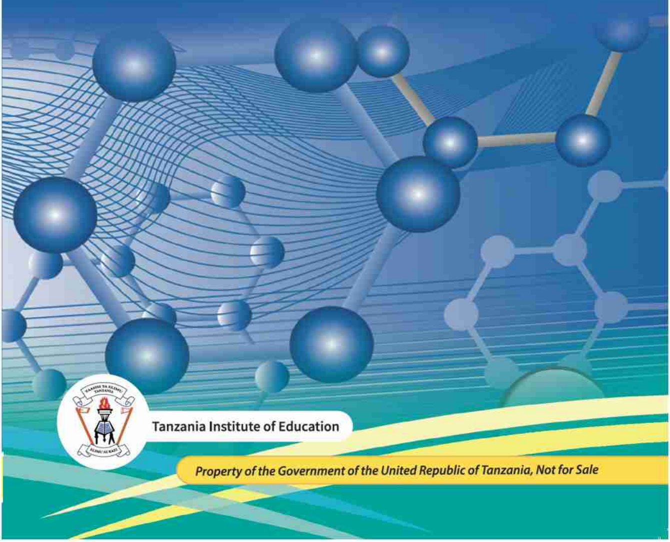
Organic Chemistry

for Advanced Level Secondary Schools

Student's Book
Form Five and Six



Tanzania Institute of Education

Property of the Government of the United Republic of Tanzania, Not for Sale

Organic Chemistry

for Advanced Level Secondary Schools

Student's Book
Form Five and Six

THE UNITED REPUBLIC OF TANZANIA
MINISTRY OF EDUCATION,
SCIENCE AND TECHNOLOGY

Certificate of Approval

No. 216

Title of Publication: Organic Chemistry for Advanced Level Secondary Schools Student's Book Form Five and Six

Publisher: Tanzania Institute of Education

Author: Tanzania Institute of Education

ISBN: 978-9987-09-028-0

This book was approved by the Ministry of Education, Science and Technology on 14th October, 2019 as a Textbook for Form Five and Six students in Tanzania Secondary Schools as per 2009 syllabus.

Dr. Lyabwene M. Mtahabwa
Commissioner for Education

Tanzania Institute of Education

Published 2019

ISBN 978 - 9987 - 09 - 028 - 0

Tanzania Institute of Education
P. O. Box 35094
Dar es Salaam

Tel: +255 22 2773005/+255 22 277 1358
Fax: +255 22 2774420
E-mail: director.general@tie.go.tz
Website: www.tie.go.tz

Preface

This book, *Organic Chemistry for Advanced Level Secondary Schools*, is written specifically for Form Five and Six students in the United Republic of Tanzania. The book is prepared according to the 2009 Chemistry Syllabus for Advanced Level Secondary Education Form V-VI issued by the Ministry of Education and Vocational Training.

The book consists of nine chapters, which are: Introduction to Organic Chemistry, Aliphatic hydrocarbons, Aromatic hydrocarbons, Halogen derivatives of hydrocarbons, Alcohols and Phenols, Carbonyl compounds, Carboxylic acids and their Derivatives, Amines, and Polymers. In addition to content, each chapter contains exercises, revision questions, illustrations, and some activities. Learners are encouraged to do all activities and answer all the questions so as to enhance their understanding, and promote the acquisition of the intended knowledge, skills, and attitudes.

Tanzania Institute of Education

Acknowledgements

The Tanzania Institute of Education (TIE) would like to acknowledge the contribution of all organisations, and individuals who participated in the design and development of this textbook.

Writers: Dr Mtabazi G. Sahini, Ms Marietha M. Belege, Mr Fixon E. Mtelesi, Mr Gerald E. Shija, Mr Peter Kyabwazi, Mr Jumanne Mwanga, Mr Elias B. Singano, Ms Anjelina P. Kanyabwoya, Mr George M. Kazi & Mr Athuman O. Mmbuji

Editors: Dr Quintino A. Mgani, Hossein M. Mwanga, Rajab A. Suleiman & Dr James E. Mgaya (Chairman of the panel)

Designer: Mr Frank P. Maridadi

Illustrators: Dr Mtabazi G. Sahini, Mr Fixon. E. Mtelesi & Alama Art and Media Production Co. Ltd.

Coordinators: Ms Marietha M. Belege & Mr Fixon E. Mtelesi

TIE also extends its sincere graditude to secondary school teachers who participated in the trial phase of the manuscript.

Likewise, the Institute would like to thank the Ministry of Education, Science and Technology for facilitating the writing of this textbook.

Dr Aneth A. Komba
Director General
Tanzania Institute of Education

Table of contents

Chapter Four: Halogen derivatives of hydrocarbons 156

Chapter Five: Alcohols and Phenols 192

Chapter One

Introduction to organic chemistry

Organic chemistry is the branch of chemistry which deals with the study of organic compounds. The major constituents of organic compounds are carbon and hydrogen elements. Other important elements in the organic compounds include oxygen, nitrogen, halogen, and few metals such as magnesium and lithium. It should be noted that, not all carbon containing compounds are organic; some compounds such as carbon dioxide, carbides, hydrogen carbonates, and carbonates are inorganic compounds. This chapter introduces the basic concepts of organic chemistry as a foundation of understanding simple to complex organic compounds such as polymers, which have laboratory, home-scale and industrial applications.

1.1 Sources of organic compounds

Previously, organic compounds were generally known to originate from living organisms such as plants, animals, algae, and microorganisms. These organic compounds are obtained from their sources either directly or indirectly. The organic compounds such as carbohydrates (cellulose, starch, and sugar), proteins (silk, wool, and food proteins), fats and oils (cooking oil), alkaloids (quinine and morphine), hormones, vitamins, perfumes, and flavours are obtained directly from plants and animals by using suitable isolation methods. The indirect sources of organic compounds include fossil fuels such as coal, natural gas, and petroleum. These indirect sources are from plants, animals, and microorganisms remains that lived millions of years ago. These remains have been converted to fossil fuels through exposure to high temperature and pressure in the earth's crust for a long time.

The major and potential sources of organic compounds in most cases are natural gas, coal, and petroleum. These are used for production of many useful organic materials such as solvents, synthetic rubber, dyes, drugs, and plastics.

For example, coal-tar which is one of the products of destructive distillation of coal, is used as a starting material for manufacturing of many useful aromatic compounds such as perfumes, dyes, and drugs. Organic compounds such as methane, acetic acid, urea, and acetylene can be synthesised from inorganic sources. For example, in 1828, a German chemist Friedrich Wöhler (1800-1882), synthesised urea (organic compound) by heating ammonium cyanate (inorganic compound). This experiment played a vital role in the development of organic chemistry.

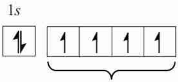
$$\underset{\text{Ammonium cyanate}}{NH_4OCN} \xrightarrow{\text{heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

1.2 Special properties of carbon

Carbon forms large groups of organic compounds, which show special features as compared to other elements. The carbon element is a major component of organic compounds due to its special properties that include tetravalency, the ability to form multiple bonds, the ability to form strong bonds, electronegativity, and catenation tendency. In this section, special properties of carbon are introduced. These properties contribute to the carbon's ability to form many different compounds and make the backbone of all organic compounds.

1.2.1 Tetravalency of carbon

The ground state electronic configuration of carbon is [He] $2s^2 2p^2$, with four electrons in its outer most shell. To become a cation (C^{4+}), carbon needs to lose four electrons, which is energetically impossible under normal conditions. Likewise, to form a carbon anion (C^{4-}), then carbon element needs to gain four electrons which is also energetically difficult. Therefore, carbon forms a maximum of four covalent bonds with either carbon atoms or other atoms to attain a filled shell known as *tetravalency*. To account for tetravalency of carbon, the $2s$ electrons should be unpaired and promoted to the vacant $2p_z$ orbital by absorbing energy in the process called *hybridisation*. This leads to the electronic configuration of the carbon atom in the excited state shown as follows:



Hybridised sp^3 orbitals

The half-filled sp^3 hybrid orbitals can take part in bonding by sharing electrons with other atoms to form four bonds and this explains the tetravalency of carbon.

1.2.2 Catenation

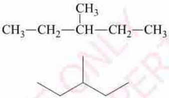
Catenation is the ability of atoms of the same element to join and form long open chains or cyclic structures. The carbon atom can undergo catenation due to its small size which results into the formation of strong bonds between the carbon atoms. Through catenation, carbon forms many chemically and thermally stable compounds which can either be open chains (linear or branched) or cyclic structures.

Examples:

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

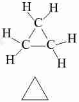
Hexane

(linear chain)



$CH_3—CH_2—\overset{\overset{\large CH_3}{|}}{C}H—CH_2—CH_3$

3-methylpentane
(branched chain)



Cyclopropane
(ring)

1.2.3 Ability to form multiple bonds

Carbon can form various types of covalent bonds which are carbon-carbon single bonds (C—C), carbon-carbon double bonds (C=C), and carbon-carbon triple bonds (C≡C) between carbon atoms themselves or with other elements such as carbon-oxygen double bonds (C=O) and carbon-nitrogen triple bonds (C≡N). The multiple bonds consist of one carbon-carbon (C—C) sigma bond, and one or two *pi* (π)-bonds which are formed by the side-way overlap of unhybridised *p*-orbitals. The ability to form *pi* (π)-bonds is contributed by the fact that the carbon-carbon (C—C) single bond is relatively short and strong such that it allows the side to side overlap of half-filled unhybridised *p*-orbitals.

1.2.4 Strengths of bonds between carbon and other elements

The covalent bonds formed between carbon-carbon (C—C) and carbon-hydrogen (C—H) bonds are very strong such that they are not easily broken during chemical reactions. This makes it easier to replace other atoms or groups of atoms, such as halogens (X) or hydroxyl (OH) attached to carbon. This allows the formation of many new compounds by carrying out organic reactions as in the case of the production of ethanol from haloalkanes and alkalis like potassium hydroxide.

$$\underset{\text{Chloroethane}}{CH_3{-}CH_2{-}Cl} + \underset{\text{Potassium hydroxide}}{KOH(aq)} \longrightarrow \underset{\text{Ethanol}}{CH_3{-}CH_2{-}OH} + \underset{\text{Potassium chloride}}{KCl(aq)}$$

1.3 Differences between organic and inorganic compounds

Organic compounds differ from inorganic compounds in many different ways as presented in Table 1.1.

Table 1.1 Comparison between organic and inorganic compounds

Organic compounds	**Inorganic compounds**
Carbon is the principle element together with hydrogen, halogens, oxygen, phosphorous, sulphur, and a few metals such as lead.	Composed of any of the known elements.
Most of the compounds are covalent in nature.	Most of the compounds are ionic in nature.
Have low melting and boiling points.	Have high melting and boiling points.
There are many classes based on functional groups.	They exist in few classes only as salts, acids or bases.
They are mostly insoluble in water but soluble in organic solvents such as benzene, cyclohexane, alcohols, and ethers.	They are mostly soluble in water but not in the organic solvents.
They are poor conductors of heat and electricity in solution.	Their solutions are good conductors.
The reactions of organic compounds generally proceed slowly.	The reactions of inorganic compounds generally proceed fast.

1.4 Isomerism

This part is concerned with how organic compounds can be accurately represented. In order to describe correctly an organic compound, it is necessary to understand how different atoms represented in the molecular formula are joined to one another, and how they are arranged in space with respect to one another. *Isomers* are compounds which have the same molecular formula but differ in the type of structural arrangement, sequence of bonding of their atoms or in the arrangement of their atoms in space. The existence of compounds in more than one isomeric forms is called *isomerism*. There are two main types of isomerism shown by organic compounds, which are constitutional isomerism (structural isomerism) and stereoisomerism.

1.4.1 Constitutional isomers

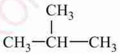
Constitutional isomers are two or more compounds with the same molecular formula but different in the arrangement of the bonded atoms. The existence of constitutional isomers is known as *constitutional isomerism* which can be divided into skeletal, functional, and positional isomerisms.

Skeletal (sequential or carbon chain) isomers

Skeletal isomers are constitutional isomers that have the same molecular formula but differ from each other in the connectivity of the carbon skeleton. For example, a compound with molecular formula C_4H_{10} has the following skeletal isomers:

$CH_3{-}CH_2{-}CH_2{-}CH_3$

n-butane



$$CH_3{-}\overset{\overset{\large CH_3}{|}}{C}H{-}CH_3$$

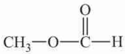
2-methylpropane

Functional group isomers

Functional group isomers are constitutional isomers that have the same molecular formula but differ from each other in their functional groups. For example, a compound with molecular formula $C_2H_4O_2$ has the following functional group isomers:

$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH$$

Ethanoic acid
(carboxylic acid)



$$CH_3{-}O{-}\overset{\overset{\large O}{\|}}{C}{-}H$$

Methylmethanoate (ester)

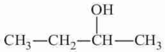
Other examples of functional group isomers include alcohols like ethanol (CH_3CH_2OH) that are isomeric to ethers like methoxymethane (CH_3OCH_3), and alkenes such as propene, which are isomeric to cycloalkanes such as cyclopropane. For an alkene to exist as an isomer of a cycloalkane, it should possess a double bond and more than two carbon atoms.

Positional isomers

Positional isomers are constitutional isomers that have the same molecular formula and the same carbon skeleton, but differ only in the positions of the substituents or functional groups. For example, the compound with molecular formula $C_4H_{10}O$ has the following positional isomers:

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$$

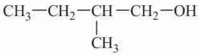
Butan-1-ol



$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_3$$

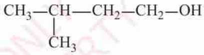
Butan-2-ol

The following are examples of the positional isomers in which the substituent group appears in different positions.



$$CH_3{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}OH$$

2-methylbutan-1-ol



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_2{-}OH$$

3-methylbutan-1-ol

Note that, in the above positional isomers, the position of the hydroxyl functional group (OH) is retained and only the position of the methyl group (substituent group) is shifted.

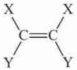
1.4.2 Stereoisomers

Stereoisomers are isomers which have the same molecular formula and even the same structural formula but differ only in the spatial arrangements of their atoms or groups of atoms. This type of isomers is divided into geometrical and optical isomers.

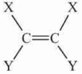
Geometrical isomers

Geometrical isomers are *cis–trans* stereoisomers which have different orientations of groups around a double bond. Geometrical isomerism exists in compounds in which the presence of a carbon-carbon double bond or a ring structure fixes the atoms or groups of atoms in their relative positions due to restricted rotation. In the carbon-carbon double bond of alkenes, the rotation is restricted because it requires high energy and if it happens, the *pi*(π) -bond would break the overlap of *p*-orbitals. Because of the restricted rotation, the *cis–trans* isomers may exist, depending on the groups attached to the adjacent carbons.

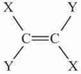
For *cis–trans* isomers to exist, the adjacent carbon atoms that form the double bond must be bonded to at least two different atoms or groups of atoms as illustrated by the following hypothetical compound.



If similar groups are located on the same side of the double bond (Y and Y or X and X), the isomer is called *cis*–isomer, and if they are on opposite sides (X and Y), the isomer is called *trans*–isomer.

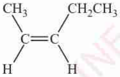


cis-isomer

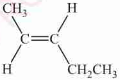


trans-isomer

The groups or atoms X, X or Y, Y are not necessarily identical. But Y, Y must be different from X, X. For example, pent-2-ene with a structural formula $CH_3CH{=}CHCH_2CH_3$ has the following geometrical isomers:

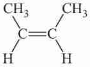


cis-2-pentene

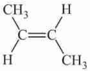


trans-2-pentene

Another example of an alkene which shows geometrical isomerism is but-2-ene. But-2-ene has two geometrical isomers; the first isomer is *cis*-2-butene which has two methyl groups on the same side of the carbon-carbon double bond (C=C), whereas the second isomer is *trans*-2-butene which has one methyl group on one side of the carbon-carbon double bond (C=C) and another methyl group on the other side of the carbon-carbon double bond (C=C).



cis-2-butene



trans-2-butene

Optical isomers

Optical isomers are a pair of stereoisomers in which a molecule and its corresponding mirror image cannot be superimposed on each other. To understand the mirror image concept, consider your hands. If you place your right hand in front of the mirror, the reflection of your right hand looks like your left hand. If your palms are aligned on top of each other pointing in the same direction, the position of the thumb of one palm lies over the baby finger of the other palm, and not over the thumb of the other palm (Figure 1.1). Therefore, they are said to be non-superimposable (not superimposed).

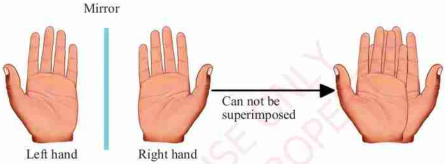
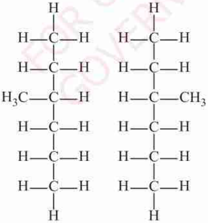
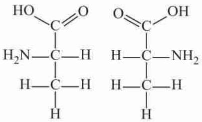


Figure 1.1 Hand palms are non-superimposable

When the molecules are mirror images of each other and cannot be superimposed, they are called *optical isomers*. The following are examples of optical isomers.



Optical isomers of 3-methylhexane



Optical isomers of alanine

Exercise 1.1

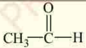
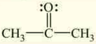
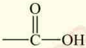
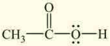
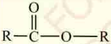
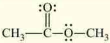
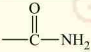
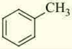
1. Describe the main sources of organic compounds.
2. Using examples, distinguish between direct and indirect sources of organic compounds.
3. Describe the concept that carbon element is the major component of organic compounds.
4. (a) Define each of the following types of isomers:
    - (i) Constitutional
    - (ii) Geometrical
    - (iii) Optical

   (b) Which types of isomers in 4 (a) are stereoisomers? Give reason(s).
5. Draw all the possible isomers of the following compounds:
    - (a) C_5H_{12}
    - (b) C_3H_8O
    - (c) $C_2H_4O_2$

1.5 Structural features and reactions of organic compounds

Organic compounds are generally characterised by their functional groups. A *functional group* is an atom, group of atoms or set of bonds which is responsible for the characteristic chemical reactions in a given class of organic compounds. For example, the carbon-carbon double bond in alkenes is responsible for the chemical reactivity of alkenes. Similarly, the carbonyl group (C=O), governs the reactions of aldehydes and ketones. Atoms outside the functional group are generally unaffected by it, although they can influence the ease and the rate of chemical reactions depending on the electronic and steric effects they impose on the functional group. Examples of the functional groups are given in Table 1.2.

Table 1.2 Important functional groups of the organic compounds

Functional group (Structure)	Compound type	Suffix or Prefix of name	Example	IUPAC name (Common name)
 $-\overset{\vert}{\underset{\vert}{C}}-$	Alkane	-ane	CH_4	Methane
$-C=C-$	Alkene	-ene	$CH_2=CH_2$	Ethene (ethylene)
$-C\equiv C-$	Alkyne	-yne	$H-C\equiv C-H$	Ethyne (acetylene)
$-OH$	Alcohol	-ol	CH_3-O-H	Methanol
$R-O-R$	Ether	Alkoxy-alkane	$CH_3-CH_2-O-CH_3$	Ethoxymethane
$-X$ X= Halogen	Haloalkane	halo	CH_3-Cl	Chloromethane (methyl chloride)
$-NH_2$	Amine	-amine	$CH_3-CH_2-NH_2$	Ethylamine
 $R-\overset{\overset{O}{\Vert}}{C}-H$	Aldehyde	-al	 $CH_3-\overset{\overset{O}{\Vert}}{C}-H$	Ethanal
 $R-\overset{\overset{O}{\Vert}}{C}-R$	Ketone	-one	 $CH_3-\overset{\overset{:O:}{\Vert}}{C}-CH_3$	2- propanone (acetone)
 $-\overset{\overset{O}{\Vert}}{C}-OH$	Carboxylic acid	-oic acid	 $CH_3-\overset{\overset{O}{\Vert}}{C}-\ddot{\underset{..}{O}}-H$	Ethanoic acid (Acetic acid)
 $R-\overset{\overset{O}{\Vert}}{C}-O-R$	Ester	-oate	 $CH_3-\overset{\overset{:O:}{\Vert}}{C}-\ddot{\underset{..}{O}}-CH_3$	Methylethanoate (methyl acetate)
 $-\overset{\overset{O}{\Vert}}{C}-NH_2$	Amide	-amide	 $CH_3-\overset{\overset{O}{\Vert}}{C}-NH_2$	Ethanamide (acetamide)
$-C\equiv N:$	Nitrile	-nitrile	$CH_3-C\equiv N:$	Ethanenitrile (acetonitrile)
	Arene	benzene		Methylbenzene (Toluene)

Key: The red colour indicates *suffix* and the blue colour indicates the *prefix*
R represents any alkyl group

1.6 Organic reactions

A chemical reaction shows how reactants undergo changes to form products. This is normally described by means of an equation. The equation normally shows reagents involved, required conditions, and products formed. In organic chemistry, it is also possible to show the detailed information on how and why a reaction occurs. Organic reactions involve the movement of electrons, thus causing the breaking and formation of covalent bonds. In most reactions, the movement of electrons between two reacting species can be predicted from the knowledge of their electronegativity values. By considering the lone pairs of electrons present in the reagents and the electronegativities of the atoms involved, it is possible to predict how compounds will react under different conditions. The effect of electronegativity of reacting atoms and the participation of electron pairs is shown by using a mechanism. A *reaction mechanism* shows the details of each stage and the movement of electron pairs (bond-electrons or lone pairs) in relation to the electronegativity of the atoms present in the organic molecules. In this section, you will learn about the types of organic reagents and reactions, bond breaking and forming processes, general rules for showing reaction mechanisms and factors affecting reaction mechanisms.

1.6.1 Types of organic reagents

Organic reagents are chemical species which react to form products. They can be divided into three main types: nucleophiles, electrophiles, and free radicals.

Nucleophiles (Nu: or $Nu^{\ominus}$)

The term nucleophile was derived from the word nucleus and the Greek word *philos* which means to love. Therefore, nucleophiles are nucleus loving species. A *nucleophile* is a reagent containing an atom with unshared or lone pair of electrons which can be shared with another atom to form a new covalent bond. Being electron rich species, nucleophiles seek electron deficient sites and therefore behave as Lewis bases. Some nucleophiles are neutral with lone pair or *pi* (π)-electrons while others are negatively charged ($Nu^{\ominus}$).

Neutral nucleophiles

Neutral nucleophiles are species which consists of either lone pair(s) or π electrons.

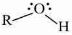
Examples of neutral nucleophiles with lone pair(s) include ammonia, amine, alcohol, and water.

$:NH_3$

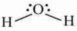
Ammonia

$R-\ddot{N}H_2$

Amine

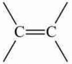


Alcohol



Water

Examples of neutral nucleophiles which consist of π-electrons include alkenes, alkynes and arenes.



Alkene

$-C\equiv C-$

Alkyne

Arene

Negatively charged nucleophiles

These are nucleophiles which carry a net negative charge. Examples of negatively charged nucleophiles include: hydroxyl ions, cyanide ions, halide ions and alkoxide ions.

$H-O^{\ominus}$

Hydroxyl

$^{\ominus}C\equiv N$

Cyanide

$X^{\ominus}$

Halide

$R-O^{\ominus}$

Alkoxide

$R-C\equiv C^{\ominus}$

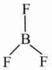
Carboanion

Electrophiles ($E^{\oplus}$)

The term electrophile was derived from the word electron and the Greek word *philos* which means to love. Therefore, electrophiles are electron loving species. *Electrophiles* are positively charged or neutral species which are deficient in electrons such that they can accept a pair of electrons to form a bond. They are of two types, positively charged species and neutral molecules with vacant orbitals.

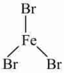
$AlCl_3$

Aluminium trichloride



BF_3

Boron trifluoride



$FeBr_3$

Iron(III) bromide

Neutral electrophiles

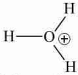
Neutral molecules which act as electrophiles have vacant orbitals for receiving electrons from nucleophiles. They include aluminium trichloride, boron trifluoride, and iron(III) bromide. They are often referred to as electron acceptors or Lewis acids.

Positively charged electrophiles

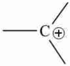
These are electrophiles which carry a net positive charge. The possession of a positive charge is an indication that they are deficient in electrons and therefore, they can receive electrons from electron rich species (nucleophiles). Examples of positively charged electrophiles include hydrogen ion (proton), hydroxonium ion, carbocation, nitronium ion, and metal cations.

$H^{\oplus}$

Proton



Hydroxonium ion



Carbocation

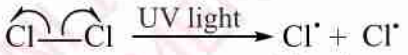
$O=\overset{\oplus}{N}=O$

Nitronium ion

The positive sign ⊕ indicates that the atom bearing the sign has less electron as compared to its electron configuration in its ground state.

Free radicals

A *free radical* is an atom or group of atoms which contains at least one unpaired electron. Free radicals are formed from homolytic breaking of a covalent bond. This is the type of bond breaking in which, each of the bonding atom goes with one of the shared electrons. For example, chlorine gas dissociates homolytically into two chlorine free radicals when exposed to ultraviolet light or any high energy source.



Chlorine radicals

Free radicals are electrically neutral and highly reactive species; therefore, they have a very short lifespan. A free radical will always react with another free radical or another reactive species.

Note that, under normal conditions there is no reaction between one electrophile with another electrophile or one nucleophile with another nucleophile. This means, an electrophile will always react with a nucleophile to form a product as shown in the following reaction.

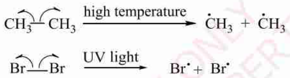
$$Nu^{\ominus} + E^{\oplus} \longrightarrow Nu\text{-}E$$

1.6.2 Bond breaking and bond forming processes

All organic reactions involve bond breaking and bond forming processes. In order for an organic reaction to occur, some or all old bonds in the reactants must be broken down and new ones must be formed in the products. A chemical bond can be broken (cleaved) by either heterolytic or homolytic mechanism.

Homolytic bond breaking

The term homolytic comes from a Greek word, *homoios* which means equal and *lysis* which means loosening or splitting. *Homolytic bond breaking* or *bond cleavage* is the breaking of a covalent bond in which the bond electron pair is split evenly in such a way that each bonded atom gets one of the shared electrons. The resulting products of homolytic bond breaking are called *free radicals*. Homolytic bond cleavage is also called *homolysis* or *homolytic fission*. It can be induced at very high temperatures or by ultraviolet light. Examples of homolytic bond breaking is in ethane and bromine molecules. This process is indicated by a half-head curled arrow which originate from the source of an electron to the destination (the sink).



$$CH_3-CH_3 \xrightarrow{\text{high temperature}} \dot{C}H_3 + \dot{C}H_3$$

$$Br-Br \xrightarrow{\text{UV light}} Br^{\bullet} + Br^{\bullet}$$

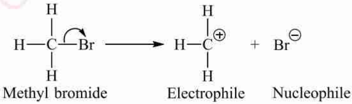
The half head curled arrow (⌒) indicates that each of the two bonding electrons is taken by the respective atom.

Heterolytic bond breaking

The term heterolytic comes from a Greek word *heteros* which means different and *lysis* which means loosening. Heterolytic bond breaking or bond cleavage is the breaking of a chemical bond in which the bond electron pair is split unevenly in such a way that one atom takes both shared electrons. The resulting products of the heterolytic bond breaking are nucleophiles and electrophiles.

Examples:

Heterolytic bond breaking of carbon-bromine (C–Br) bond in methylbromide.



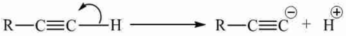
$$CH_3-Br \longrightarrow CH_3^{\oplus} + Br^{\ominus}$$

Heterolytic bond cleavage of HCl

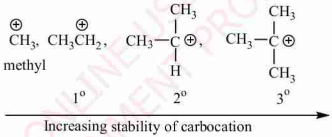
$$H-Cl \longrightarrow H^{\oplus} + Cl^{\ominus}$$

A full head curved arrow (↷) indicates that all the bonding electrons are taken by one atom. During heterolytic bond breaking, electrons are taken by the more electronegative atom. The more electronegative atom becomes negatively charged (nucleophile) and the other species become positively charged (electrophile). If the positive charge is on the carbon atom, the positively charged species is called *carbocation*. In the previous example, the heterolytic bond breaking of methyl bromide generates a methyl carbocation and bromide ion. If the resulting negative charge is on carbon, the negatively charged species is called *carbanion*.

Example:



Note that, most of the organic reactions involve the formation of carbocations and rarely carbanions. Carbocations can be classified as methyl, primary (1°), secondary (2°), and tertiary (3°) depending on the number of alkyl or aryl group attached to it. The number of electrons donating group influences the stability of carbocation in the following order:



1.7 General rules for showing reaction mechanisms

In the preceding subsection, it was observed that all organic reactions involve bond breaking and bond forming processes. The way in which electrons move from one species to another is indicated by a reaction mechanism. Reaction mechanisms help organic chemists to understand and predict the movement of electrons during chemical reactions. The mechanism of a reaction is guided by the following general rules that must be considered in any reaction;

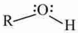
1. The movement of electrons during a chemical reaction is indicated by arrows. The arrow tail points the source of electrons and the arrow head points in the direction where the electrons are destined.
2. Full headed curved arrow (↷) is used to indicate the movement of the two bond electrons, while a half headed curved arrow or a single sided arrow (↷) is used to indicate the movement of one electron.

3. All lone pairs of electrons on the reacting species must be clearly shown. The lone pairs are always indicated by dots.

   Examples:

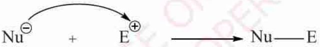
   $:NH_3$

   One lone pair of electrons on nitrogen



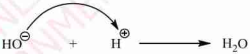
   Two lone pairs of electrons on oxygen

4. In the process of forming new bonds, the arrows point from the electron source to the electron sink. An example of the electron source is a nucleophile ($Nu^{\ominus}$), while the electrophile ($E^{\oplus}$) is an example of the electron destination (sink). Therefore, the process of forming a bond between an electrophile and a nucleophile always involves the movement of electrons from the nucleophile to the electrophile and not vice versa.



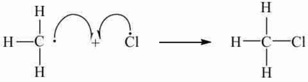
Electron source　Electron sink　Chemical bond

Example:



Electron source (Nucleophile)　Electron sink (Electrophile)

If the bond is to be formed between free radicals, then the two half-headed curled arrows one from each radical must meet at the sink which becomes a bond. This is exemplified by the formation of chloromethane from methyl and chlorine radicals:

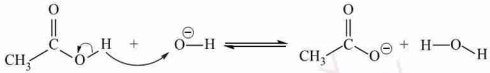


Methyl radical　Chlorine radical　Chloromethane

5. The arrows show only the movement of electrons, and not the movement of the entire atom.

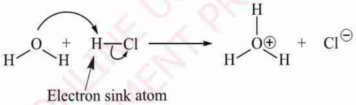
Example:

Correct use of arrow
(Arrow start from electron source)



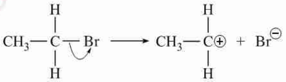
Incorrect use of arrow
(Arrow points in the wrong direction)

6. Bond breaking occurs to avoid overfilling of the valence shell of the electron sink atom.

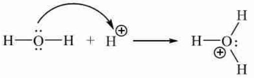


7. If the source of the moving electrons is a bond (single or multiple bond), a positive charge is formed on the atom which loses its bond electron.

Example:



8. If the source of bond electrons is a lone pair the atom which loses its lone pair of electron becomes positively charged.



Exercise 1.2

1. Define the following terms and give two examples in each case:
   (a) Nucleophiles
   (b) Electrophiles
   (c) Free radicals

2. Giving examples, explain the meaning of homolysis and heterolysis.

3. (a) Describe the differences between carbocation and carbanion.

   (b) Why is a secondary carbocation more stable than a primary carbocation while a secondary carbanion is less stable than a primary carbanion?

4. Identify each of the following species as an electrophile or a nucleophile:

$$I^{\ominus}, H^{\oplus}, BF_3, OH^{\ominus}, \overset{\oplus}{C}H_3, H_2O, \overset{\ominus}{C}H_3$$

5. Identify the electrophile and nucleophile in the following reaction:

$$BCl_3 + 4NH_3 \longrightarrow BN + 3NH_4Cl$$

6. (a) Briefly explain how free radicals are formed.
   (b) Why do free radical, have a very short lifespan?

7. Give differences between the following terms:
   (a) Half curved arrow and full curved arrow
   (b) Electron source and electron sink

8. Write down the structure of the functional groups of the following organic compounds:
   (a) Carboxylic acids
   (b) Aldehydes
   (c) Ketones
   (d) Alkenes
   (e) Alkynes

1.8 Types of organic reactions

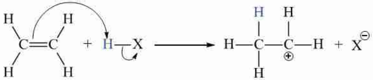
Organic reactions are chemical reactions which involve organic compounds. There are many types of organic reactions that occur naturally or in the laboratory. In this section, only three common types of organic reactions are discussed: addition, substitution, and elimination reactions.

1.8.1 Addition reactions (A)

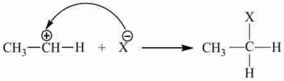
An *addition reaction* is a type of organic reaction in which an atom or groups of atoms are added to adjacent atoms linked by multiple bonds. Addition reactions occur in unsaturated compounds which consist of multiple bonds such as alkenes (C=C), alkynes (C≡C), and carbonyls (C=O). In the process of adding new atoms to the molecules, the π-bond is cleaved leaving the sigma bond intact. There are two types of addition reactions depending on the nature of the reacting species which adds first to the reacting compound. If an electrophile adds first, the reaction is called *electrophilic addition reaction*, and if a nucleophile adds first, the reaction is called *nucleophilic addition reaction*.

Electrophilic addition reaction (A_E)

An *electrophilic addition reaction* is a chemical reaction in which an electrophile is added first to an electron rich carbon atom of unsaturated organic compound, followed by addition of the nucleophile. Electrophilic addition reaction occurs at multiple bonds between two adjacent identical atoms, for example carbon double bond (C=C) or carbon triple bond (C≡C). If the unsaturated organic compound consist of C=C bond, the resulting product will be a saturated organic compound. But if a carbon triple bond (C≡C) is involved in the electrophilic addition reaction by involving one mole of reagent, an unsaturated organic compound with C=C bond will be formed. One example of an electrophilic addition reaction is the addition of hydrogen halide to ethene (hydrohalogenation). In hydrogen halide (HX), hydrogen ion $H^{\oplus}$ acts as an electrophile and the halide ion ($X^{\ominus}$) acts as a nucleophile. Electrophile ($H^{\oplus}$) adds first to ethene, forming an intermediate carbocation.



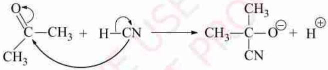
Then, the intermediate carbocation react with the nucleophile (halide ion) to form haloalkane.



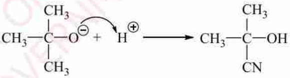
Nucleophilic addition reaction (A_N)

A *nucleophilic addition reaction* is a chemical reaction in which a nucleophile is added first to an electron deficient carbon atom followed by the addition of electrophile. Nucleophilic addition reaction occurs at the localised multiple bonds between two different adjacent atoms, for example carbon-oxygen double bonds (C=O) or carbon-nitrogen triple bonds (C≡N). An example of nucleophilic addition reaction is the addition of hydrogen cyanide (HCN) to propanone.

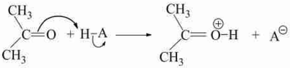
The first step is the nucleophilic attack by the cyanide ion on the slightly positive carbon atom.



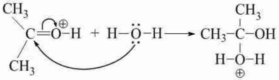
The second step is the electrophilic reaction of the negative ion with the hydrogen ion ($H^{\oplus}$).



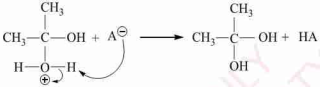
Note that, the given reaction involves the addition of both nucleophile and electrophile. Since the nucleophile is added first followed by the electrophile, the reaction is called nucleophilic addition. The previous example involves a strong nucleophile. If the reaction involves a weaker nucleophile like the C=O in propanone, it needs to be activated before being attacked by nucleophile. The activation can be done using an acid catalyst which protonates the oxygen atom, therefore, making the system more electrophilic.



The resulting protonated species is more electrophilic and therefore, easier to react with a weak nucleophile. Consider water (H_2O) as a weak nucleophile. Then, the nucleophile is added to the protonated carbonyl species.



The negatively charged species from the acid catalyst attacks hydrogen on the positively charged H−O−H.



Being a catalyst, the acid (HA) remains unchanged at the end of the reaction.

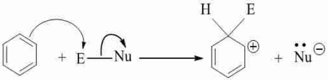
1.8.2 Substitution reactions (S)

Substitution reaction is a type of organic reaction in which an atom or a group of atoms in one reacting species is replaced by another atom or a group of atoms from another reacting species. There are three types of substitution reactions depending on the type of reacting species involved: electrophilic substitution, nucleophilic substitution and free radical substitution reactions.

Electrophilic substitution reaction (S_E)

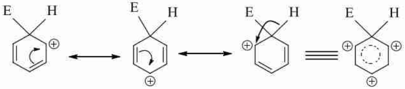
Electrophilic substitution reaction is a type of substitution reaction in which a weak electrophile in one molecule is replaced by a strong electrophile. This type of reaction occurs in aromatic rings for which the electrophile attaches on the ring and forms an intermediate which is stabilised by resonance. The resulting intermediate is then converted into a stable product by the release of hydrogen ion ($H^{\oplus}$). In this type of reaction, the electrophile replaces the hydrogen atom from the aromatic ring, hence electrophilic substitution. Since this type of reaction occurs only in aromatic compounds, it is also called *electrophilic aromatic substitution*. The mechanism of electrophilic aromatic substitution reaction is shown in the following reaction mechanisms:

The first step involves the formation of the intermediate arenium ion.

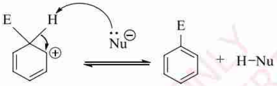


Intermediate arenium ion

The intermediate is stabilised by resonance which is the movement of electrons from one place to another and then back to their original place to stabilise the carbocation.



The second step involves the removal of hydrogen ion from the aromatic ring by a nucleophile to reform the aromatic ring.

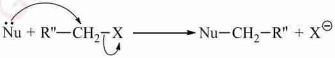


Nucleophilic substitution reaction (S_N)

Nucleophilic substitution reaction is a type of substitution reaction in which an electron pair donor (the nucleophile) reacts with an electron pair acceptor (the electrophile) which has a good leaving group (one that is substituted during the reaction). Nucleophilic substitution reaction occurs in compounds which have saturated *sp*^{3} hybridised carbon atoms. There are two different ways in which nucleophilic substitution reactions occur: S_N2 and $S_N1$mechanisms.

S_N2 mechanism of nucleophilic substitution

This is the nucleophilic substitution reaction in which the replacement of a leaving group occurs simultaneously with the backside attack by the nucleophile. This reaction does not involve the formation of a carbocation as an intermediate.



$$\ddot{Nu} + R''{-}CH_2{-}X \longrightarrow Nu{-}CH_2{-}R'' + X^{\ominus}$$

$X^{\ominus}$ is called leaving group

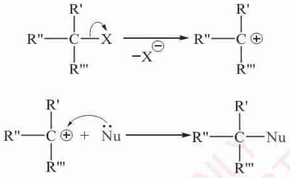
Example:

$$CH_3{-}CH_2{-}Br + OH^{\ominus} \longrightarrow CH_3{-}CH_2{-}OH + Br^{\ominus}$$

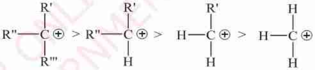
In S_N2 reaction, 'S' stands for substitution, 'N' stands for nucleophilic and '2' stands for bimolecular.

S_N1 mechanism of nucleophilic substitution

This is a nucleophilic substitution reaction in which the leaving group leaves first, resulting into the formation of a carbocation intermediate which is then attacked by the nucleophile, to form final product.



In this mechanism, the reaction proceeds through one step at a time, hence it is called S_N1 mechanism. Since the first step in S_N1 mechanism is the loss of a leaving group to form an intermediate carbocation, the rate of reaction will depend on the stability of the carbocation. The stability of carbocation increases with the increase in number and sizes of the substituent groups.



Tertiary Secondary Primary Methyl

In S_N1 reaction, 'S' stands for substitution, 'N' stands for nucleophilic and '1' stands for unimolecular.

Free radical substitution reaction (S_R)

A *free radical substitution reaction* is a type of substitution reaction in which a free radical replaces an atom or a group of atoms in a compound. An example is the reaction between methane and chlorine gas under UV light.

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

Methane Chloromethane

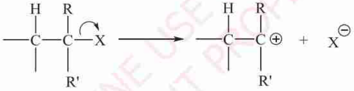
The free radical substitution reaction involves three steps; the initiation, propagation, and termination. The mechanisms of these steps will be discussed in chapter two.

1.8.3 Elimination reactions (E)

Elimination reaction is a type of organic reaction which involves the removal of an atom or a group of atoms from a molecule or compound. Thus, the mechanism of elimination reaction involves the loss of a leaving group leading to the formation of π-bonds. The elimination reaction can take place in two different mechanisms: E_1 and E_2 elimination mechanisms.

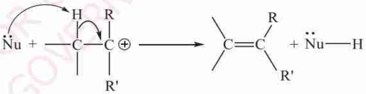
E_1 elimination mechanism

The E_1 elimination mechanism involves the formation of an intermediate carbocation followed by a nucleophilic attack which removes the proton. The elimination reaction shown below demonstrates the E_1 mechanism. The E_1 elimination reaction occurs in one step at a time hence E_1 elimination mechanism. In E_1 reaction; 'E' stand for elimination and '1' for unimolecular.



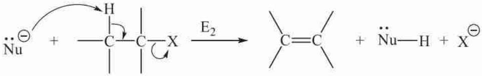
Carbocation intermediate

This is followed by the loss of a proton from the intermediate carbocation in the presence of a nucleophile.



E_2 elimination mechanism

The E_2 mechanism is the elimination mechanism in which both the attack of a nucleophile and the elimination of the leaving group occur simultaneously to form a C═C bond.

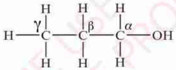


In E_2 reaction; 'E' represents elimination, and '2' represents bimolecular.
There are two types of elimination reactions depending on whether the reaction is triggered by acid or base that is, acid induced elimination and base induced elimination reactions.

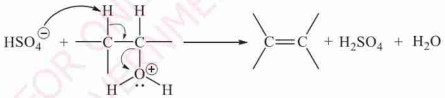
Acid induced elimination

This is a type of elimination reaction which is triggered by the acid. The reaction occurs in alcohols and involves the protonation of the hydroxyl group attached to the alpha (α)-carbon atom.

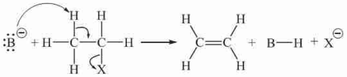
An alpha (α)-carbon, is a carbon atom that is directly bonded to the carbon containing a functional group. The carbon atom, which is adjacent to the α-carbon is called a beta (β)-carbon and the one next to the β carbon is a gamma (γ)-carbon. The hydrogens attached to these carbons are α-hydrogen, β-hydrogen and γ-hydrogen, respectively. During the elimination reaction, the C=C bond is formed between the α-carbon and the β-carbon.



An example of this type of reaction is the acid catalysed dehydration of alcohols.



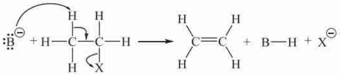
The protonation of the hydroxyl (OH) group on α-carbon is followed by the removal of hydrogen atom from the β-carbon using the conjugate base of an acid ($HSO_4^{\ominus}$).



Since the reaction involves the elimination of water, it is sometimes called *dehydration reaction* and the acid acts as both a dehydrating agent and catalyst.

Base induced elimination

This is a type of elimination reaction which is triggered by a base. The reaction occurs in haloalkanes and involves the removal of a leaving group from α-carbon and hydrogen atom from β-carbon by using a strong base. The attack on hydrogen atom by a base and the removal of the leaving group occur simultaneously.



$X^{\ominus}$ is the leaving group (halides)

Since the base induced elimination reaction involves the removal of hydrogen and halide ions, it is also known as *dehydrohalogenation reaction* of alkyl halides.

Predicting whether substitution or elimination will occur in a given reaction

Since every nucleophile can act as a base, any organic compound that has a lone pair of electrons can react with alkyl halide by either substitution or elimination. Whether in acidic, neutral or basic conditions, the guidelines for predicting whether the reaction will be substitution or elimination are different.

Basic conditions

Both S_N1 substitution and E_1 elimination reactions occur only under acid conditions. Therefore, the reactions in the basic conditions will either be S_N2 substitution or E_2 elimination. Whether substitution or elimination will occur, depends on the basicity of the base or nucleophilicity of the nucleophile. Both bases and nucleophiles react with electrophiles. However, the ability of an atom that has lone pairs to attack hydrogen ion ($H^{\oplus}$) or hydrogen halide (H—X) defines the basicity. Its ability to attack the electrophilic carbon halide (C—X) defines the nucleophilicity. As the nucleophilicity increases, the basicity increases.

(a) Nucleophilicity increases down the group in the periodic table, that is, $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ and $^{\ominus}SH > {}^{\ominus}OH$.

(b) Nucleophilicity and basicity are relatively similar in the same row of the periodic table.

(c) Nucleophilicity increases as the bulkiness of the nucleophile increases.

Examples:

(i) Primary alkyl centres undergo S_N2 substitution with good nucleophiles regardless of whether a weak or strong base is involved. However, if the base is strong and the nucleophile is weak, E_2 elimination occurs.

(ii) Tertiary alkyl centres never undergo S_N2 substitution because they are highly sterically hindered.

(iii) Secondary alkyl centres undergo S_N2 substitution with strong nucleophiles which are weak bases. However, with strong bases, regardless of whether they are strong or weak nucleophiles, E_2 elimination will occur.

Acidic conditions

Both E_1 and S_N1 occur under acidic conditions and require the formation of carbocation at the electrophilic carbon. The occurrence of substitution or elimination reactions under acidic conditions depends on the groups attached on the electrophilic carbon as well as the concentrations of the nucleophiles. Both secondary and tertiary alcohols and alkyl halides form stable carbocations. After the formation of stable carbocation, either E_1 or S_N1 can occur. If there is a very high concentration of nucleophile, the S_N1 substitution reaction will occur. If the concentration of the nucleophile is low, E_1 elimination reaction will occur.

Neutral conditions

The following guidelines help to predict the reaction mechanism under neutral conditions:

(a) If there is a good nucleophile and a poor base S_N2 substitution may occur.
(b) If there is a tertiary halide in an aprotic solvent S_N1 reaction may occur.
(c) If there is a secondary or a tertiary halide in a polar aprotic solvent, E_1 elimination reaction may occur.

Protic solvent is a type of solvent which has a hydrogen atom bound to a more electronegative atom (example, O or N) such that it can easily donate its protons to the reagent. An *aprotic* solvent is a type of solvent which has a hydrogen atom bound to a least electronegative atom such that it cannot donate it to the reagent.

Exercise 1.3

1. Describe the three common types of organic reactions and give one example in each case.
2. Using simple mechanisms show how the following reactions occur:
   (a) Nucleophilic substitution
   (b) Electrophilic substitution
   (c) Nucleophilic addition

   (d) Electrophilic addition
   (e) Elimination

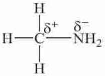
3. Show how the S_N2 mechanism differs from the S_N1 mechanism.
4. Explain the difference between E_2 and E_1 reactions.
5. Explain the similarities between the following:
   (a) E_2 elimination mechanism and S_N2 substitution mechanism
   (b) E_1 elimination mechanism and S_N1 substitution mechanism
6. Using one example, explain the term free radical substitution.
7. Outline the factors that can be used to predict types of substitution or elimination reaction mechanisms under the following conditions:
   (a) Acidic condition
   (b) Neutral condition
   (c) Basic condition

1.9 Factors affecting reaction mechanisms

Organic reactions are influenced by three important factors: inductive effect, mesomeric effect, and reactivity of lone pairs.

Inductive effect

Inductive effect is a slight shift of bonded electrons towards the more electronegative atom resulting in a polarised bond. For example, in methylamine (CH_3NH_2), nitrogen is more electronegative than carbon. Therefore, the carbon-nitrogen single bond (C—N) would be polarised, with the carbon atom acquiring a partial positive charge and the nitrogen atom acquiring a partial negative charge.



$$H_3\overset{\delta+}{C}—\overset{\delta-}{N}H_2$$

Assume that, the alkylamine has two or more carbon atoms in the chain, the carbon atom that is directly bonded to the nitrogen atom needs more electrons because it is more positive than the neighbouring carbon atom. Therefore, it pulls the bonded pair of electrons from the next carbon atom making it slightly positive.

This effect is then shifted along the entire carbon chain, but as the number of carbon atoms increases the partial positive charges decreases.
There are two types of inductive effects which are negative inductive (−I) effect and positive inductive (+I) effect.

Negative inductive (−I) effect

A *negative inductive* effect is the type of inductive effect in which electrons are slightly withdrawn away from the carbon atom. Examples of atoms or a group of atoms that cause negative inductive effect include F, Cl, Br, −OH and $-NH_2$. Since many non-metals are more electronegative than carbon, they exhibit a negative inductive effect with respect to carbon. The greater the difference in electronegativity the larger the negative inductive effect and hence the more the polarisation of the bond. The typical trend in bond polarisation due to the difference in the electronegativity is shown as follows.

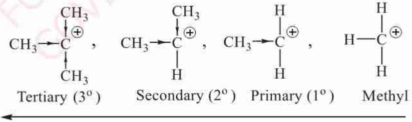
$$CH_3C{\equiv}N > H_2C{=}O > CH_3{-}F > CH_3{-}Cl > CH_3{-}Br > CH_3{-}I > CH_3{-}OH$$

$$\xrightarrow{\hspace{10cm}}$$

Increase in polarisation

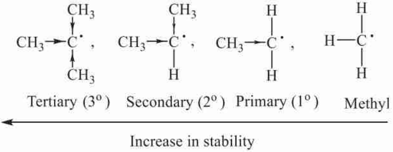
Positive inductive (+I) effect

Positive inductive effect is the type of inductive effect in which the substituent group or an atom bonded to a carbon atom partially releases electrons to the carbon atom. The positive inductive effect is commonly observed in the carbon atom bonded to alkyl groups. If an organic reaction involves the formation of an intermediate carbocation, the positive inductive effect stabilises the carbocation. The stability of carbocation increases with an increase of the number of alkyl group due to their +I effect.

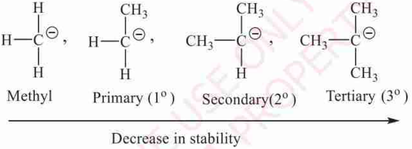


Increase in stability

Similarly, if an organic reaction involves the formation of an intermediate free radical, the stability of a free radical due to +I effect increases with an increase in the number of alkyl group.



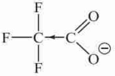
However, the trend in stability is opposite for the reactions which form intermediate carbanions, where the stability decreases with an increase in the number of alkyl groups.



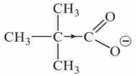
The positive inductive effects cause some abnormalities in organic bases (amines) and organic acids which are carboxylic acids and phenols. The main effects in these compounds are to decrease acid strength and increase base strength.

Acid strengths of carboxylic acids and phenols

In carboxylic acids (R—COOH), the electron withdrawing group decreases the negative charge on the carboxylate ion, hence stabilising it. As a result, the acid strength increases.

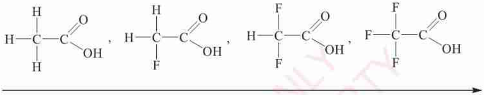


However, the positive inductive effect (+I) destabilises the carboxylate ion and therefore decreases the acid strength. The destabilisation of the carboxylate ion by the +I effect is shown as follows:



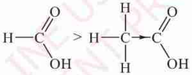
The consequences of the inductive effects are summarised in the following examples:

(a) In carboxylic acids, the acid strength increases with an increase in the number of electron withdrawing groups on the α-carbon due to its negative inductive effect (–I).



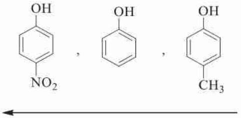
Increase in acid strength

(b) Formic acid (methanoic acid) is stronger than acetic acid because the methyl group (– CH_3) destabilises the carboxylate ion by positive inductive effect.



Positive inductive effect increases the electron density on the carboxylate ion making the hydrogen atom tightly held. Therefore, the ability to release proton (acidity) decreases. The case is opposite for a negative inductive effect.

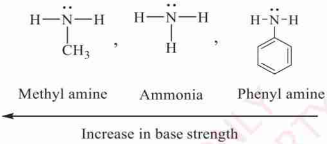
(c) The acid strength of phenols increases when bonded with an electron withdrawing group (negative inductive effect) and decreases when bonded with an electron donating group (positive inductive effect).



Increase in acid strength

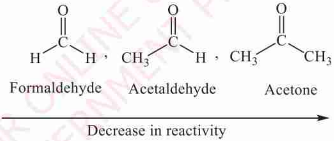
Base strengths of amines

The electron donating groups such as alkyl groups increase the base strengths of amines by +I effect. This is because the release of electrons increases the electron density on the amine group ($-NH_2$) and therefore the ability to attract proton ($H^{\oplus}$) increases. Contrary, the electron withdrawing groups such as aryl decrease the base strength by negative inductive effects. The order of basicity of alkyl and aryl amines with respect to ammonia is:



Reactivity of carbonyl compounds

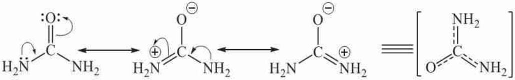
The trend in the reactivity of carbonyl compounds towards nucleophiles is in the following order:



The reason for low reactivity of acetone relative to acetaldehyde and formaldehyde is due to +I effect caused by two methyl ($-CH_3$) groups. The positive inductive (+I) effect increases the electron density on the carbonyl carbon, therefore lowering the ability to attract nucleophile. Acetaldehyde has only one methyl ($-CH_3$) group, and hence low +I effect and formaldehyde which has no methyl group is the most reactive of the three.

Mesomeric effects (mesomerism) or resonance effects

Mesomeric effect is the effect of withdrawing or releasing electrons, attributed to a particular substituent through the delocalisation of *pi* (π) -bond electrons. The resonance or mesomeric structures are hypothetical structures with different arrangements of electrons but with identical positions of atoms. However, these resonance structures are only imaginary, and the true structure is assumed to be the average or hybrid of all the valid resonance structures. The mesomeric effect is observed in compounds containing alternating single and multiple bonds. For example, the resonance structures of urea are shown as follows:

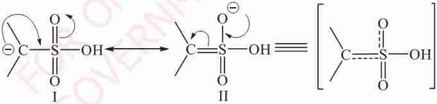


Resonance hybrid of urea

There are two types of mesomeric effects: negative mesomeric or resonance effect (–M or –R) and positive mesomeric or resonance effect (+M or +R).

Negative mesomeric or resonance effects (–M or –R)

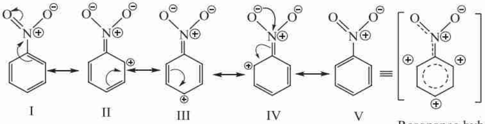
Negative mesomeric effects occur when a compound containing a substituent group withdraws electrons by delocalisation mechanism from the rest of the compound. Typical groups that show negative mesomeric effects include nitro group (–NO_2), carbonyl group (–C═O), cyanide group (–C≡N), carboxylic acid group (–COOH) and sulphonic acid group (–SO_3H). Negative mesomeric effect by sulphonic acid group is shown below.



Resonance hybrid of sulphonic acid group

The –M or –R effects stabilise the negatively charged carbon atom (carbanion) by delocalising the negative charge that is present on the carbanion. The –M or –R effect also destabilises the positively charged carbon atom (carbocation) by withdrawing an electron and making it more electron deficient hence very unstable. Since the negatively charged carbons (carbanions) are not very common, the influence of –M or –R effects is more pronounced in species that form carbocation.

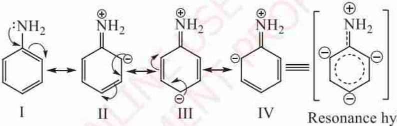
An example of negative mesomeric effect of a nitro group in nitrobenzene is shown as follows;



Resonance hybrid of nitrobenzene

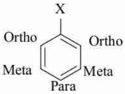
Positive mesomeric or Resonance effects (+M or +R)

Positive mesomeric effects occur when a compound containing a substituent group releases electrons by delocalisation mechanism to the rest of the compound. Typical groups that show +M or +R effect include hydroxyl group (–OH), alkoxyl group (–OR), sulphydryl group (–SH), sulphanyl group (–SR) and amine group (–NH_2). An example is shown by +M or +R effect by phenyl amine.



Resonance hybrid of phenylamine

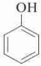
The amine group releases electrons towards benzene ring by positive mesomerism. The electrons are delocalised throughout the benzene ring, as a result, the electron density increases on the benzene ring especially at the *ortho* and *para* positions.



Because of the increased electron density on benzene ring, phenyl amine (aniline) becomes more reactive towards the electrophilic substitution reaction. Also, the positive mesomerism lowers the electron density on nitrogen of the amine group (–NH_2). As a result, phenylamine is less basic than alkyl amine due to a decrease in its ability to attract protons ($H^{\oplus}$). Similarly, the positive mesomeric effect makes phenol more acidic than alcohol.

R—OH

Alcohol
(less acidic)



Phenol
(more acidic)

The strength of mesomeric or resonance effects against inductive effects

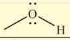
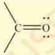
In most cases, the strength of mesomeric effects is higher than that of inductive effects. For example, both –OH and –NH_2 groups release electrons by a positive mesomeric effect. However, since both consist of electronegative atoms, they also tend to withdraw electrons by a negative inductive effect. The positive mesomeric effect is stronger than the negative inductive effect, therefore the net result is the release of electrons toward the rest part of the molecule. This concept explains why phenol and aniline are more reactive toward substitution electrophilic reactions than benzene.

Reactivity of lone pairs

A *lone pair* is a pair of electrons present in an atom's valence shell but is not involved in the covalent bond formation. Lone pairs in organic molecules play a major role in both nucleophilic addition or substitution and mesomeric effects. However, the reactivity of lone pairs in these organic reactions is largely contributed by the type of hybridisation of atoms in the molecule and hence the distance of lone pair electron from the nucleus. Nitrogen and oxygen atoms mainly have reactive lone pairs when they are sp^3 hybridised. The sp^3 hybrid orbitals consist of one *s* and three *p* ($p + p + p$) orbitals. That is, a 75% *p* character and 25% *s*-character. For the case of sp^2 hybrid orbitals, which have one *s* and two *p* ($p + p$) orbitals the percentages of *s* and *p* characters are 33.3% and 66.7%, respectively. The *sp* hybrid orbitals, which have one *s* and one *p*-orbitals have 50% *s*-character and 50% *p*-character. The percentage of *s* and *p* characters in the hybrid orbitals is directly related to the distance of the lone pair electrons from the nucleus. Because of a larger percentage of the *p* character in the sp^3 hybrid orbitals, the lone pair of electrons are relatively far from the nucleus compared to those in sp^2 and *sp* hybrid orbitals. As a result, the lone pair electrons in sp^3 hybrid orbitals experience a weaker nuclear attractive force and therefore are more reactive. In sp^2 hybrid orbitals, the lone pair of electrons are relatively closer to the nucleus, and experience strong nuclear attractive forces. therefore, they are unreactive.

The lone pair electrons in *sp* hybrid orbitals, which have the highest percentage of *s*-character (50%), are closest to the nucleus. Therefore, they experience stronger nuclear forces of attraction compared to the sp^2 and sp^3 hybrid orbitals. As a result, these lone pair electrons in *sp* hybrid orbitals are very unreactive. The reactivity of lone pairs in nitrogen and oxygen with different types of hybridisation are summarised in Table 1.3.

Table 1.3 The reactivity of lone pair of electrons in nitrogen and oxygen

Element	Number of lone pairs	Functional group	Hybridisation	Reactivity
Nitrogen	1	$-\ddot{N}H_2$	sp^3	Reactive
		$—C\equiv N:$	sp	Unreactive
Oxygen	2		sp^3	Reactive
			sp^2	Unreactive

In alkynes (—C≡C—), the carbon atoms are *sp* hybridised. Because of the high percentage of *s*-character, (50%) the bonding electrons are strongly attracted to the nucleus. As a result, the bonding electrons can be completely removed from the bond and exist as a lone pair in the *sp* hybrid orbital. This makes the carbon hydrogen (C—H) bond very weak and hence easy to break, and therefore releasing the proton ($H^{\oplus}$). This phenomenon explains why alkynes that consists of a terminal hydrogen like R—C≡C—H have an acidic property (proton releasing property).

For the case of sp^2 hybrid orbitals, the bonding electrons experience less force of attraction from the nucleus because they are further away from it. Consequently, sp^2 hybridised carbon atoms are said to be less electron attracting (less electronegative) than *sp* hybridised carbon atoms. Similarly, the sp^3 hybrid orbitals of carbon atoms are less electron attracting (less electronegative) than the sp^2 hybrid orbitals of carbon atoms. The trend of electronegativity of hybridised carbon atoms is in the order:

$$\xrightarrow{sp^3,\ sp^2,\ sp}$$

Increase in electronegativity

Exercise 1.4

1. (a) Define the term inductive effect.
   (b) Why is chloroacetic acid a stronger acid than acetic acid?
2. State whether the following groups show a negative or a positive inductive effect:

   (a) $-NO_2$ (b) $-OCH_3$ (c) $-COOH$ (d) $-CH_3$

   (e) $-CH_2CH_3$ (f) $-C_6H_5$ (g) $-NH_2$ (h) $-C(CH_3)_3$
3. Explain the comparative stability of primary, secondary, and tertiary carbocations using inductive effect.
4. (a) Explain the meaning of mesomeric effect or mesomerism.
   (b) What are the conditions necessary for mesomeric effect to occur?
5. Explain the influence of inductive effect on the acidity of carboxylic acids and basicity of amines.

Revision exercise 1

1. (a) What is meant by the term isomerism?
   (b) Describe the two main types of isomerism.
2. Draw structures for the *cis*- and *trans*-isomers of 1, 2-dichloropropene.
3. Using examples, summarise the general rules that are used in writing organic reaction mechanisms.
4. Label each of the following as 1°, 2°, 3° or methyl carbocation and then arrange them in the order of increasing stability (from least stable to most stable). $CH_3^{\oplus}$, $(CH_3)_3C^{\oplus}$, $CH_3CH_2^{\oplus}$, $(CH_3)_2CH^{\oplus}$. Explain your answer.

5. How many reactants are involved in the formation of the reaction intermediate in an S_N1 type reaction?

6. Which of the following reactants will undergo S_N1 type of reaction? Give reasons for your answer.

   (a) CH_3CH_2Cl

   (b) $CH_3CH(CH_3)Cl$

   (c) $CH_3C(CH_3)_2Cl$

   (d) $(CH_3)_3CCH_2Cl$

7. Show how the stability of carbocation increases with an increase in the number of substituent groups.

8. Arrange the following groups in the order of decreasing negative inductive effect:

   $-Br$, $-CONH_2$, $-CN$, $-SO_3H$, $-NO_2$, $-CHO$, $-OH$, $-F$,
   $-I$, $-COOH$, $-OR$, $-NH_2$, $-Cl$,

9. Why are cyanides and carbonyl compounds less reactive than alcohols and amines?

10. Among unsaturated hydrocarbons (alkenes, alkynes, and arenes), it is only alkenes which show *cis-trans* isomerism. Explain.

11. Explain why the lone pair of compounds with sp^3 hybrid orbital is more reactive than compounds with sp^2 and sp hybrid orbitals.

12. Why alkynes with terminal hydrogens have acidic properties, while alkenes and alkanes with terminal hydrogens have no acidic properties?

Chapter Two

Aliphatic hydrocarbons

Introduction

Aliphatic hydrocarbons (alkanes, alkenes, and alkynes) are either open chains or non-aromatic organic compounds containing carbon and hydrogen as the only elements. They exist as gases, liquids, and solids with the wide range of uses such as in making solvents, constituents of rubber and plastics as well as source of energy on combustion processes. Thus, in this chapter you will learn about properties, preparation, and uses of aliphatic hydrocarbons.

2.1 Properties of aliphatic hydrocarbons

Generally, aliphatic hydrocarbons are flammable. They undergo combustion reaction with oxygen in the atmosphere to form carbon dioxide, water vapour, and energy. In this section you will learn about general physical and chemical properties as well as the nature of bonding in aliphatic hydrocarbons.

2.1.1 General physical and chemical properties of aliphatic hydrocarbons

Elements that form hydrocarbon molecules are covalently bonded to each other which make hydrocarbons to be insoluble in water but soluble in organic solvents. The boiling and melting points of aliphatic hydrocarbons increase with the increase in the number of carbon atoms and hence the molecular masses. The physical states of aliphatic hydrocarbons are determined by the number of carbon atoms. Hydrocarbons with few carbon atoms exist as gases. As the number of carbon atoms increases, the physical state changes from gas to liquid and finally to solid.

Hydrocarbons that consist of only carbon-carbon single bonds are least reactive than those containing carbon-carbon double bonds and triple bonds. This is because it is very difficult to break a strong sigma bond than the *pi* (π) -bond.

2.1.2 Nature of bonding in aliphatic hydrocarbons

There are two main classes of aliphatic hydrocarbons; saturated and unsaturated hydrocarbons. *Saturated hydrocarbons* that consist of only carbon-carbon single bonds (C—C) are called alkanes. *Unsaturated hydrocarbons* consist of carbon-carbon multiple bond(s). These include alkenes which consist of carbon-carbon double bonds (C═C) and alkynes which consist of carbon-carbon triple bonds (C≡C).

2.2 Alkanes

Alkanes are saturated aliphatic hydrocarbons which contain only carbon-carbon single bonds. All carbon atoms in alkanes are sp^3 hybridised. The sp^3 hybridisation of carbon is shown in Figure 2.1.

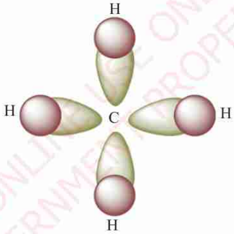


Figure 2.1 sp^3 hybrid orbitals overlapping in methane

The sp^3 hybrid orbitals of carbon contain four unpaired electrons, which has the ability of forming a maximum of four sigma bonds with other atoms. It is said to be saturated, and hence alkanes are generally known as saturated hydrocarbons. The general formula for alkanes is C_nH_{2n+2} where n is the number of carbon atoms. For example, if n equals to 1, the molecular formula of the alkane will be CH_4 and if n equals to 2, the molecular formula of the alkane will be C_2H_6 and when n equals to 3 the molecular formula will be C_3H_8. In this section, homologous series, sources of alkanes, IUPAC nomenclature of alkanes, laboratory and industrial preparation, physical and chemical properties, and uses of alkane will be covered.

2.2.1 Homologous series

A *homologous series* is a series of organic compounds with the same functional group, similar properties and each member differs from the other by a methylene ($-CH_2$) group. Members of the same homologous series are represented by the same general molecular formula and also members have the same mode of preparations. For example, the homologous series of alkanes have the general molecular formula C_nH_{2n+2}. Some of the members of the homologous series of alkanes are shown in Table 2.1.

Table 2.1 Homologous series of alkanes

Alkanes			**Alkanes**		
Number of carbon atoms	Molecular formula	IUPAC name	Number of carbon atoms	Molecular formula	IUPAC name
1	CH_4	Methane	6	C_6H_{14}	Hexane
2	C_2H_6	Ethane	7	C_7H_{16}	Heptane
3	C_3H_8	Propane	8	C_8H_{18}	Octane
4	C_4H_{10}	Butane	9	C_9H_{20}	Nonane
5	C_5H_{12}	Pentane	10	$C_{10}H_{22}$	Decane

Alkyl group

An *alkyl group* is a hydrocarbon group which is formed when one hydrogen is removed from an alkane. The general formula for alkyl group is C_nH_{2n+1}; where n represents the number of carbon atoms in that group and it assists on writing the molecular formula of an alkyl group. For example, if n equals to 1, the molecular formula for the alkyl group will be $-CH_3$ (methyl) if n equals to 2, the molecular formula will be $-C_2H_5$ (ethyl) and if n equals to 3 the molecular formula will be $-C_3H_7$ (propyl). The names of the alkyl groups are obtained by replacing the suffix *–ane* from the corresponding alkane with *–yl*. For example, the removal of one hydrogen from methane (CH_4) forms a methyl group ($-CH_3$). Similarly, ethane (C_2H_6) forms an ethyl group ($-C_2H_5$). Some of the alkyl groups are shown in Table 2.2.

Table 2.2 Homologous series of alkyl groups

Alkyl groups, R-			**Alkyl groups, R-**		
Number of carbon atoms	Molecular formula	Name	Number of carbon atoms	Molecular formula	IUPAC name
1	$-CH_3$	Methyl	6	$-C_6H_{13}$	Hexyl
2	$-C_2H_5$	Ethyl	7	$-C_7H_{15}$	Heptyl
3	$-C_3H_7$	Propyl	8	$-C_8H_{17}$	Octyl
4	$-C_4H_9$	Butyl	9	$-C_9H_{19}$	Nonyl
5	$-C_5H_{11}$	Pentyl	10	$-C_{10}H_{21}$	Decyl

2.2.2 Sources of alkanes

The major source of alkanes is petroleum. The term *petroleum* originates from the Latin word *petra*, rock, and *oleum*, oil. It is used to describe a broad range of hydrocarbons that are found as gases or liquids beneath the earth's surface. The two most common forms are natural gas and crude oil. Also, coal is another important source of hydrocarbons (alkanes).

Natural gas is a mixture of lightweight alkanes obtained from its reserve in the earth's crust. A typical sample of natural gas from its source contains 80% methane (CH_4), 7% ethane (C_2H_6), 6% propane (C_3H_8), 4% butane and isobutane (C_4H_{10}), and 3% pentanes (C_5H_{12}). The propane, butane and pentane are isolated from the mixture before the gas is sold. The commercial natural gas delivered to the customer is therefore a mixture of methane and ethane.

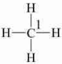
Crude petroleum is a complex mixture that is between 50 and 95% hydrocarbon by weight. The first step in refining crude oil involves separating the oil into different hydrocarbon fractions by fractional distillation. Since there are a number of factors that influence the boiling points of hydrocarbons such as branching and number of carbons, petroleum fractions are complex mixtures. For example, more than 500 different hydrocarbons have been identified in the gasoline fractions.

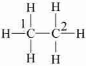
Coal is a sedimentary rock that burns to give out heat energy and other by-products. It was formed by the decomposition of plant matter and it is a complex substance that can be found in many forms. *Destructive distillation* is the process of heating coal in the absence of air to form coke, coal tar, and coal gas. Coal gas which is a mixture of hydrogen, methane and carbon monoxide is used as a fuel.

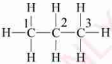
2.2.3 IUPAC nomenclature of alkanes

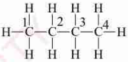
IUPAC is an abbreviation for the International Union of Pure and Applied Chemistry. This union has put forward the rules for naming of organic compounds. The following are the rules for naming alkanes:

1. Identify the parent chain of an alkane. The parent chain is the longest continuous chain of carbon atoms in the molecule. The number of carbon atoms in the parent chain gives the name of the parent alkane. The name of the parent chain of alkanes ends with the suffix *–ane*. Thus, the parent names with 1, 2, 3, and 4 carbon atoms are methane, ethane, propane, and butane, respectively and the names of other alkanes proceed to the nth carbon atom.

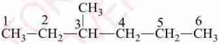






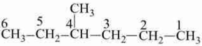


2. Any carbon chain branching off the parent chain is named as alkyl group, because it has one hydrogen less than a normal alkane. For example, when a hydrogen atom is removed from propane the group left is called propyl. The names of the common alkyl groups are shown in Table 2.2. When one or more hydrogen atoms of the parent chain are replaced by other groups, the parent chain is numbered from the end nearest to the branch to identify the locations of carbon atoms where the replacement is made. Consider the following naming of the same compound by using two different systems:



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

3-methylhexane
Compound I (Correct)



$$\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

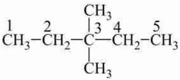
4-methylhexane
Compound II (Incorrect)

Compound (I) is correctly named because the methyl group is located at carbon number three of the parent chain (hexane) which is the nearest end, while compound (II) is incorrectly named because the methyl group is located at carbon number four which is far to the end.

Note that, the branch and the parent names are written as a single word, a hyphen is used to separate the number and alkane name, and the commas are used to separate the numbers, *example*; 3,3-dimethylhexane.

3. The prefix such as *di-, tri- tetra-*, and *pent-* are used when there are more than one alkyl groups of the same kind on the same parent chain. The numbers indicate the locations of identical alkyl groups.

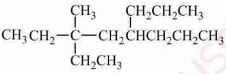
Example:



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{CH_3}{\underset{CH_3}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

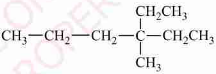
3,3-dimethylpentane

4. If there are two or more different alkyl groups on the same parent chain, the names of the groups are written by the following alphabetical order.
Example:



$$CH_3CH_2-\overset{CH_3}{\underset{CH_2CH_3}{C}}-CH_2\overset{CH_2CH_2CH_3}{CH}CH_2CH_2CH_3$$

3-ethyl-3-methyl-5-propyloctane



$$CH_3-CH_2-CH_2-\overset{CH_2CH_3}{\underset{CH_3}{C}}-CH_2CH_3$$

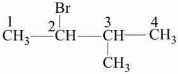
3-ethyl-3-methylhexane

5. Alkanes may have many different types of substituent groups such as nitro ($-NO_2$), amine ($-NH_2$), and halide ($-X$) groups. When the substituent group is a halogen, the suffix *-ine* is dropped and replaced by suffix "*-o*". Table 2.3 shows the list of some common substituent groups.

Table 2.3 Names of some common substituent groups

Substituent group	Name	Group	Name
$-F$	Fluoro	$-NO$	Nitroso
$-Cl$	Chloro	$-OCH_3$	Methoxy
$-Br$	Bromo	$-OC_2H_5$	Ethoxy
$-I$	Iodo	$-OR$	Alkoxy
$-NO_2$	Nitro		
$-NH_2$	Amino		

Examples:



$$\overset{1}{CH_3}-\overset{2}{CH}(Br)-\overset{3}{CH}(CH_3)-\overset{4}{CH_3}$$

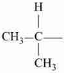
2-bromo-3-methylbutane

$$\overset{1}{CH_3}-\overset{2}{CH}(F)-\overset{3}{CH_3}$$

2-fluoropropane

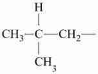
Sometimes, the alkyl groups are named with prefixes such as *iso*-, *sec*-, *neo*- and *tert*-. The alkyl group where a methyl ($-CH_3$) group is present at the end of the chain is called the *iso*alkyl group. That is, if the second carbon atom from the end of the chain contains $-CH_3$, the substituent is called an isoalkyl group.

Examples:



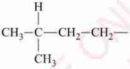
$$CH_3-\underset{CH_3}{\overset{H}{C}}-$$

1-methylethyl
(*iso*-Propyl)



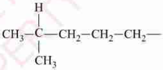
$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-$$

2-methylpropyl
(*iso*-Butyl)



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2-$$

3-methylbutyl
(*iso*-Pentyl)

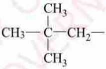


$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2-CH_2-$$

4-methylpentyl
(*iso*-Hexyl)

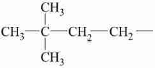
If two methyl groups are present at the secondary carbon atom of the chain, the alkyl group is called *neo*alkyl.

Examples:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$$

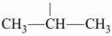
2,2-dimethylpropyl
(*neo*-Pentyl)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-$$

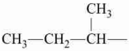
3,3-dimethylbutyl
(*neo*-Hexyl)

When the hydrogen atom of the alkyl substituent group is removed from the secondary carbon, then the prefix *-sec* is used to mean secondary carbon.



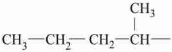
$$CH_3-\overset{|}{CH}-CH_3$$

1-methylethyl
(*sec*-Propyl)



$$CH_3-CH_2-\overset{CH_3}{CH}-$$

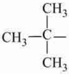
1-methylpropyl
(*sec*-Butyl)



$$CH_3-CH_2-CH_2-\overset{CH_3}{CH}-$$

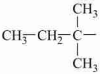
1-methylbutyl
(*sec*-Pentyl)

If the hydrogen atom has been removed from the tertiary carbon of the alkyl group, then the prefix-*tert* is used.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-$

1,1-dimethylethyl
(*tert*-Butyl)



$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$

1,1-dimethylpropyl
(*tert* -Pentyl)

Note that, the prefixes *iso*- and *neo*- form part of the name of the alkyl groups, consequently, the letters *i* and *n* must be considered when naming substituent groups in the alphabetical order.

Isomerism in alkanes

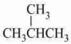
Isomerism is the tendency of a compound to exist in two or more forms with the same molecular formula but different properties due to different arrangements of atoms. Types of isomers that exist in alkanes are constitutional isomers and stereoisomers.

Types of constitutional isomers are skeletal (structural), functional, and positional isomers. In alkanes, structural isomers can exist, because they possess carbon-carbon single bond as a functional group. Note that, in cyclic alkanes both structure and positional isomers can exist. Butane (C_4H_{10}) is the smallest alkane that exhibits structural isomerism.

Examples:

$CH_3CH_2CH_2CH_3$

n-Butane



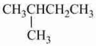
$CH_3\overset{CH_3}{C}HCH_3$

2-methylpropane

Pentane (C_5H_{12}) has three isomers:

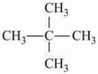
$CH_3CH_2CH_2CH_2CH_3$

n-Pentane



$CH_3\underset{CH_3}{C}HCH_2CH_3$

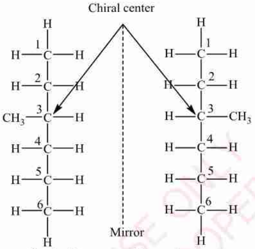
2-methylbutane



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

2,2-dimethylpropane

The second type of isomerism that exists in alkanes is stereoisomerism. The type of stereoisomerism which is exhibited by alkanes is optical isomerism. Optical isomerism exists when two molecules are mirror images of each other, and they cannot be superimposed because each one is asymmetric. In other words there is no plane of symmetry that divides them into two equal parts. These asymmetric molecules are called chiral, because they contain carbon atom that is bounded to four different groups. An example of optical isomerism in alkane is shown as follows:



Optical isomers of 3-methylhexane

The molecule 3-methylhexane has a carbon chiral centre, bonded to four different groups which are hydrogen, methyl, ethyl, and propyl groups. Since the mirror images of 3-methylhexane are non-superimposable, this implies that the two molecules are optical isomers (enantiomers).

2.2.4 Preparation of alkanes (paraffins)

Alkanes as saturated aliphatic hydrocarbons can be prepared by various methods. These methods can be divided into two categories, namely laboratory preparation and industrial production.

Laboratory preparation of alkanes

In the laboratory, alkanes can be prepared in large or small scales depending on the need of a compound. In both cases, the preparation methods can be categorised into three main types depending on whether they maintain the same number of carbon atoms, reduce the number of carbon atoms or increase the number of carbon atoms.

The reactions which maintain the number of carbon atoms

The reactions which produce alkanes by maintaining the number of carbon atoms of the original compound include: hydrogenation of unsaturated hydrocarbons, hydrolysis of Grignard reagents, and reduction of alkyl halides (RX).

Hydrogenation of unsaturated hydrocarbons (alkenes and alkynes)

Hydrogenation is the reaction which involves the addition of hydrogen atoms to unsaturated hydrocarbon compounds. This reaction is normally catalysed by catalysts such as platinum, nickel or palladium.

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Hydrogen gas}}{H_2(g)} \xrightarrow{\text{Ni, 200 °C}} \underset{\text{Ethane}}{CH_3CH_3}$$

$$\underset{\text{Ethyne}}{HC{\equiv}CH} + \underset{\text{Hydrogen gas}}{2H_2(g)} \xrightarrow{\text{Ni, 200 °C}} \underset{\text{Ethane}}{CH_3CH_3}$$

Nickel catalyst in these reactions is used in finely powdered form. When platinum or palladium are used as catalysts instead of nickel, the reactions take place at normal temperature.

Hydrolysis of Grignard reagents

Grignard's reagents are organic compounds in which a magnesium metal is directly bonded to a carbon atom of alkyl group on one side and halogen on the other side. The reagents were discovered in 1900 by a French chemist Victor Grignard (1871-1935). Organic compounds which contain metallic atom directly bonded to a carbon atom of that compound are generally known as organometallic compounds. Grignard's reagents are prepared by reacting an alkyl or aryl halide with magnesium metal in dry ether.

$$\underset{\text{Alkyl halide}}{R{-}X + Mg} \xrightarrow[\text{heat}]{\text{dry ether}} \underset{\text{Grignard reagent}}{RMgX}$$

The Grignard reagents undergo double decomposition with water or other compounds having an active hydrogen atom (H) to give alkanes and other products. The active hydrogen (H) atom is the one which is bonded to more electronegative elements such as oxygen (O), nitrogen (N), fluorine (F), and terminal alkynes ($R{-}C{\equiv}C{-}H$).

When water is used to hydrolyse the Grignard reagent, the products formed are alkane and magnesium hydroxide halide ($[Mg(OH)X]$).

$$\overset{\ominus\oplus}{RMgX} + \overset{\oplus}{H}{-}\overset{\ominus}{OH} \xrightarrow{H^{\oplus}} R{-}H + [Mg(OH)X]$$

Example:

$$CH_3CH_2Br + Mg \xrightarrow[\text{ether}]{\text{dry}} CH_3CH_2MgBr \xrightarrow{H_2O,\ H^{\oplus}} CH_3CH_3 + Mg(OH)Br$$

Bromoethane   Ethylmagnesium bromide   Ethane

When the alcohol is used to decompose the Grignard reagent,alkaneand alkoxy magnesium halides are formed.

Example:

$$CH_3CH_2MgBr + CH_3CH_2OH \longrightarrow CH_3CH_3 + Mg(OC_2H_5)Br$$

Ethylmagnesium bromide   Ethanol   Ethane   Ethoxymagnesium bromide

Reduction of haloalkanes (alkyl halide)

Haloalkanes can be reduced through various reactions to produce alkanes and other products depending on the reagent(s) involved.

(a) Reduction of alkyl halide by nascent hydrogen

The haloalkanes can be reduced by reactive hydrogen (nascent hydrogen) to form alkanes and metal halides.

$$RX + Zn + HX \longrightarrow RH + ZnX_2$$

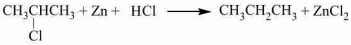
The nascent hydrogen can be prepared by mixing a metal with acid or alcohol.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

Nascent hydrogen

The gaseous hydrogen produced during this chemical reaction is called *nascent hydrogen* and always occurs in atomic state. When the alkyl halide is present, it reacts with nascent hydrogen and reduces it to alkane, in the absence of a substance to react with, it recombines into a molecular hydrogen (H_2).

Example:



$$\underset{\displaystyle Cl}{CH_3\underset{|}{C}HCH_3} + Zn + HCl \longrightarrow CH_3CH_2CH_3 + ZnCl_2$$

2-chloropropane   Propane

(b) Reduction of alkyl halides by using hydrogen gas in the presence of Pt

The heating of an alkyl halide (RX) with reducing agents such as $LiAlH_4$/ether, Pd/H_2, Pt/H_2 and Zn/conc. HCl produce alkanes and hydrogen halides.

$$RX + H_2 \xrightarrow[\text{heat}]{\text{Pt or Pd}} RH + HX$$

Examples:

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_2 \xrightarrow[\text{heat}]{\text{Pt or Pd}} \underset{\text{Ethane}}{CH_3CH_3} + HBr$$

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow[\text{heat}]{\text{Pt or Pd}} CH_3CH_2CH_3 + HCl$$

(c) Reduction of alkyl halide with red phosphorus and hydrogen iodide

When an alkyl halide is mixed with hydrogen iodide and heated in the presence of red phosphorus, the alkane and iodine are formed. In the absence of red phosphorus, the iodine will react with formed alkane to form alkyl halide. Therefore, the role of red phosphorus is to react with I_2 to prevent reaction reverting to reactants.

Example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + 2HI \xrightarrow[\text{red P}]{167\ ^{o}C} \underset{\text{Ethane}}{C_2H_6} + HBr + I_2$$

$$2P + 3I_2 \longrightarrow 2PI_3$$

Reduction of alcohols, aldehydes and ketones by using hydrogen iodide

Hydrogen iodide (HI) is used to reduce alcohols, aldehydes, and ketones to alkanes in the presence of red phosphorus.

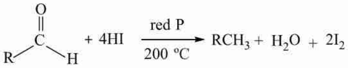
(a) Reduction of alcohols

$$R{-}OH + 2HI \xrightarrow[200\ ^{o}C]{\text{red P}} RH + H_2O + I_2$$

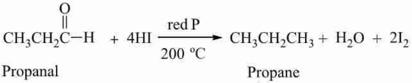
Example:

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + HI \xrightarrow[200\ ^{o}C]{\text{red P}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O + I_2$$

(b) Reduction of aldehyde



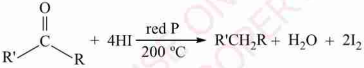
Example:



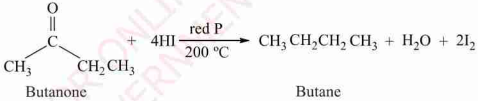
$$CH_3CH_2\overset{\overset{O}{\|}}{C}-H + 4HI \xrightarrow[200\ ^{\circ}C]{red\ P} CH_3CH_2CH_3 + H_2O + 2I_2$$

Propanal Propane

(c) Reduction of ketone



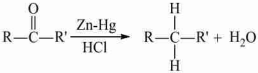
Example:



Clemmensen reduction (reduction of carbonyl compounds)

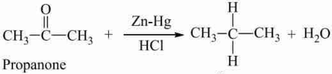
The reduction of carbonyl compounds by using amalgamated zinc in concentrated HCl is called *Clemmensen reduction*. The reduction was named after the Danish chemist, Erick Christian Clemmensen (1876-1941) who discovered this reduction process.

The carbonyl compounds can be reduced by using amalgamated zinc and concentrated hydrochloric acid (HCl) to form alkanes. The amalgamated zinc in HCl is used as a reducing agent. The reaction is suitable for the reduction of carbonyl compounds which are stable to strong acidic medium.



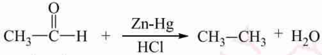
$$R-\overset{\overset{\large O}{\|}}{C}-R' \xrightarrow[HCl]{Zn\text{-}Hg} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{C}}-R' + H_2O$$

Examples:



$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3 + \xrightarrow[HCl]{Zn\text{-}Hg} CH_3-\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{C}}-CH_3 + H_2O$$

Propanone Propane

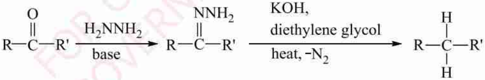


$$CH_3-\overset{\overset{\large O}{\|}}{C}-H + \xrightarrow[HCl]{Zn\text{-}Hg} CH_3-CH_3 + H_2O$$

Ethanal Ethane

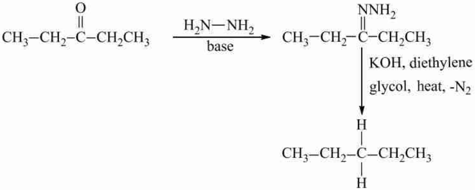
Wolff-Kishner reduction (reduction of carbonyl compounds)

In basic conditions, *Wolff-Kishner reduction* is suitably used to reduce all acid sensitive carbonyls which are stable in strong basic conditions to form alkanes. The Wolff-Kishner reduction was named after German chemist Ludwig Wolff (1857-1919) and Russian chemist, Nikolai Kishner (1867-1935) who discovered this reduction process in 1911. The reduction process involves conversion of carbonyl group to methylene group. The carbonyl compound is first treated with excess hydrazine to form an intermediate hydrazone which on heating in the presence of a strong base, forms an alkane.



$$R-\overset{\overset{\large O}{\|}}{C}-R' \xrightarrow[base]{H_2NNH_2} R-\overset{\overset{\large NNH_2}{\|}}{C}-R' \xrightarrow[\text{heat, }-N_2]{\text{KOH, diethylene glycol}} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{C}}-R'$$

Example:



$$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-CH_2CH_3 \xrightarrow[base]{H_2N-NH_2} CH_3-CH_2-\overset{\overset{\large NNH_2}{\|}}{C}-CH_2CH_3 \xrightarrow[\text{glycol, heat, }-N_2]{\text{KOH, diethylene}} CH_3-CH_2-\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{C}}-CH_2CH_3$$

By hydrolysis of carbides

The hydrolysis of aluminium and beryllium carbides forms hydroxides and methane, the only alkane compound formed by the method.

$$\mathrm{Al_4C_3 + 12H_2O \xrightarrow{heat} 4Al(OH)_3 + 3CH_4}$$

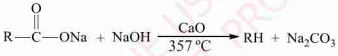
$$\mathrm{Be_2C + 4H_2O \xrightarrow{heat} 2Be(OH)_2 + CH_4}$$

Reactions which decrease the number of carbon atoms of the reagents

Reactions involving the decrease in the number of carbon atoms of the reactants include soda lime decarboxylation of carboxylic salts and cracking of the larger saturated hydrocarbons to smaller molecules.

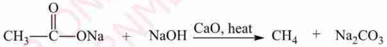
Decarboxylation of carboxylate salts

The treatment of carboxylate salts and carboxylic acids with soda lime (NaOH and CaO) produces a carbonate and an alkane.



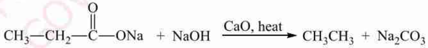
$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}ONa + NaOH \xrightarrow[357\,^{\circ}C]{CaO} RH + Na_2CO_3}$$

Examples:



$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}ONa + NaOH \xrightarrow{CaO,\ heat} CH_4 + Na_2CO_3}$$

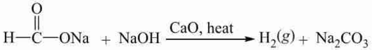
Sodium ethanoate　　Methane



$$\mathrm{CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}ONa + NaOH \xrightarrow{CaO,\ heat} CH_3CH_3 + Na_2CO_3}$$

Sodium propanoate　　Ethane

The calcium oxide (CaO), in this reaction helps in fusing the reaction mixtures and keeps NaOH dry but does not participate in the reaction. However, the decarboxylation of sodium formate yields hydrogen gas and a carbonate.



$$\mathrm{H{-}\overset{O}{\overset{\|}{C}}{-}ONa + NaOH \xrightarrow{CaO,\ heat} H_2(\mathit{g}) + Na_2CO_3}$$

Cracking of higher alkanes to produce lower alkanes

Cracking process is the method of preparing smaller alkanes from higher alkanes. This concept will be discussed in detail in the industrial production of alkanes.

Reactions which increase the number of carbon atoms of the reagents

In the preparation of saturated hydrocarbons, there are reactions which involve the coupling of reacting molecules to increase the number of carbon atoms. These reactions include: Wurtz synthesis, Kolbe electrolytic method, and Corey-House synthesis.

Wurtz synthesis

The Wurtz synthesis is named after Charles Adolphe Wurtz (1817-1884), a French chemist who discovered it in 1855. The reaction involves the coupling of two alkyl halide molecules in the presence of sodium metal in dry ether to form a higher alkane. When only aryl halides are subjected to coupling, the reaction is called *Fittig's reaction*; and if it involves both alkyl and aryl halides it is known as Wurtz- Fittig's reaction.

$$2RX + 2Na \xrightarrow{\text{dry ether}} R{-}R + 2NaX$$

Example:

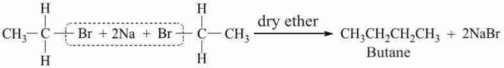
$$2CH_3CH_2I + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3 + 2NaI$$

The Wurtz synthesis is suitable for the synthesis of symmetrical alkanes, that is, those with even number of carbon atoms. The number of carbon atoms of the alkane produced is double compared to alkyl halide used as a reactant. The use of different alkyl halides as reactants in Wurtz synthesis produces a mixture of alkanes which is usually difficult to separate. Thus, Wurtz synthesis is not suitable for the preparation of asymmetrical alkanes, that is, with odd number of carbon atoms because of side reactions of alkyl halides themselves and with each other.

$$3RX + 3R'X + 6Na \xrightarrow{\text{dry ether}} R{-}R' + R'{-}R' + R{-}R + 6NaX$$

A mixture of ethyl bromide and methyl bromide for example, in the presence of sodium or other metals such as Zn, Ag and Fe and dry ether produces a mixture of propane, butane and ethane as shown in the following reactions:

$$CH_3{-}\boxed{Br + 2Na + Br}{-}CH_2CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Propane}}{CH_3CH_2CH_3} + 2NaBr$$



$$CH_3-\overset{H}{\underset{H}{C}}-\boxed{Br + 2Na + Br}-\overset{H}{\underset{H}{C}}-CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

$$CH_3-\boxed{Br + 2Na + Br}-CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

Overall equation,

$$3CH_3Br + 3CH_3CH_2Br + 6Na \xrightarrow{\text{dry ether}} CH_3CH_3 + CH_3CH_2CH_3$$
$$+ CH_3CH_2CH_2CH_3 + 6NaBr$$

Note that, the suitable alkyl halides which are used in Wurtz synthesis are those formed by least electronegative halogens such as bromine (Br) and iodine (I). This is because when highly electronegative halogens are used, the alkyl halide which is formed will be stable. Hence, it will be difficult to form alkyl radical which is important in forming an alkyl-metal intermediate ($R-M^{\oplus}$). Since Wurtz synthesis is an example of a substitution reaction, which depends on the electronegativity of halides, the order of substitution (S_N2) reaction is:

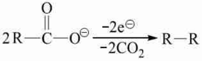
$$I > Br > Cl > F$$

Also depending on the position of halide group on the alkyl group, the halide group on the primary carbon is easily substituted compared to secondary and tertiary alkyl halides. The order of the substitution reaction in Wurtz synthesis is as follows:

$$1^{o} \text{ alkyl halide} > 2^{o} \text{ alkyl halide} > 3^{o} \text{ alkyl halide}$$

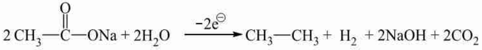
Kolbe electrolytic method

The Kolbe electrolytic method is an organic reaction named after Hermann Kolbe (1818-1884) a German chemist who discovered it. This reaction involves the electrolysis of carboxylic acid salts, which leads to the formation of alkyl radicals that dimerise to form alkanes as shown in Figure 2.2. Like in the Wurtz synthesis, the reaction is suitable for synthesis of symmetrical alkanes.



$$2R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow[-2CO_2]{-2e^{\ominus}} R-R$$

Example:



$$2\,CH_3-\overset{O}{\overset{\|}{C}}-ONa + 2H_2O \xrightarrow{-2e^{\ominus}} CH_3-CH_3 + H_2 + 2NaOH + 2CO_2$$

During this reaction, carbon dioxide is released at the anode along with the formation of alkanes, and hydrogen gas is released at the cathode.

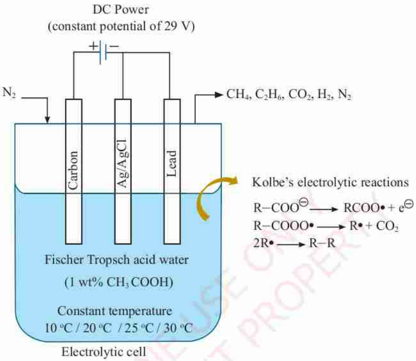


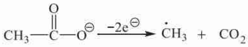
Figure 2.2 Experimental set up for Kolbe's electrolysis

Electrolytic mechanism,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + Na^{\oplus}$$

$$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$$

At anode



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} \xrightarrow{-2e^{\ominus}} \dot{C}H_3 + CO_2$$

$$2\dot{C}H_3 \xrightarrow{\text{dimerises}} \underset{\text{Ethane}}{CH_3CH_3}$$

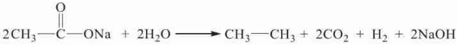
At cathode

$$2H_2O \rightleftharpoons 2OH^{\ominus} + 2H^{\oplus}$$

$$2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2(g)$$

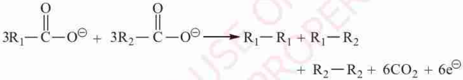
Net reaction $$2H_2O + 2e^{\ominus} \longrightarrow H_2(g) + 2OH^{\ominus}$$

Overall reaction,



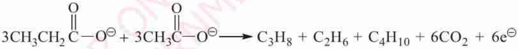
$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + 2H_2O \longrightarrow CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

Therefore, at the cathode, hydrogen gas is liberated and the solution around the cathode becomes alkaline due to the accumulation of NaOH. If a mixture of two different carboxylic salts are used in Kolbe's electrolysis, a mixture of alkanes is produced. The general reaction is:



$$3R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + 3R_2-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} \longrightarrow R_1-R_1 + R_1-R_2 + R_2-R_2 + 6CO_2 + 6e^{\ominus}$$

For example, the electrolysis of a mixture of sodium ethanoate and sodium propanoate produces a mixture of ethane, propane, and butane as shown in the following equation:



$$3CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + 3CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} \longrightarrow C_3H_8 + C_2H_6 + C_4H_{10} + 6CO_2 + 6e^{\ominus}$$

When a dicarboxylic acid salt is used in the Kolbe's electrolysis, the products are only unsaturated hydrocarbons. The Kolbe electrolytic method is also known as decarboxylative dimerisation or Kolbe reaction or Kolbe decarboxylation reaction.

Corey-House synthesis

This is another type of organic coupling reaction developed in 1990 by an American organic chemist; Elias James Corey (1928). The coupling involves the reaction between lithium dialkyl cuprate with an alkyl halide to form a saturated hydrocarbon, an organometallic compound and a lithium halide.

R_2CuLi	+	$R'X$	$\longrightarrow$	$R-R'$	+	RCu	+	LiX
Lithium dialkyl cuprate		Alkyl halide		Alkane		Alkyl copper		Lithium halide

The Corey-House synthesis occurs in three main steps:

Step 1: Formation of alkyl lithium.

The alkyl lithium is formed when an alkyl halide is treated with lithium metal and solvated in dry ether.

$$RX + 2Li \longrightarrow RLi + LiX$$

The alkyl halide which is used can be primary, secondary, or tertiary.

Step 2: The formation of lithium dialkyl cuprate

The lithium dialkyl cuprate is obtained by treating alkyl lithium with cuprous iodide.

$$2RLi + CuI \longrightarrow R_2CuLi + LiI$$

Step 3: Coupling of alkyl halide with lithium dialkyl cuprate with a second alkyl halide.

$$R_2CuLi + R'X \longrightarrow R{-}R' + RCu + LiX$$

For example, chloroethane (ethyl chloride) reacts with lithium to form ethyl lithium. When the ethyl lithium reacts with copper iodide, it forms lithium diethyl cuprate. Then, the lithium diethyl cuprate reacts with ethyl chloride to produce butane, organo copper and lithium chloride.

$$CH_3CH_2Cl + 2Li \xrightarrow{\text{dry ether}} CH_3CH_2Li + LiCl$$

Chloroethane	Ethyllithium	Lithium chloride

$$2CH_3CH_2Li + CuI \longrightarrow Li(CH_3CH_2)_2Cu + LiI$$

Ethyllithium	Copper(I) iodide	Lithium diethyl cuprate	Lithium iodide

$$Li(CH_3CH_2)_2Cu + CH_3CH_2Cl \longrightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2Cu + LiCl$$

Lithium diethyl cuprate	Butane	Ethyl copper

Like the Kolbe and Wurtz reactions, in Corey-House synthesis if the second alkyl halide used is different from the first one, a mixture of alkanes will be formed.

This reaction works successfully if the second alkyl halide is a methyl halide, benzyl halide, primary alkyl halide or a secondary cycloalkyl halide. The Corey-House synthesis is highly suitable in the synthesis of alkanes with odd number of carbon atoms.

Industrial production of alkanes

In industry, alkanes are prepared in large quantities by using one of the following methods: cracking of higher alkanes to produce lower alkanes, by direct synthesis from elements and catalytic hydrogenation of carbon monoxide.

Cracking of higher alkanes

When higher alkanes are heated to 400–600 ºC cracking take place and simple alkanes and alkenes are produced.

Example:

$$CH_3CH_2CH_2CH_3 \xrightarrow{400-600\ ^{\circ}C} \underset{\text{Ethane}}{CH_3CH_3} + \underset{\text{Ethene}}{CH_2{=}CH_2}$$

Direct synthesis from elements

When hydrogen is ignited in an electric arc, between carbon electrodes alkanes are produced.

Example:

$$C + 2H_2 \xrightarrow{\text{electric arc}} CH_4$$

Catalytic hydrogenation of carbon monoxide

When carbon monoxide reacts with hydrogen gas in the presence of iron (Fe) or Nickel (Ni), an alkane is formed.

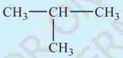
Example:

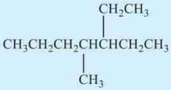
$$nCO + (2n+1)H_2 \xrightarrow{\text{heat (Fe)}} C_nH_{2n+2} + nH_2O$$

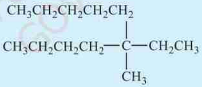
$$3CO + 7H_2 \xrightarrow{\text{heat (Fe)}} C_3H_8 + 3H_2O$$

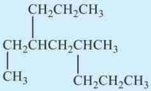
Exercise 2.1

1. (a) What are aliphatic hydrocarbons?
   (b) Mention the classes of aliphatic hydrocarbons.
2. (a) Draw the structures of the ground state, excited states and the sp^3 hybridised state of carbon.
   (b) By using the sp^3 hybrid orbital of carbon, explain the phenomenon that alkanes are saturated hydrocarbons.
3. Explain with examples, the difference between alkanes and alkyl groups.
4. (a) Define the term homologous series.
   (b) State three characteristic features of compounds that belong to the same homologous series.
5. Draw the structural formula of each of the following compounds:
   (a) 2,2,3,3-tetramethylpentane
   (b) 2,2,4-trimethylpentane
   (c) 3-ethyl-4-methylhexane
6. By using IUPAC rules, name the following alkanes:

(a)

$CH_3-CH(CH_3)-CH_3$

(c)

$CH_3CH_2CH_2CH(CH_3)CH(CH_2CH_3)CH_2CH_3$

(b)

$CH_3CH_2CH_2CH_2-C(CH_2CH_2CH_2CH_2CH_3)(CH_3)-CH_2CH_3$

(d)

$CH_2(CH_3)CH(CH_2CH_2CH_3)CH_2CH(CH_2CH_2CH_3)CH_3$

7. (a) Define the term isomerism.
   (b) Describe with examples types of isomers that exist in alkanes.
8. Draw the structures of isomers with the following formulas:
   (a) C_4H_{10} (b) C_7H_{16} (c) $C_5H_{11}Br$ (d) $C_4H_8F_2$

2.2.5 Properties of alkanes

Physical properties

The physical properties of alkanes are largely dependent on the length of the carbon chains and hence, on the relative molecular mass and the degree of branching.

Physical state

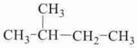
Alkanes consist of carbon-carbon (C—C) and carbon-hydrogen (C—H) sigma bonds. These bonds are almost non-polar due to the small difference in electronegativity between carbon and hydrogen. As a result, the type of intermolecular forces that exist in alkanes are weak van der Waal's forces. Due to weak intermolecular forces, the first four members of alkanes (methane to butane) are gases, the next thirteen members (C_5 to C_{17}) are liquids and the members with more than seventeen carbon atoms are waxy solids.

Boiling points

Generally, alkanes have low boiling points, which increase with an increase in the number of carbon atoms in the linear chain (n-alkane). For example, the boiling points of ethane, propane, butane, pentane, and hexane are -89, -42, -0.5, 36, and 69 °C, respectively. The increase in boiling points with an increase in the number of carbon atoms is due to an increase of the magnitude of van der Waal's forces. For alkanes with the same molecular formula, branched chain isomers have lower boiling points than the corresponding linear chains, due to a decrease of the surface area for the van der Waal's forces to act. For example, the boiling points of the three isomers of pentane (C_5H_{12}) are shown in the following structures:

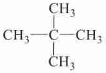
$CH_3-CH_2-CH_2-CH_2-CH_3$

n-Pentane,
b.p.= 36 °C



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2-CH_3$

2-methylbutane,
b.p.= 28 °C



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

2,2-dimethylpropane,
b.p.= 9.5 °C

Melting point

The trend in the melting points of alkanes is generally similar to that of the boiling points, where the melting points increase with an increase in the number of carbon atoms. However, alkanes which have odd numbers of carbons have relatively lower melting points than those with even numbers. This is because, in alkanes with even number of carbons there is closer packing of molecules and hence have relatively stronger van der Waal's forces that are more difficult to break. Figure 2.3 shows the plot of the melting point of alkanes as a function of the number of carbons.

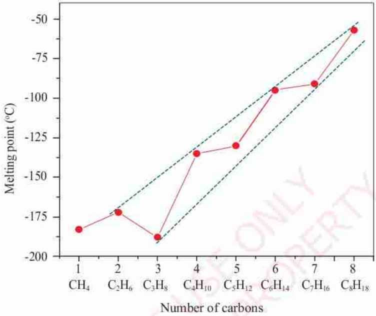


Figure 2.3 The melting points of alkanes as a function of the number of carbon atoms

Solubility

Considering that alkanes are non-polar, they dissolve in non-polar solvents such as ether and carbon tetrachloride. Alkanes are insoluble in polar solvents such as water.

Density

Density of alkanes increases with an increase in the molar masses up to about 0.8 g/cm^3. This means that, the most dense alkane has lower density than that of water (1.0 g/cm^3). Therefore, all alkanes are lighter than water.

Chemical properties

Alkanes are relatively unreactive compared to other aliphatic hydrocarbons because they contain C—C sigma bonds which are stable and therefore difficult to break. Because they are inert or unreactive against ionic or other polar compounds, they are called *paraffins*. The word paraffin was derived from the Latin word *Para* + *ffinis* which means lacking affinity. Alkanes do not react with strong acids or alkalis, sodium metal as well as strong oxidising agents such as potassium permanganate. The most common reactions of alkanes include free radical substitution, combustion, nitration at high temperature, cracking and reformation.

Reactions with oxygen (oxidation or combustion)

All alkanes react with oxygen in a combustion reaction to form water and carbon dioxide. The general equation for a complete combustion of alkanes is;

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + \text{heat}$$

Examples:

$$CH_4(g) + 2O_2(g) \longrightarrow 2H_2O(g) + CO_2(g) + \text{heat}$$

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 6H_2O(g) + 4CO_2(g) + \text{heat}$$

$$C_9H_{20}(l) + 14O_2(g) \longrightarrow 10H_2O(g) + 9CO_2(g) + \text{heat}$$

During the combustion reaction, heat energy is released. It is this energy which is generated during combustion that makes alkanes good fuels. The combustion of alkanes with limited supply of oxygen generates, water vapour and carbon monoxide, or water vapour and soot, or water vapour, carbon monoxide and soot.

$$2CH_4(g) + 3O_2(g) \longrightarrow 2CO(g) + 4H_2O(g) + \text{heat}$$

$$CH_4(g) + O_2(g) \longrightarrow C(s) + 2H_2O(g) + \text{heat}$$

$$4CH_4(g) + 5O_2(g) \longrightarrow 2CO(g) + 2C(s) + 8H_2O(g) + \text{heat}$$

Free radical substitution reactions

Alkanes undergo substitution reaction with halogens to form haloalkanes. The reactions occur in the presence of ultraviolet light (UV light) or controlled temperature. A good example is the free radical substitution of alkane with chlorine (chlorination of alkanes).

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

The mechanism for free radical substitution involves three steps:

Initiation

The initiation step involves the symmetric or homolytic splitting of halogen molecule to form two atoms with unpaired electrons (free radicals).

$$Cl_2 \xrightarrow{\text{UV light}} 2Cl^{\bullet}$$

Propagation

The free radicals that were formed are so reactive that they pull off a hydrogen atom from the alkane to form alkyl radicals.

$$CH_4 + Cl^{\bullet} \longrightarrow \dot{C}H_3 + HCl$$

The methyl radical then pulls chlorine atom from Cl_2 molecule to form another chlorine radical.

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

Termination

Termination of the reaction occurs by the recombination of two free radicals in a random fashion.

$$\dot{C}H_3 + Cl^{\bullet} \longrightarrow CH_3Cl$$

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3CH_3$$

In the presence of UV light and excess of chlorine, the reaction will proceed until all the hydrogen atoms of alkane are replaced.

$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

The free radical substitution reactions of halogens are different depending on the halogen involvement. The substitution reaction with fluorine is difficult to control. The substitution reactions with chlorine and bromine are moderate, but the reaction with bromine is much slower than the one with chlorine while iodine is unreactive.

Cracking

Cracking is the process by which alkanes with many carbon atoms (higher alkanes) are converted into alkanes and alkenes with few carbon atoms (lower alkanes) by the application of high temperature and catalyst.

$$\text{Higher alkanes} \xrightarrow[\text{catalyst}]{400\text{ - }700\ ^{\circ}\text{C}} \text{Lower alkanes + alkenes}$$

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{catalyst}]{400\text{ - }700\ ^{\circ}\text{C}} CH_3CH_3 + CH_2{=\!=}CH_2$$

This process is used in crude oil refineries when there is high demand of petrol while the crude oil contains only a small amount of petrol.

Reforming

Reforming is a chemical process in which the molecular structure of a hydrocarbon is rearranged to change its properties. The process involves heating of alkanes with hydrogen in the presence of catalysts. For example, the properties of low grade naphtha can be changed by converting the molecules into those with high octane number under high temperature and pressure. The *octane number* is a measure of the ability of a fuel to resist knocking when ignited.

Nitration

In the nitration of alkanes, the hydrogen atom is replaced by a nitro group ($-NO_2$). The occurrence of this reaction requires very high temperature of about 400 - 500 °C.

$$RH + HNO_3 \xrightarrow{400\text{ - }500\ ^{\circ}\text{C}} RNO_2 + H_2O$$

Because of high temperature application during nitration of alkanes, the reaction is accompanied with the breaking of much C—C and C—H bonds. As a result, several other products are formed which include a mixture of different nitro alkanes as well as oxidation products which are carbon dioxide (CO_2) and water (H_2O). This chemical process is therefore carried out only in the industrial scale.

2.2.6 Uses of alkanes

Alkanes have a wide range of applications depending on the size of the molecules (number of carbon atoms). Most of the applications are related to the energy released following the combustion of the alkanes. The uses of some of the alkanes are summarised in Table 2.4.

Table 2.4 Uses of some alkanes

Alkanes	Uses
Methane (CH_4)	• As fuel for homes, burn without smoke. • In the generation of electricity. • As fuel for vehicles in the form of liquefied natural gas (LNG). It is more environmentally friendly than gasoline and diesel. • As a rocket fuel when highly refined.
Ethane (C_2H_6)	• In the preparation of ethene and other higher hydrocarbons. • In the production of ethylene used in the manufacture of various chemical products such as plastics and detergents. • As a refrigerant in cryogenics systems.
Propane (C_3H_8)	• As fuel for domestic and industrial purposes. • As fuel for hot air balloons. • As a propellant for sprays, example, air freshener.
Butane (C_4H_{10})	• In the production of synthetic rubber. • As fuel in cigarette lighters. • As a liquefied petroleum gas (LPG) when mixed with other gases. • Used as fuel in cooking equipment.
Pentane (C_5H_{12})	• As a laboratory solvent. • In the synthesis of pesticides. • As a solvent for liquid chromatography.
Hexane (C_6H_{14})	• In the extraction of cooking oil from seeds. • In the synthesis of glues for shoes, leather products and roofing. • In the cleaning and degreasing purposes.
Heptane (C_7H_{16})	• In paints and coatings. • As a minor component of gasoline. • As a nonpolar solvent in laboratories.
Octane (C_8H_{18})	• As a component of gasoline or petrol. • In the prevention of engine damage.
Nonane (C_9H_{20})	• Used in automotive fuel and jet fuel. • As a component of organic solvents.

Exercise 2.2

1. (a) What are the physical properties of alkanes?
   (b) Explain the trend in boiling and melting points of alkanes with an increase in the number of carbon atoms.
   (c) Why alkanes do not dissolve in water?

2. (a) Why are alkanes less reactive than the unsaturated hydrocarbons?
   (b) Write the general equation for the combustion of alkanes and the corresponding reaction equations for the combustion of methane (CH_4), butane (C_4H_{10}), and hexane (C_6H_{14}).

3. Write the balanced chemical equations for the complete combustion of methane in;
   (a) an ample supply of oxygen.
   (b) a limited supply of oxygen.

4. Write the mechanism of free radical substitution of methane with chlorine under ultraviolet light.

5. Crude oil is separated into fractions by fractional distillation. Outline how different fractions are obtained by this process.

6. (a) Define the term catalytic cracking.
   (b) Give two main types of catalytic cracking and two main types of products obtained by catalytic cracking.

7. Complete and balance the following reactions:
   (a) $C_2H_5MgBr + C_2H_5OH \longrightarrow$
   (b) $CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}}$
   (c) $C_2H_5MgBr + H_2O \xrightarrow{H^{\oplus}}$

8. Give equations for a suitable laboratory method of preparing the following alkanes starting from compounds that have four carbon atoms or less. Indicate the conditions and the reagents which are required.
   (a) Pentane
   (b) 2-methylpropane
   (c) 2,3-dimethylbutane
   (d) 2,4-dimethylpentane

2.3 Alkenes

Alkenes are unsaturated hydrocarbons which contain carbon-carbon double bonds (C=C). In alkenes, carbon-carbon bonds are sp^2 hybridised. The sp^2-hybrid orbitals of carbon consist of three combined orbitals. (one *s*- and two *p*-orbitals), therefore they have the ability of forming three sigma bonds with other atoms. The remaining unhybridised *p*-orbital undergo sideway overlap with another unhybridised *p*-orbital of the adjacent carbon atom and form a π bond. Therefore, the carbon-carbon double bond in alkene consists of one strong sigma (σ) bond and one weak π bond formed by a sideway overlap of unhybridised *p*-orbital. The formation of carbon-carbon double bond is illustrated in the Figure 2.4.

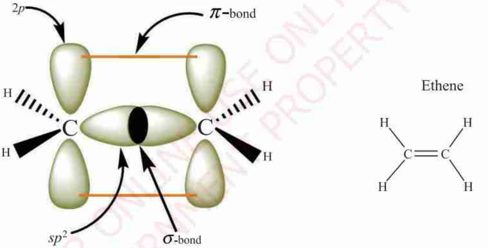


Figure 2.4 The formation of carbon-carbon double bond by overlaping of atomic orbitals

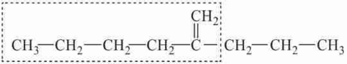
Alkenes form three sigma bonds at the adjacent sp^2 hybridised carbons, one C─C bond and two C─H bonds. Because sp^2 hybridised carbon does not have as many hydrogen atoms as they possibly could, alkenes are therefore said to be unsaturated. The general formula for alkenes is C_nH_{2n}, where n is the number of carbon atoms. The simplest alkene in the homologous series is ethene with n equals to 2, (C_2H_4). If n equals to 3, the molecular formula of the alkene is C_3H_6, and if n equals to 4, the molecular formula of the alkene is C_4H_8. In this section, you will learn about, IUPAC nomenclature, preparations, properties, and uses of alkenes.

2.3.1 IUPAC nomenclature of alkenes

The IUPAC rules of nomenclature for alkanes are also applicable to alkenes, with few exceptions.

1. The suffix *-ane* used in alkanes is replaced by *-ene* in alkenes. For example, *n*-propane in alkane becomes *n*-propene in alkenes.
2. The longest continuous chain is the one bearing the carbon with double bond.

Example:

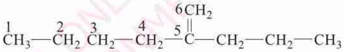


$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}{-}CH_2{-}CH_2{-}CH_3}$$

In the structural formula of above example, the parent chain consists of six carbons, and not eight.

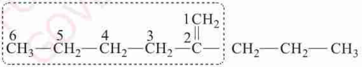
3. Numbering of the parent chain is done in such a way that the carbon containing the double bond is assigned the lowest possible number. If the double bond is at the centre, the numbering is done by considering the lowest number of substituents present.

Examples:



$$\mathrm{\overset{1}{CH_3}{-}\overset{2}{CH_2}\ \overset{3}{CH_2}{-}\overset{4}{CH_2}{-}\overset{5}{\overset{\overset{\displaystyle 6\,CH_2}{\|}}{C}}{-}CH_2{-}CH_2{-}CH_3}$$

Incorrect

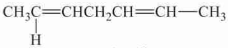


$$\mathrm{\overset{6}{CH_3}{-}\overset{5}{CH_2}{-}\overset{4}{CH_2}{-}\overset{3}{CH_2}{-}\overset{2}{\overset{\overset{\displaystyle 1\,CH_2}{\|}}{C}}{-}CH_2{-}CH_2{-}CH_3}$$

Correct

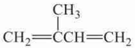
$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$	But-2-ene	Incorrect
$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$	But-1-ene	Correct

4. If more than one double bonds are present, the name of compounds will depend on the number of double bonds. For example if compound has two double bonds is named as diene and three double bonds as triene.



$$CH_3\underset{H}{\underset{|}{C}}=CHCH_2CH=CH-CH_3$$

Hepta-2,5-diene

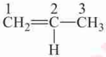


$$CH_2=\overset{CH_3}{\overset{|}{C}}CH=CH_2$$

2-methylbuta-1,3-diene

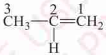
Isomerism in alkenes

Just like in alkanes, alkenes exhibit both constitutional and stereo isomerism. However, constitutional isomers in alkanes exhibit only structural isomers while alkenes exhibit both structural and positional isomers due to the presence of carbon–carbon double bond. The position of the double bond accounts for positional isomerism in alkenes. Both ethene and propene which are the first and second members of alkene respectively exist in one structural formula.



$$\overset{1}{CH_2}=\underset{H}{\underset{|}{\overset{2}{C}}}-\overset{3}{CH_3}$$

Shifting the position of double bond to the other two carbons gives the same structure.

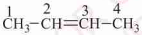


$$\overset{3}{CH_3}-\underset{H}{\underset{|}{\overset{2}{C}}}=\overset{1}{CH_2}$$

Therefore, there are no isomers in open chain propene.

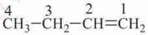
Constitutional isomerism in butene

Butene (C_4H_8) is the first member of alkenes to exhibit isomerism. The molecule has three constitutional isomers:



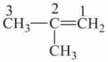
$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3}$$

But-2-ene



$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

But-1-ene



$$\overset{3}{CH_3}-\underset{CH_3}{\underset{|}{\overset{2}{C}}}=\overset{1}{CH_2}$$

2-methylprop-1-ene

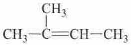
Pentene (C_5H_{10}) has five constitutional isomers as shown in the following structures:

$CH_2=CH-CH_2-CH_2-CH_3$

Pent-1-ene

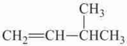
$CH_3-CH=CH-CH_2-CH_3$

Pent-2-ene



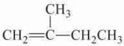
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$$

2-methylbut-2-ene



$$CH_2=CH-\overset{CH_3}{\overset{|}{C}}HCH_3$$

3-methylbut-1-ene



$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2CH_3$$

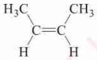
2-methylbut-1-ene

The second type of isomers in alkenes is stereoisomers, which are divided into optical and geometrical isomers. Alkenes possess both optical and geometrical isomers due to the existence of restricted rotations between carbons of the double bond.

Geometrical isomerism in alkenes

The two groups attached on each carbon in the double bond are held rigidly in a specific spatial orientation because of the restricted rotation about the C=C bond (the double bond is rigid). As a result, geometrical isomers have different orientations in space, hence differ in both physical and chemical properties despite having the same molecular formula and the same connectivity.

When similar groups or priority groups are attached on the same side, the isomer is said to be a *cis*-isomer, and when they are attached on the opposite sides, the isomer is said to be a *trans*-isomer. The geometrical isomers are also called *cis-trans* isomers.



cis-But-2-ene

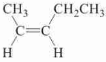
trans-But-1-ene

Note that, if all the priority groups are attached on the same carbon, geometrical isomers are not possible.

No geometrical isomerism

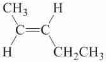
2-methylprop-1-ene

Geometrical isomerism also exists in pentene (C_5H_{10}) and hexene (C_6H_{12}). Geometrical isomers of pentene (C_5H_{10}) are:



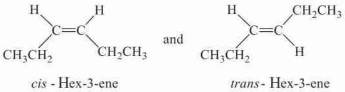
cis-Pent-2-ene

and



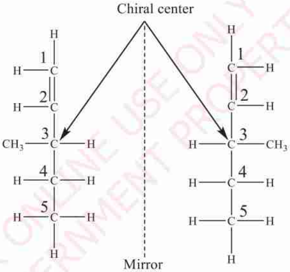
trans-Pent-2-ene

Geometrical isomers of hex–3–ene (C_6H_{12}) are:



Optical isomerism in alkenes

Optical isomers must have non-superimposable mirror images, and exists in asymmetric molecules which have a chiral center (that is a carbon bonded to four different groups) or a stereo-centre. The following example of alkene (3-methyl pentene) shows an optical isomerism with a chiral centre on the third carbon.



The two isomers are optical isomers because they consist of non- superimposable mirror images and they can rotate a plane of polarised light.

2.3.2 Preparations of alkenes

Alkenes being among the important groups of unsaturated aliphatic hydrocarbons, can be prepared by using a number of methods. These methods can be categorised into laboratory preparation and industrial production depending on the nature of reagents used and the quantity of alkene produced.

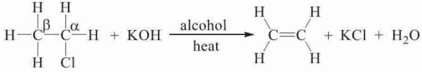
Laboratory preparation of alkenes

The laboratory preparation of alkenes includes the following methods: dehydrohalogenation of alkyl halides, dehydration of alcohols, reduction of alkynes, dehalogenation of vicinal dihalides, and Kolbe reaction.

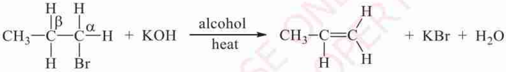
Dehydrohalogenation of alkyl halides

Dehydrohalogenation is a chemical reaction that involves the removal of a hydrogen halide (HX) from an alkyl halide molecule. This reaction occurs when an alkyl halide is heated with a strong base in alkaline medium to form a corresponding alkene. The reaction involves the elimination of hydrogen halide at the α and β carbon atoms, hence it is called 1,2 or β-elimination reaction.

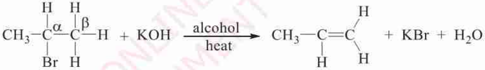
Example:



Ethylchloride Ethene

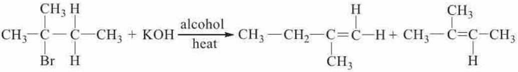


1-bromopropane Prop-1-ene



2-bromopropane Prop-1-ene

In many cases, the elimination reactions in alkyl halides give a mixture of isomeric alkenes, but with one formed in excess (major product) over another (minor product). The dehydrohalogenation of 2-bromo-2-methylbutane for example gives 2-methylbut-1-ene as a minor product and 2-methylbut-2-ene as a major product.

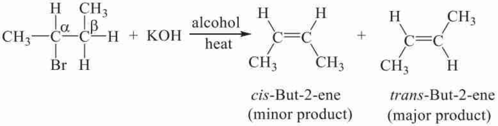


$$CH_3-\overset{CH_3}{\underset{Br}{C}}-\overset{H}{\underset{H}{C}}-CH_3 + KOH \xrightarrow[heat]{alcohol} CH_3-CH_2-\underset{CH_3}{C}=\overset{H}{C}-H + CH_3-\overset{CH_3}{C}=\underset{H}{C}-CH_3$$

2-bromo-2-methylbutane 2-methylbut-1-ene (minor product) 2-methylbut-2-ene (major product)

However, the elimination reactions of alkyl halide often favours, the more stable *trans*-alkene over the *cis*-alkene when the produced alkenes are *cis-trans* isomers.

For example, the dehydrohalogenation of 2-bromobutane gives mainly *trans*-but-2-ene and minor *cis*-but-1-ene as shown in the following equation:

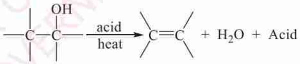


The relative elimination reactivity order of alkyl halides and their halide groups are: $3^{o} > 2^{o} > 1^{o}$ and I > Br > Cl > F respectively.

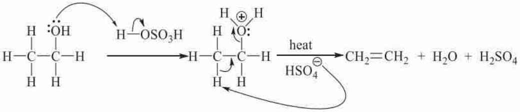
Generally, the elimination in alkyl halides is governed by *Zaitsev's rule* which predicts that the most substituted alkene products in the elimination reaction is the most stable and hence the most favoured product. This rule was named after a Russian chemist, Alexander M. Zaitsev (1841-1910) who developed it in 1875.

Dehydration of alcohols

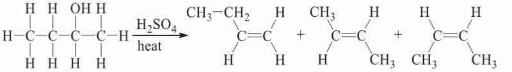
Dehydration is a chemical reaction that involves loss of a water molecule from the reacting substances. The dehydration of alcohols to form alkenes involves the loss of hydroxyl (OH) group and hydrogen ion $(H^{\oplus})$ from an alcohol. At a high temperature hydrogen ion $(H^{\oplus})$ from strong acid combines with OH group from alcohol to form a water molecule.



The reaction above takes place through the following mechanism:

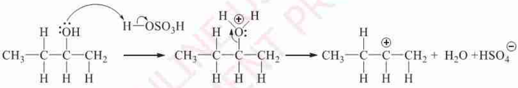


Like elimination in alkyl halide, the elimination in dehydration of alcohols to form alkenes follows this order: $3^{o} > 2^{o} > 1^{o}$ for this case, only 1^{o} alcohols form one alkene. 2^{o} and 3^{o} alcohols form a mixture of two or more alkenes, one as a major product and others as minor products. For example, when a mixture of butan-2-ol (a secondary alcohol) and concentrated sulphuric acid is heated three isomers of alkenes are produced which are but-1-ene (minor), *trans*-but-2-ene (major) and *cis*-but-2-ene (minor).



But-1-ene (minor product) *trans*-But-2-ene (major product) *cis*-But-2-ene (minor product)

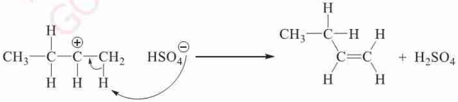
Both secondary and tertiary alcohols are dehydrated resulting in the formation of *cis* or *trans* isomers. Water molecules leave first to form a carbocation as the reaction intermediate. The hydrogen sulphate ions pick a proton from an adjacent carbon to form a double bond. The alkene formed depends on which proton is picked by hydrogen sulphate ion. Its mechanistic detail is illustrated in the following equation.



Carbocation

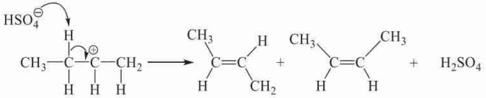
When hydrogen sulphate ion picks a proton from the first carbon (C_1) atom, the less substituted but-1-ene is formed as minor product.

Example:



But-1-ene
Less substituted alkene (minor)

However, when hydrogen sulphate ion picks a proton from the third carbon (C_3) atom, the two *cis-trans* isomers are formed: *trans*-but-2-ene (stable and major product) and *cis*-but-2-ene (less stable and minor product).



trans-But-2-ene (major product)

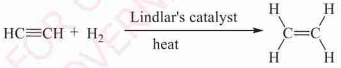
cis-But-2-ene (minor product)

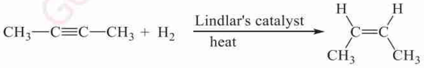
Note that, the heating of alcohols in the concentrated acid requires a specific range of temperature depending on the type of alcohols; 3° alcohols require 25-80 °C, 2° alcohol (100-140 °C) and 1° alcohols (170 -180 °C). If the mixture is not sufficiently heated, alcohols react with each other to form ethers.

$$CH_3CH_2OH + CH_3CH_2OH \xrightarrow[\text{temp.}]{\text{insuficient}} CH_3CH_2OCH_2CH_3 + H_2O$$

Partial hydrogenation of alkynes

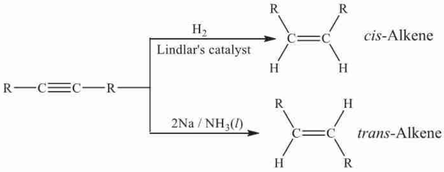
Partial hydrogenation of alkynes involves treatment of alkynes with hydrogen gas and a metal catalyst. The role of the catalyst is to weaken the sigma H—H bond and to prevent the complete hydrogenation of alkynes. The catalyst used is a mixture of palladium and calcium carbonate deactivated by lead acetate and an aromatic amine. It is commonly known as Lindlar's catalyst named after its inventor by a British-Swiss chemist, Herbert Lindlar (1909-2009).





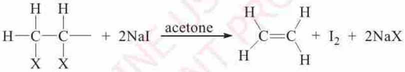
cis-But-2-ene

However, the reduction of alkynes may yield either *cis*-or *trans*-alkenes depending on the reaction conditions, with the exception of terminal alkynes (R—C≡C—H). If the reduction takes place using sodium metal in liquid ammonia, the *trans*-alkene is formed and if hydrogenated in the presence of Lindlar's catalyst, the *cis*-alkene is formed.

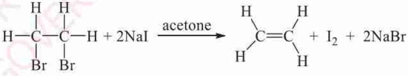


Dehalogenation of vicinal dihalides

Dehalogenation is a chemical reaction that involves the removal of a halogen atom from an alkyl halide molecule. Vicinal halides are dihaloalkanes in which the halogen atoms are attached to the adjacent carbon atoms. When they are attached to the same carbon atom the molecule is known as germinal dihalide. The vicinal dihalides undergo dehalogenation when they are treated with sodium iodide solution in acetone or a mixture of zinc dust in acetic acid or ethanol as shown below.

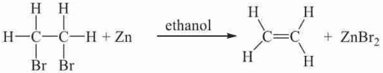


Examples:



1,2-dibromoethane

Ethene

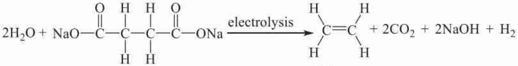


1,2-dibromoethane

Ethene

Kolbe electrolytic method

Kolbe electrolytic method involves the electrolysis of carboxylic acid salts to form alkanes. But when it involves the electrolysis of aqueous solution of sodium or potassium salt of saturated dicarboxylic acids, the products formed are alkenes. Sodium succinate for example, is electrolysed to form ethene and carbon dioxide at the anode and sodium hydroxide and hydrogen at the cathode.



Sodium succinate

Ethene

Industrial production of alkenes

Alkenes can be obtained from higher hydrocarbons by a process called cracking. Many of the higher alkanes produced from the fractional distillation of crude oil are cracked; for example, naphtha is cracked to produce gasoline. Cracking also produces extra alkenes, which are needed for making plastics. Breaking of these chemical substances can be achieved by two methods which are thermal and catalytic cracking.

Thermal cracking is a process of breaking down large complex molecules of hydrocarbon at high temperature range of 500 - 700 °C and high pressure of 70 atmospheres into smaller hydrocarbons. This involves the breaking of C─C and C─H bonds leading to the formation of smaller hydrocarbons, which will also include unsaturated hydrocarbons like alkenes. The reaction is highly endothermic and therefore more energy is needed to make the reaction happen.

$$C_{15}H_{32} \xrightarrow{500 - 700\,^{o}C} C_8H_{18} + 2C_2H_4 + C_3H_6$$

Catalytic cracking uses lower pressure and temperature of approximately 550 °C and a catalyst known as a zeolite which is a mixture of aluminium oxide and silicon oxide (Al_2O_3 and SiO_2). In this method, catalysts used facilitate the breaking down of the bigger chains at a lesser temperature and pressure than the thermal cracking. The advantage of catalytic cracking is that by this method the yield of more useful fractions is high.

$$C_{10}H_{22} \xrightarrow[(Al_2O_3\ \&\ SiO_2)]{550\,^{o}C} C_5H_{12} + C_5H_{10}$$

Exercise 2.3

1. (a) Using illustrations, explain the type of hybridisation in alkenes.
   (b) Describe the formation of sigma and *pi*-bonds in alkenes.
2. Describe the type of isomers that exist in alkenes and give one example in each case.
3. (a) Briefly describe the main distinguishing properties of geometrical isomers.
   (b) Why do the *cis* isomers of alkenes have higher boiling points than the *trans* isomers?
4. How many alkenes have the molecular formula C_5H_{10}? Write their structures and IUPAC names. Specify the configuration of the stereoisomers as *cis* or *trans* as appropriate.
5. Give the structure of the product formed when each of the following alkenes reacts with bromine in water:
   (a) 2-methylbut-1-ene
   (b) 3-methylbut-1-ene
   (c) 2-methylbut-2-ene
6. Describe the preparation of alkene by dehydration of alcohol. Give the mechanism of the reaction.
7. (a) What is dehydrohalogenation of alkyl halides?
   (b) Explain using a mechanism, how alkenes can be obtained by dehydrohalogenation reaction?
8. Identify the alkene obtained from dehydration of each of the following alcohols:
   (a) 3-ethylpentan-3-ol
   (b) Propan-2-ol
   (c) Propan-1-ol
   (d) 2,3,3-trimethylbutan-2-ol

2.3.3 Properties of alkenes

Physical properties of alkenes

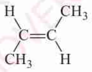
Being unsaturated compounds, alkenes show different physical properties compared to alkanes which are saturated. The physical properties of alkenes depend on the molecular masses or number of carbons, degree of branching and also the configurations of the structures (*cis*-*trans* isomers).

Physical states

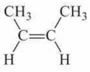
The polarity of bonds in alkenes is very small such that the type of intermolecular forces that exist are weak van der Waals forces. Therefore, alkenes exist in all three states, the gaseous, liquid, and solid states at room temperature. This depends on the number of carbon atoms (molecular mass). The first three members of alkenes (ethene, propene, and butene) are colourless gases, the next eleven members (five to fifteen carbons) are colourless liquids, and higher alkenes are solids. Excluding ethene which has a faint sweet smell, all other alkenes are colourless and odourless.

Boiling points

In alkenes, the boiling points increase with an increase in the number of carbons (molecular masses) due to the increase in the strength of the intermolecular forces. For example, the boiling points of ethene, propene, butene, pentene, and hexene are -104, -47, -6.3, 30, and 63 °C, respectively. The boiling points of the *cis* isomers are higher than that of the *trans* isomers. For example, the boiling point of *cis*-but-2-ene is 3.7 °C while the boiling point of *trans*-but-2-ene is 0.9 °C.



trans-But-2-ene,
b.p. = 0.9 °C



cis-But-2-ene,
b.p.= 3.7 °C

The reason for the above behaviour is that despite the same molecular mass, the two isomers have different polarities. The dipole moment in the *trans* isomer is zero because the bonds are exactly the opposite of each other giving a zero-resultant dipole moment. The *cis* isomer on the other hand, is slightly polar, therefore more strongly attracted to each other. The graph of the boiling points of alkenes as a function of the number of carbon atoms is shown in the Figure 2.5.

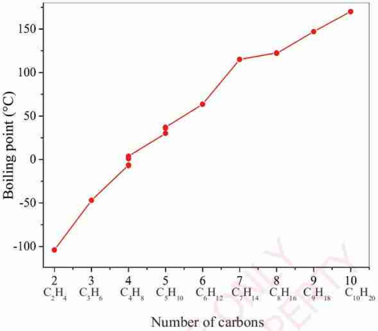


Figure 2.5 The boiling points of alkenes as a function of number of carbon atoms

Generally, the boiling points increase with the number of carbon atoms. At 4th and 5th carbons, the *cis* isomers have higher boiling points compared to the corresponding *trans* isomers. Alkenes have lower boiling points than the corresponding alkanes. Recall that, the boiling points increases with an increase of the strength of the intermolecular forces. Alkanes have two more hydrogens than alkenes of the same number of carbon atoms. Therefore, they have greater contribution to the strength of intermolecular forces. Stronger intermolecular forces, therefore, explain the higher boiling points of alkanes relative to alkenes.

Melting points

The trend in the melting points of alkenes is generally similar to that of boiling points, where the melting points increase with an increase in the number of carbon atoms. However, the melting point of alkenes, just like the boiling point are affected by the configurations of the groups bonded to the double bond. *Trans* isomers have higher melting points than the *cis*-isomers. The melting points are highly affected by the packing of the molecules in a solid state. Molecules with good packing have higher melting points. This is observed for *trans* isomers which are symmetrical in shape. *Cis*-isomers are packed in a U bending shape that diplay lower melting points. The melting points of some alkenes are shown in Table 2.5.

Table 2.5 The melting points of some selected alkenes

Compound	**Structure**	**Melting Point (°C)**
Ethene	$CH_2{=}CH_2$	-169
Propene	$CH_3CH{=}CH_2$	-185
cis-but-2-ene	$CH_3\text{-}CH{=}CH\text{-}CH_3$	-138
trans-but-2-ene	$CH_3\text{-}CH{=}CH\text{-}CH_3$	-105.5
But-1-ene	$CH_2{=}CH\text{-}CH_2CH_3$	-185.0
3-methylbut-1-ene	$CH_2{=}CH\text{-}CH(CH_3)_2$	-135
2-methylbut-2-ene	$CH_3\text{-}C(CH_3){=}CH\text{-}CH_3$	-123
2,3-dimethylbut-2-ene	$CH_3\text{-}C(CH_3){=}C(CH_3)\text{-}CH_3$	-74
Iso-butylene	$CH_2{=}C(CH_3)_2$	-141
trans-pent-2-ene	$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$	-135
cis-pent-2-ene	$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$	-180
Hex-1-ene	$CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$	-138
Hept-1-ene	$CH_2{=}CH\text{-}CH_2CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$	-119
Dec-5-ene	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2CH{=}CH\text{-}CH_2CH_2\text{-}CH_2\text{-}CH_3$	-66.3

Solubility

Being non-polar, alkenes are generally insoluble in water and other polar solvents but soluble in non-polar solvents such as ether, benzene and carbon tetrachloride. Like dissolves the like.

Density

Just like in alkanes, the densities of alkenes are less than the density of water (1 g/cm^3). Thus, when mixed with water alkenes form a separate layer at the top because they are insoluble in water, and less denser than water.

Chemical properties of alkenes

Alkenes are relatively reactive compared to alkanes because of the presence of the

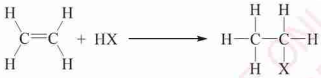
π-bond that is weak and easy to break. The chemistry of alkenes is thus very much dependent on the unsaturation of the molecules, and mostly involves additional reactions, resulting into saturated compounds that are more energetically stable.

Addition reactions (electrophilic addition, A_E)

An *electrophilic addition reaction* is a reaction which occurs at multiple bonds to form one product. Electrophilic addition reactions include the following:

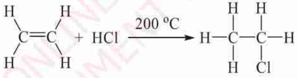
Addition of hydrogen halide (Hydrohalogenation)

Alkenes react with hydrogen halides to give haloalkanes. The reaction is known as electrophilic addition because the first species to attack the molecule is an electrophile.

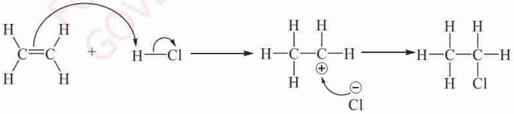


where X = Cl, Br or I

The typical hydrohalogenation reaction is the reaction between ethene and hydrogen chloride.

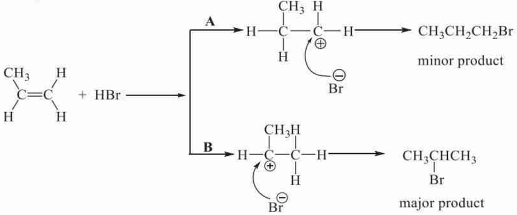


The hydrohalogenation reaction follows the following reaction mechanism:



When the reaction involves the use of an unsymmetrical alkene, *Markovnikov's rule* of electrophilic addition applies. The rule states that, when the electrophilic addition reaction involves the use of unsymmetrical alkene the electrophile attacks the carbon which already contains a large number of hydrogen (less substituted carbon) or electrophile adds so as to form a more stable carbocation intermediate.

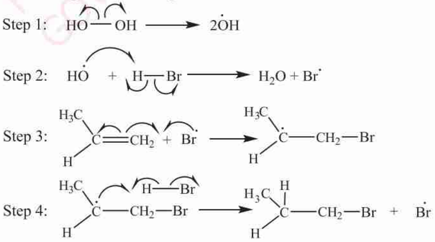
Example:



Route **B** forms a secondary carbocation intermediate which is more stable than the intermediate formed in route **A**. This is due to the positive inductive effect of the alkyl groups, which stabilises the carbocation by releasing electrons on the ion. Therefore, the resulting haloalkane formed in route **A** is the minor product. The Markovnikov's rule is obeyed due to the stabilisation of carbocation in the carbon atom bearing more alkyl groups. In general, the trend of the stability of carbocation is shown as follows:

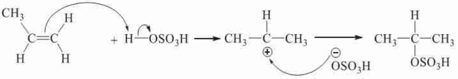
Increase in stability of carbocation

If the addition on the unsymmetrical alkene occurs under hydrogen peroxide (H_2O_2) medium or organic peroxide, anti-Markovnikov's product is formed as a sole product through the following mechanism.



Addition of sulphuric acid (H_2SO_4)

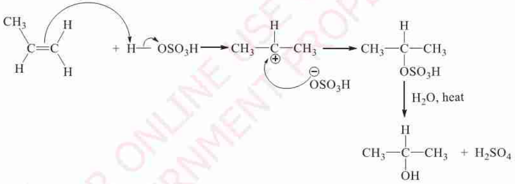
In sulphuric acid, the electrophile and nucleophile are proton ($H^{\oplus}$) and bisulphate ($HSO_4^{\ominus}$), respectively. The addition of H_2SO_4 to unsymmetric alkene follows the Markovnikov's rule where the electrophile $H^{\oplus}$ adds first to the unsaturated carbon that is bonded with more hydrogen atoms.



Alkylhydrogen sulphate
(major product)

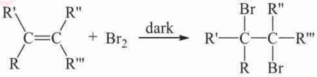
Addition of water (hydration)

The addition of water is an acid, (H_2SO_4) catalysed reaction which begins with the formation of alkyl hydrogen sulphate intermediate. So, the first step is the same as the previous reaction. The resulting alkyl hydrogen sulphate is then hydrolysed by heating with excess water.

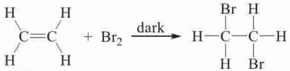


Halogenation

Chlorine and bromine react readily with alkenes at room temperature to form vicinal dihaloalkanes. This reaction takes place in the dark in other words, there is no need of light energy. The general bromination equation is:



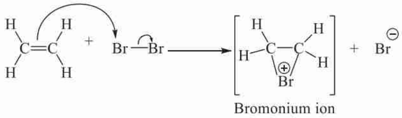
Example:



Ethene

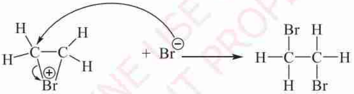
1,2-dibromoethane

The given reaction is very important because it is used to test for the unsaturation in the compound. Bromine water which is brown in colour changes to colourless when treated with any compound containing carbon-carbon double (C=C) bond. This reaction takes place through the following mechanism:

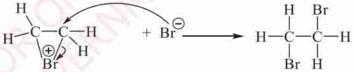


The formation of the final product from the intermediate bromonium ion can occur in two steps:

Step 1: Bromide ion reacts with the carbon to the left.



Step 2: Bromide ion reacts with the carbon to the right.



Combustion reaction

This reaction takes place in excess or limited supply of oxygen and temperature. When it takes place in the excess of oxygen and at high temperatures, carbon dioxide (CO_2) and water (H_2O) are formed as shown in the following example:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g) + \text{heat}$$

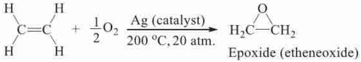
On the other hand, if the temperature is insufficient and the supply of oxygen is limited, carbon monoxide (CO) and carbon (soot) may be formed. Generally, the combustion of alkenes under these conditions gives more sooty flame than alkanes.

Oxidation

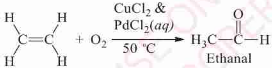
Oxidation, specifically addition of oxygen to alkenes can occur in a variety of ways other than the combustion reaction.

(a) Direct combination with oxygen using suitable catalysts

When silver is used as a catalyst, ethene reacts with oxygen to form an epoxide which is a three-membered cyclic ether.

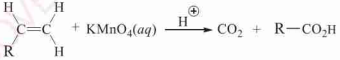


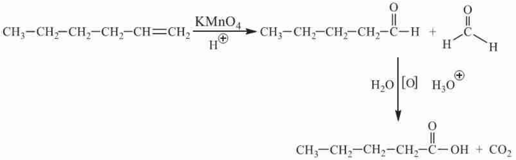
When an aqueous mixture of Cu(II) and Pd(II) chloride is used as a catalyst, ethene reacts with oxygen to form an aldehyde (ethanal).

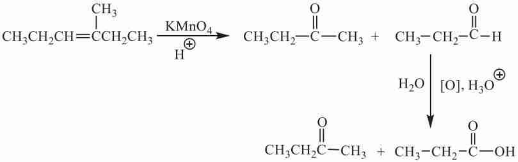


(b) Oxidation using potassium permanganate ($KMnO_4$)

Potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$) being strong oxidising agents, give different oxidation products depending on whether the reaction is carried out in acidic or alkaline medium. If the oxidation is done in acidic medium, the breaking down of the carbon chain to give lower carboxylic acids and carbon dioxide occurs depending on the structure of the alkene.



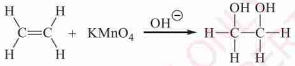




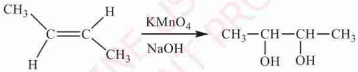
$$CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3 \xrightarrow[H^{\oplus}]{KMnO_4} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$\xrightarrow[{[O],\ H_3O^{\oplus}}]{H_2O} CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

On the other hand, when the oxidation reaction is carried out in the basic medium, the strength of potassium permanganate or potassium dichromate as oxidising agents is weakened, thus giving vicinal diols.



Ethane-1,2-diol

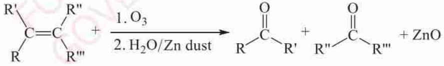


trans-But-2-ene

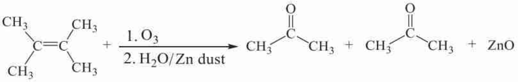
Butane-2,3-diol

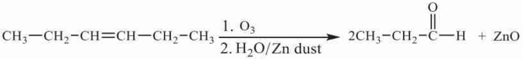
(c) Ozonolysis

Ozonolysis is the oxidative cleavage of the carbon-carbon double bond with ozone, followed by hydrolysis to form carbonyl compounds.



Example:

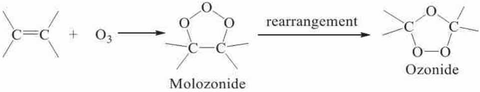




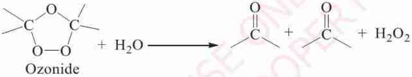
$$CH_3-CH_2-CH{=}CH-CH_2-CH_3 \xrightarrow[2.\ H_2O/Zn\ dust]{1.\ O_3} 2CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + ZnO$$

The ozonolysis occurs in two main steps:

Step 1:
Addition of ozone (O_3) across the double bond to form an intermediate ozonide.



Step 2:
Hydrolysis of ozonide without presence of zinc dust to give carbonyl compounds and hydrogen peroxide.



If the reaction is carried out with zinc dust, the peroxide formed in the above reaction react with zinc dust to produce zinc oxide and water. Thus zinc dust prevents the oxidation of aldehyde to carboxylic acid.

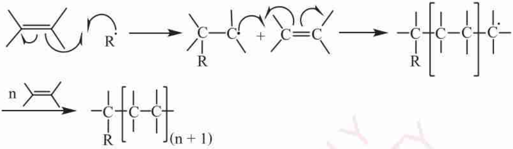
$$H_2O_2 \xrightarrow{\text{Zn dust}} H_2O + ZnO$$

In absence of zinc dust, an aldehyde will be oxidised by the hydrogen peroxide formed to produce a carboxylic acid.

Ozonolysis may be used to determine the structure of the alkene by examining the carbonyl fragments formed. That is, by using ozonolysis technique, the position and number of carbon-carbon double (C=C) bonds in a molecule can be determined.

Polymerisation

Alkenes can be attacked by a reactive species such as cations, anions or free radicals to form reactive species that can further react with alkene species and form a long chain molecule known as polymer.



2.3.4 Uses of alkenes

Production of various polymers

One of the most important uses of alkenes is in the synthesis of polymers. Simple alkene molecules are used as raw materials (monomers) for the production of polymers either directly or in modified forms. These small molecules containing carbon-carbon double bonds are called vinyl monomers and the resulting polymers are called vinyl polymers. Plastics which are obtained from polymers have a wide range of applications, from packaging and wrapping to clothing and building materials and various domestic containers.

Manufacturing of industrial chemicals

Alkenes are used as raw materials in the manufacturing of industrial chemicals such as ethanol, aldehydes and ethane-1,2- diol.

Artificial ripening of fruits

The simplest alkene (ethylene) is used for artificial ripening of fruits. Ethylene also plays roles in other plant development processes such as seed germination, leaf abscission, flowering, and vegetative growth.

Exercise 2.4

1. Write the structure of the major organic products formed in the reaction of hydrogen chloride with each of the following:
   (a) 2-methylbut-2-ene
   (b) 2-methylbut-1-ene
   (c) *cis*-But-2-ene

2. Write a balanced chemical equation for each of the following:
   (a) An addition reaction between but-2-ene and Cl_2
   (b) A substitution reaction between $CH_3–CH_2–CH_2–Br$ and NaOH
   (c) The elimination of H_2O from $(CH_3)_3C–OH$

3. Determine the reaction type and predict the product(s) for each of the following reactions:
   (a) $CH_3-CH_2-CH_2-I + NaOH \longrightarrow$
   (b) $CH_3-CH_2-Br + CH_3-CH_2-CH_2-NH_2 \longrightarrow$

4. (a) State the Markovnikov's rule of electrophilic addition.
   (b) Describe the two possible products formed when propene reacts with hydrogen chloride and indicate with reasons, which one is the major product and which one is the minor product.

5. Using a reaction equation, explain how you can differentiate pent-1-ene from pent-2-ene.

6. Explain the various applications of alkenes in industries, domestic, and agriculture.

7. Predict the major organic product(s) for each of the following reactions:
   (a) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} A$
   (b) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} B \xrightarrow{NaBH_4} C$
   (c) $(CH_3)_2CHCH{=}CH_2 \xrightarrow{BH_3{:}THF} D \xrightarrow{H_2O_2,\ NaOH} E$

2.4 Alkynes

Alkynes are unsaturated hydrocarbons which contain a carbon–carbon triple bonds (—C≡C—). The carbon atoms of the carbon-carbon triple bonds are sp-hybridised. The *sp* hybrid orbital of carbon, which consists of two combined orbitals (one *s* and one *p*), can therefore form two σ-bonds with other atoms. The remaining two unhybridised *p*-orbitals undergo a sideway overlap with other two unhybridised *p*-orbitals of the adjacent carbon atom and form two π-bonds. Therefore, the carbon-carbon triple bonds in alkynes consist of one strong σ-bond and two weak π-bonds formed by a sideway overlap of unhybridised *p*-orbitals. The formation of carbon-carbon triple bond is illustrated in Figure 2.6.

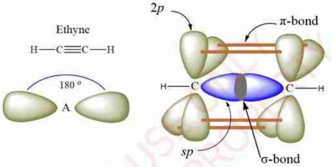


Figure 2.6 The formation of carbon–carbon triple bond by overlaping of atomic orbital

Alkynes form two sigma bonds at the adjacent *sp* hybridised carbons namely, C—C sigma bond and C—H sigma bond. Just like alkenes, alkynes are said to be unsaturated because the *sp*-hybridised carbon do not have as many hydrogen atoms as they could possibly occupy. The general formula for alkynes is C_nH_{2n-2} where n is the number of carbon atoms. The simplest alkyne in the homologous series is ethyne with n = 2 (C_2H_2). If n = 3, the molecular formula for alkyne is C_3H_4 and if n = 4, the molecular formula of the alkyne is C_4H_6. In this section IUPAC nomenclature, preparation, properties, and uses of alkynes will be covered.

2.4.1 Nomenclature of alkynes

There are two main systems of naming alkynes which are: common and IUPAC systems. Under the common nomenclature system, alkynes are named as derivatives of the first member of this homologous series. Ethyne, which is the first member of alkyne homologous series, is also called acetylene and other alkynes are named as derivatives of acetylene. The following examples give the common names of some selected alkynes:

$HC\equiv CH$
Acetylene

$CH_3-C\equiv C-CH_3$
Dimethyl acetylene

$CH_3-C\equiv C-CH_2CH_3$
Ethylmethyl acetylene

$CH_3-CH_2-CH_2-C\equiv C-H$
Propyl acetylene

$CH_3-C\equiv CH$
Methyl acetylene

Contrary to the common system, the International Union of Pure and Applied Chemistry (IUPAC) rules of nomenclature for alkanes and alkenes are also applicable for alkynes, except that the suffix *–ane* from alkane or-ene from alkene is replaced by *–yne* for alkynes.

Example:

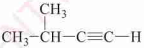
$CH_3CH_2C\equiv CH$

But-1-yne

Isomerism in alkynes

Different isomers that exist in alkynes include structural and positional isomers. For example, pentyne has the following isomers as shown below in Table 2.6.

$CH_3-CH_2-CH_2-C\equiv C-H$ and



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-C\equiv C-H$$

as structural isomers

Pent-1-yne

3-methylbut-1-yne

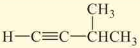
$CH_3CH_2CH_2C\equiv C-H$ and $CH_3CH_2C\equiv C\,CH_3$ as positional isomers.

Pent-1-yne

Pent-2-yne

Table 2.6 Isomers of alkynes

Member	Open chain isomers
$H-C\equiv C-H$ Ethyne	No isomers
$H-C\equiv C-CH_3$ Prop-1-yne	No isomers
Butyne	$H-C\equiv C-CH_2CH_3$ and $CH_3-C\equiv C-CH_3$ But-1-yne But-2-yne

Member	Open chain isomers
Pentyne	 $H-C\equiv C-\overset{CH_3}{\overset{\vert}{C}}HCH_3$ 3-Methylbut-1-yne $CH_3CH_2CH_2C\equiv C-H$ Pent-1-yne $CH_3CH_2C\equiv C\,CH_3$ Pent-2-yne

2.4.2 Preparation of alkynes

Alkynes are unsaturated aliphatic hydrocarbons that can be prepared by a number of methods. These methods can be categorised into laboratory preparation and industrial production methods.

Laboratory preparation of alkynes

The laboratory preparation of alkynes includes the following methods; reaction of calcium carbide with water, dehydrohalogenation of alkyl dihalides, the reaction of alkyl halides with acetylides, dehalogenation, and substitution reaction.

Reacting calcium carbide with water

This is the simplest method for the preparation of acetylene as a simple form of alkynes. The method involves reacting calcium carbide with water. In this simple reaction, the mixture of sand and calcium carbide are put into the conical flask, then, water is added drop by drop into the mixture through the funnel as shown in the Figure 2.7.

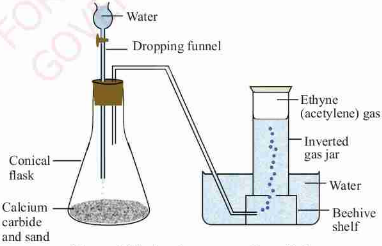


Figure 2.7 Laboratory preparation of ethyne

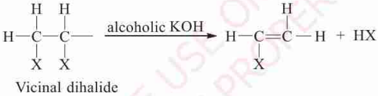
The reaction of calcium carbide with water yields calcium hydroxide and acetylene (ethyne).

$$CaC_2(s) + 2H_2O(l) \longrightarrow HC{\equiv}CH(g) + Ca(OH)_2(aq)$$

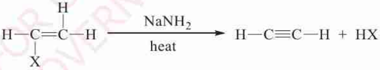
This reaction is exothermic; therefore, calcium carbide is mixed with sand to prevent breaking of conical flask.

Dehydrohalogenation of alkyl dihalides

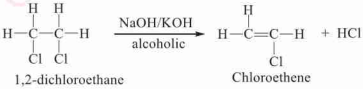
Dehydrohalogenation is a chemical reaction that involves the removal of hydrogen halide from alkyl halides to form alkenes or alkynes depending on the number of moles of hydrogen halide being removed per mole of alkyl halide. When one mole of hydrogen halide is removed from one mole of alkyl halide, an alkene is formed, whereas if two moles of hydrogen halide are removed from either a germinal dihalides or vicinal dihalide, an alkyne is formed. This reaction takes place through E_2 mechanism as illustrated in the following reaction:

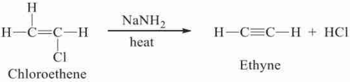


The second dehydrohalogenation step is carried out at high temperature and under extreme strong basic conditions. The strong and non-polarisable bases such as sodium amide are suitable because a weak base favours substitution or E_1 reaction.

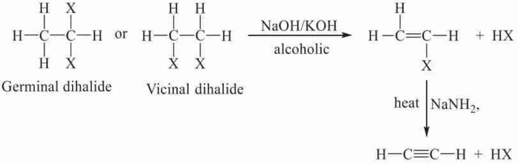


Example:





The reaction is summarised as follows:

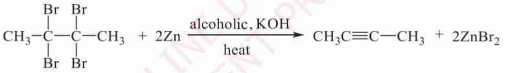


$$H-CH_2-CX_2-H \text{ or } H-CHX-CHX-H \xrightarrow[\text{alcoholic}]{NaOH/KOH} H-CH=CX-H + HX \xrightarrow[\text{heat}]{NaNH_2} H-C\equiv C-H + HX$$

Dehalogenation of tetrahaloalkanes

Dehalogenation is a chemical reaction that involves the removal of halogen atoms from an alkyl halide compound. This reaction is an elimination reaction, it only differs from dehydrohalogenation in that the alkyl group contains four halogen atoms. They are called tetrahalogen compounds. The vicinal tetrahaloalkanes can be treated with zinc metal in an organometallic reaction to form alkynes. The reaction takes place in a strong basic solution in alcohol like dehydrohalogenation.

Example:



$$CH_3-CBr_2-CBr_2-CH_3 + 2Zn \xrightarrow[\text{heat}]{\text{alcoholic, KOH}} CH_3C\equiv C-CH_3 + 2ZnBr_2$$

Alkylation substitution in alkynes

Alkylation reaction is a chemical reaction that involves the transfer of an alkyl group as a carbocation, free radical, or carbonium from one molecule to another. The alkylating agent, usually an alkyl halide, adds the desired aliphatic carbon chain to the chosen starting organic molecule. The terminal alkynes for example are easily deprotonated by an appropriate base to generate an acetylide carbanion. The acetylide carbanion undergoes nucleophilic substitution (usually S_N2) with 1° or 2° alkyl halides which have electrophilic carbon to form an internal alkyne. The 3° alkyl halides undergo elimination rather than substitution.

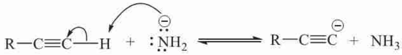
$$R-C\equiv C-H \xrightarrow[R'X]{NaNH_2} R-C\equiv C-R'$$

$$CH_3-C\equiv C-H \xrightarrow[CH_3CH_2X]{NaNH_2} CH_3-CH_2C\equiv C-CH_3$$

Alkylation substitution reactions of alkynes proceed through two steps mechanism:

Step 1: An acid base reaction (reaction between an alkyne and base)

The amide ion ($NH_2^{\ominus}$) acts as a base, generates an acetylide ion by removing the acidic terminal hydrogen.



Step 2: A nucleophilic substitution reaction

The acetylide carbanion reacts with the electrophilic carbon in the ethyl bromide with a loss of the bromide ion as a leaving group forming a new C—C bond.

This reaction is very important as it is used to increase the number of carbon atoms.

Industrial production of alkynes

The industrial production of alkynes is similar to the laboratory preparation. The only difference is that, the industrial methods involve a large scale production. The methods used in the preparation of alkynes include: Thermal cracking of higher alkanes, the *pyrolysis* of natural gas, and the action of water on calcium carbide.

Thermal cracking of higher alkanes

The ethyne, (acetylene) is one of the alkynes which is largely made industrially from hydrocarbons by cracking petroleum. Butane as a raw material for the production of ethyne is thermally cracked with steam as a diluent in the following subsequent reactions:

$$3C_4H_{10}(g) + 2H_2O(g) \longrightarrow 2C_2H_2(g) + 2C_2H_4(g) + 2CH_4(g) + 2CO(g) + 7H_2(g)$$

This reaction yields a mixture of acetylene, ethene, methane, carbon monoxide, and hydrogen gases. The reaction involves dehydrogenation of alkane (methane) to acetylene.

$$2CH_4 \xrightarrow[-6H]{Ni} HC\equiv CH + 3H_2(g)$$

These reactions take a very short time, the high yield of acetylene is obtained through the recycling of the products.

Pyrolysis of natural gas

Pyrolysis is the thermal decomposition of organic materials in absence of air. In this method, methane is undergoing combustion under limited supply of oxygen. The heat evolved in this reaction is used as a source of energy for pyrolysis whereby methane is converted to ethyne.

$$2CH_4(g) + O_2(g) \longrightarrow 2CO(g) + 4H_2(g) + \text{heat}$$

$$2CH_4(g) \xrightarrow{1700\text{ -}1800\ ^{o}C} HC{\equiv}CH(g) + 3H_2(g)$$

Action of water on calcium carbide

Acetylene can be prepared in a small scale in the laboratory by the action of water on calcium carbide. This method is also used industrially to prepare acetylene in large scale. In industry, the reaction can be categorised into two steps: preparation of calcium carbide and the reaction of water on calcium carbide.

Step 1: Preparation of calcium carbide.

Calcium carbide is prepared by reacting coke and calcium oxide at very high temperature (2500 °C) in a furnace.

$$3C(s) + CaO(s) \xrightarrow{2500\ ^{0}C} \underset{\text{Calcium carbide}}{CaC_2(s)} + CO(g)$$

Step 2: The action of water on calcium carbide.

The calcium carbide reacts rapidly with water at room temperature to form acetylene and calcium hydroxide.

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

The action of water on calcium carbide was the basis of the industrial manufacturing of acetylene (C_2H_2). However, today acetylene is mainly manufactured in the industry by thermal cracking of hydrocarbons and pyrolysis of natural gas.

Exercise 2.5

1. (a) By using illustration, explain the type of hybridisation in alkynes.
   (b) Describe the formation of sigma and *pi*-bonds in alkynes and draw the structure to show the overlap of *pi*-orbitals.
2. Name the following alkynes by applying IUPAC rules:
   (a) $H-C\equiv C-CH(CH_3)_2$
   (b) $CH_3CH(CH_3)C(CH_3)_2C\equiv C-CCH_3$
   (c) $CH_3CH(CH_3)CH(CH_3)C\equiv CCH(CH_3)CH_3$
3. Draw the structural formula for each of the following compounds:
   (a) 3-ethylpent-1-yne
   (b) 3,3-dimethylbut-1-yne
   (c) 4,4,5-trimethylhex-2-yne
   (d) 4-ethyl-4-methylpent-2-yne
4. Why do alkynes not exhibit geometrical isomerism?
   Write all the possible isomers of hexyne.
5. Explain how you would prepare each of the following compounds at the laboratory scale:
   (a) Pent-2-yne from pent-2-ene
   (b) But-2-yne from butan-1-ol
   (c) Pent-2-yne from but-1-yne
   (d) Propyne from calcium carbide
   (e) But-2-yne from but-1-yne
   (f) 2,5-dimethylhex-3-yne from ethyne
6. Using appropriate chemical equations, show how each of the following compounds could be converted to hex-1-yne:
   (a) 1,1-dichlorohexane
   (b) Hex-1-ene
   (c) Acetylene
   (d) Iodohexane
7. When 1,2-dibromodecane was treated with potassium hydroxide in aqueous ethanol, it yielded a mixture of three isomeric compounds of molecular formula $C_{10}H_{19}Br$. Each of these compounds was converted to dec-1-yne on reaction with sodium amide in dimethyl sulphoxide. Identify the three compounds.

2.4.3 Properties of alkynes

In this section, the physical and chemical properties of alkynes will be covered. The physical properties include physical states, boiling points, melting points, solubility, and density. The chemical properties are electrophilic addition, formation of acetylides, combustion, and oxidation.

Physical properties of alkynes

The physical properties of alkynes resemble closely those of alkenes and alkanes. Generally, alkynes are non-polar. Just like the other hydrocarbons, the physical properties of alkynes depend much on the sizes of the molecules.

Physical states

Alkynes consist of carbon-carbon single and triple bonds, and carbon-hydrogen bonds. The type of intermolecular forces in alkynes are weak van der Waal's forces. Due to the weak intermolecular forces, the first three members of the alkyne homologous series namely ethyne, propyne, and butyne are gases, the next eight members (C_5 to C_{12}) are liquids and the higher alkynes with thirteen carbons and above are solids. All members of the alkyne homologous series are odourless, except acetylene which has a characteristic garlic smell due to the presence of phosphine as a contaminant.

Boiling points

The boiling point of alkynes increase with an increase in molar masses (number of carbons). For example, the boiling points of ethyne, propyne, 1-butyne, 1-pentyne, and 1-hexyne are -84, -23, 8.1, 39, and 71 °C, respectively. Because of the presence of carbon-carbon triple bonds, alkynes have higher boiling points than the corresponding alkenes and alkanes. For example, the boiling points of hexane, hexene, and hexyne are 69, 63, and 71 °C, respectively.

Note that, the boiling points of alkanes and alkenes are lower than the boiling point of alkynes. High boiling points of alkynes can be explained by the presence of carbon-carbon triple bond between two carbon atoms. The two carbon atoms are strongly attracted to each other. If a hydrogen atom is directly attached to a triple bond it forms what is called a terminal alkyne. The terminal hydrogen is weakened by a strong attraction between the $C\equiv C$ triple bond, and is therefore slightly polarised. The polarisation of the C—H bond of terminal alkyne increases the strength of the intermolecular dipole-dipole attractions, hence the higher boiling points of alkynes.

Melting points

The melting points of alkynes are very low and increase with an increase in the number of carbon atoms (molecular masses). The melting of alkynes relative to alkenes and alkanes show the same trend as the boiling points.

Solubility

Alkynes are non-polar like other hydrocarbons, therefore, they are insoluble in water but soluble in organic solvents such as carbon tetrachloride, ether, hexane, and benzene.

Density

The density of alkynes increases as the number of carbon atoms increase. This is due to the increase in molecular masses. However, densities of alkynes are less than the density of water (1.0 g/cm^3). Therefore, alkynes are lighter than water.

Chemical properties of alkynes

The chemical properties of alkynes are largely contributed by the presence of carbon-carbon triple bond ($-C\equiv C-$) and the acidic terminal hydrogen ($-C\equiv C-H$) if present. *Acidic terminal hydrogen* is the hydrogen that is directly attached to a triple bond. The hydrogen is easily lost as proton because its bonding electrons are already attracted to the triple bond, hence it is called acidic terminal hydrogen. The corresponding alkyne is called a terminal alkyne. The chemical reactions of alkynes are discussed as follows:

Electrophilic addition reactions

The principal reaction of alkynes is electrophilic addition across the triple bond to form alkanes, which is analogous to the addition reactions of alkenes.

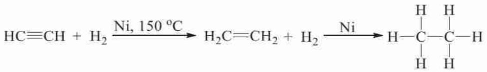
Hydrogenation

Hydrogenation of alkynes can be carried out in two different ways: catalytic hydrogenation and hydrogenation with sodium in liquid ammonia.

(a) Catalytic hydrogenation

Alkynes undergo hydrogenation in the presence of a catalyst (Ni or Pd or Pt, or Rh), just like alkenes, to form alkenes. It is difficult to stop the reaction when alkenes form, therefore the reaction proceeds to form alkanes.

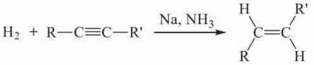
Example:



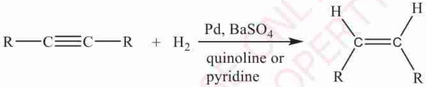
$$HC\equiv CH + H_2 \xrightarrow{Ni,\ 150\ ^{o}C} H_2C{=}CH_2 + H_2 \xrightarrow{Ni} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

(b) Hydrogenation with sodium in liquid ammonia

This is a chemical reduction rather than a catalytic process. The hydrogen is generated in the system by the reaction between sodium and ammonia and approaches the alkyne from different directions. It may form *trans* alkene depending on the groups bonded to the alkene. The reaction does not proceed to form alkane.



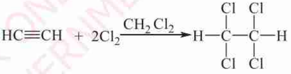
When the hydrogenation is carried out under calculated amounts of hydrogen in the presence of Pd on $BaSO_4$ in pyridine or quinoline (Lindlar's catalyst), it proceeds only up to alkenes. The reaction is specific to the formation of the *cis*-isomer of an alkene.



(c) Halogenation

Alkynes react with halogens in the same way as alkenes do. The order of reactivity of halogens follows the trend: $Cl_2 > Br_2 > I_2$.

Chlorine react with ethyne explosively, and the reaction proceeds until a saturated tetrachloroalkane is formed.

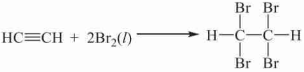


$$HC\equiv CH + 2Cl_2 \xrightarrow{CH_2Cl_2} CHCl_2-CHCl_2$$

1,1,2,2-tetrachloroethane

It is possible to stop the reaction at the stage of dichloroethene by conducting the experiment at a temperature slightly below 0 °C.

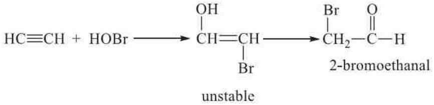
If the reaction is carried out using bromine (Br_2), the product will depend on the state of bromine used. When pure liquid bromine is used, the reaction is the same as in chlorine.



$$HC\equiv CH + 2Br_2(l) \longrightarrow CHBr_2-CHBr_2$$

1,1,2,2- tetrabromoethane

However, if aqueous bromine (bromine water) is used, the reaction gives 2-bromoethanal.

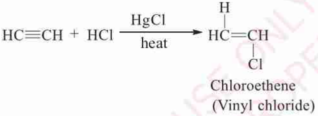


$$HC\equiv CH + HOBr \longrightarrow \underset{\text{unstable}}{\overset{OH}{CH}=\underset{Br}{CH}} \longrightarrow \underset{\text{2-bromoethanal}}{\overset{Br}{CH_2}-\overset{O}{\overset{\|}{C}}-H}$$

(d) Hydrohalogenation (addition of hydrogen halide)

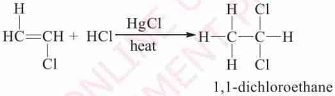
Hydrogen halides react with alkynes in the same way as they react with alkene. The reaction occurs in two steps; the first step forms a haloalkene and the second step forms a dihaloalkane. It is possible to isolate the product after the first addition.

Step 1:



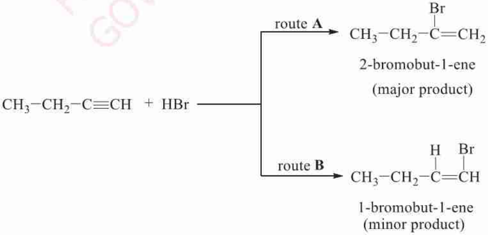
$$HC\equiv CH + HCl \xrightarrow[\text{heat}]{HgCl} \underset{\substack{\text{Chloroethene}\\ \text{(Vinyl chloride)}}}{\overset{H}{HC}=\underset{Cl}{CH}}$$

Step 2:



$$\overset{H}{HC}=\underset{Cl}{CH} + HCl \xrightarrow[\text{heat}]{HgCl} \underset{\text{1,1-dichloroethane}}{H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-H}$$

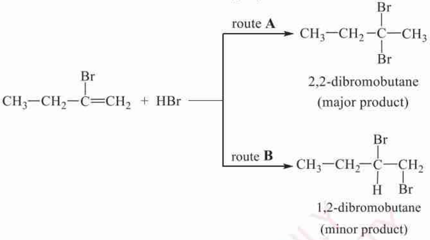
Just like in alkenes, the addition of hydrogen halide to an unsymmetrical alkyne follows Markovnikov's rule. For example, addition of hydrogen bromide to but-1-yne gives 2-bromobut-1-ene as a major product, as shown in the following scheme:



$$CH_3-CH_2-C\equiv CH + HBr \xrightarrow{\text{route }\mathbf{A}} \underset{\substack{\text{2-bromobut-1-ene}\\ \text{(major product)}}}{CH_3-CH_2-\overset{Br}{C}=CH_2}$$

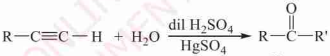
$$CH_3-CH_2-C\equiv CH + HBr \xrightarrow{\text{route }\mathbf{B}} \underset{\substack{\text{1-bromobut-1-ene}\\ \text{(minor product)}}}{CH_3-CH_2-\overset{H}{C}=\overset{Br}{CH}}$$

Following Markovnikov's rule, the reaction of 2-bromobut-1-ene in the second step forms 2, 2-dibromobutane as the major product.



(e) Hydration (addition of H_2O)

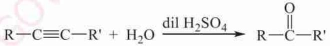
The addition of water to alkynes depend on the type of alkynes (terminal or internal alkynes). Addition of water to terminal alkyne requires mercuric(II) sulphate and dilute sulphuric acid as a catalysts at the temperature of about 60 °C. Mercuric(II) sulphate is used because terminal alkynes are less reactive than the internal alkynes toward the addition of water.



$$R-C\equiv C-H + H_2O \xrightarrow[HgSO_4]{\text{dil } H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

Ketone

On the other hand internal alkyne being relatively more reactive requires acid-catalysed condition without incorporating the use of mercuric(II) sulphate.



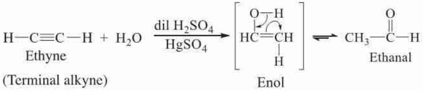
$$R-C\equiv C-R' + H_2O \xrightarrow{\text{dil } H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

(Internal alkyne)
(R, R' = alkyl group)

Ketone

The hydration reaction follows Markovnikov's rule incase an unsymmetrical alkyne is used. During hydration reaction, an intermediate *enol* is formed first, which is then interconverted to its *keto* or *aldo* product which is more stable. The term enol is derived from alkene (en) and alcohol (ol). If hydration is done on ethyne, the final product is an aldehyde, and if any other alkyne is used, the final product is a ketone.

Example:



Tautomerisation is the rapid isomerisation of the unstable vinyl alcohol (enol) intermediate to form carbonyl product (aldehyde or ketone).

Formation of acetylides

Alkynes react with a heated sodium metal which replaces the terminal hydrogen to form metal alkynides.

$$2H-C\equiv C-H + 2Na \longrightarrow 2H-C\equiv C-Na + 2H_2$$

For ethyne, which has a terminal hydrogen on both sides, further reaction of the acetylide with sodium gives disodium ethynide.

$$H-C\equiv C-H + 2Na \longrightarrow Na-C\equiv C-Na + H_2$$

Also, alkyne with terminal hydrogen(s) reacts with either solution of copper(I) chloride or silver nitrate in ammonia solution (*ammoniacal* solution) to form coloured precipitates.

$$H-C\equiv C-H + 2CuCl(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{Red ppt}}{Cu-C\equiv C-Cu} + H_2O + 2NH_4Cl$$

$$H-C\equiv C-H + 2AgNO_3(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{White ppt}}{Ag-C\equiv C-Ag} + 2NH_4NO_3 + H_2O$$

The given reactions are used as chemical tests for the presence of terminal alkynes. In the absence of terminal hydrogen, no precipitates of copper(I) or silver are formed.

$$CH_3-C\equiv C-CH_3 + 2AgNO_3(aq) + 2NH_4OH(aq) \longrightarrow \text{No reaction}$$

Combustion

Like in alkanes and alkenes, alkynes undergo combustion reaction with oxygen to form carbon dioxide water and heat energy.

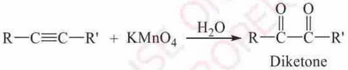
$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g) + \text{heat}$$

The flame temperature during the combustion of acetylene is very high (above 2500 °C). This property makes acetylene useful for welding purposes. Alkynes give very sooty flames when burned. This behaviour is partly used as an evidence for the high degree of unsaturation. The use of acetylene in welding is caused by the fact that the combustion process raises the temperature of the flame up to a temperature that is capable of melting various metals.

Note that, ethyne and oxygen form a mixture that is highly explosive, therefore they need to be handled with extra care.

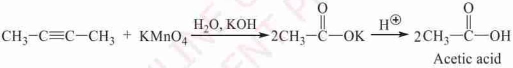
Oxidation

Alkynes are oxidised in the same way as alkenes using strong oxidising agents such as potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$). Vicinal diketones or dialdehydes or carboxylic acid can be formed.



$$R-C\equiv C-R' + KMnO_4 \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R'$$

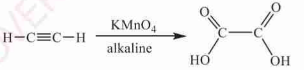
Diketone



$$CH_3-C\equiv C-CH_3 + KMnO_4 \xrightarrow{H_2O,\ KOH} 2CH_3-\overset{\overset{O}{\|}}{C}-OK \xrightarrow{H^{\oplus}} 2CH_3-\overset{\overset{O}{\|}}{C}-OH$$

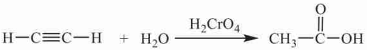
Acetic acid

Alkaline $KMnO_4$ oxidises ethyne to dicarboxylic acid.



Oxalic acid
(Ethanedioic acid)

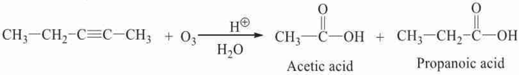
When oxidation is carried out in the presence of chromic acid (a mild oxidising agent), ethyne gives ethanoic acid.



$$H-C\equiv C-H + H_2O \xrightarrow{H_2CrO_4} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

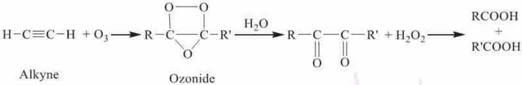
Acetic acid

Oxidation of alkynes using ozone in the absence of zinc followed by hydrolysis form carboxylic acid.



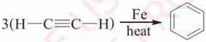
$$CH_3-CH_2-C\equiv C-CH_3 + O_3 \xrightarrow[H_2O]{H^{\oplus}} CH_3-\overset{\overset{O}{\parallel}}{C}-OH + CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-OH$$

The general equation is:-



Polymerisation

Alkynes can be polymerised in the same way as alkenes. However, polymerisation of alkynes gives short chain products. For example, polymerisation of ethyne in a hot copper or iron tube form benzene. This process is called trimerisation.



Chemical tests for alkynes

(a) Alkynes burn in large supply of oxygen with a luminous sooty flame.

(b) Alkynes slowly decolourise bromine water and acidified potassium permanganate, resulting into the formation of bromoalkane and acids. Decolourisation of these reagents signifies the presence of triple bonds (unsaturation).

(c) Formation of white precipitates with ammoniacal silver nitrate and red precipitates with ammonical copper(I) chloride solutions are useful tests for terminal alkynes.

2.4.4 Uses of alkynes

Acetylene (ethyne) is the simplest and widely used alkyne. The compound is useful because it can undergo several chemical reactions which are useful in manufacturing of products such as ethanal (acetaldehyde), chlorinated acetylene solvents, and vinyl chloride monomer which is used in the industrial manufacturing of plastics such as poly(vinyl chloride) (PVC). Acetylene is also used as fuel for the oxyacetylene blow-lamp in cutting and welding metal for fabrication purposes.

In agriculture, alkynes such as aliphatic *n*-alkynes and acetylene (ethyne) have shown the ability of measuring the process of nitrogen fixation in the soil. Plants, naturally produce *capillin*, a biologically active substance which has a strong antifungal activity.

In pharmaceutical, naturally occurring alkynes and their synthetic products have been used as antifungal and anti cancer drugs. For example enediynes are natural product from bacteria containing alternating two carbon-carbon triple bonds and one carbon-carbon double bond which are clinically used as anti-cancer drugs.

Exercise 2.6

1. Describe by using chemical equations, how you would carry out the following conversions:
   (a) Acetylene into oxalic acid
   (b) Propyne into 2,2-dibromopropane
   (c) But-2-yne into acetic acid
   (d) Propyne into propanone
   (e) Acetylene into vinyl acetate

2. Arrange the following compounds in the order of increasing acidity of their terminal hydrogens. Give reasons for your choice.

   $HC{\equiv}CH$, $CH_3C{\equiv}CH$, $(CH_3)_3C{-}C{\equiv}CH$, $Cl{-}C{\equiv}CH$, $O_2N{-}C{\equiv}CH$

3. Account for the variation in the acidity of ethyne, ethane, and ethene.

4. With the aid of a balanced chemical equation, explain what will be observed when acetylene is passed through dilute sulphuric acid containing mercuric sulphate at 70 ºC.

5. By applying Markovnikov's rule of electrophilic addition reaction, explain using chemical equations the possible products of hydrobromination of but-1-yne and indicate the major and minor products.

6. Predict the organic product(s) in each of the following:

(a) $CH_3C{\equiv}CH \xrightarrow[HgSO_4]{H_2SO_4,\ H_2O}$

(b) $CH_3C{\equiv}CCH_3 \xrightarrow[\text{Lindlar's catalyst}]{H_2}$

(c) $CH_3C{\equiv}CCH_3 \xrightarrow[NH_3,\ \text{liquid}]{Li}$

7. Explain the applications of alkynes in industry, agriculture, and medicine.

Revision exercise 2

1. (a) Name a catalyst used in the catalytic cracking.
   (b) Outline the necessary conditions used in the;
   (i) thermal cracking process (ii) catalytic cracking.
2. Write the series of reactions occuring when the free radical substitution of methane occurs in the presence of excess chlorine gas.
3. Draw a structural formula for the following molecules:
   (a) 4-ethyloctane
   (b) 2-methylnonane
   (c) 3-ethyl-2-methylheptane
   (d) 3-ethyl-2,2-dimethylhexane
   (e) 2,3,4,5,6,7-hexamethyloctane
   (f) 2-ethyl-2-methylbutane
4. Write a balanced chemical equation for the complete combustion of nonane (C_9H_{20}).
5. Why does only tertiary alkyl halide undergo elimination in Wurtz reaction?
6. Why do alkynes undergo nucleophilic addition reactions while alkanes do not?
7. Write equations for the reactions and name the products formed when isobutylene reacts with:
   (a) Cl_2 and water
   (b) HBr

(c) HBr in presence of peroxide

(d) H_2O in presence of $H^{\oplus}$

8. The addition of hydrogen chloride to 3,3-dimethylbut-1-ene gives a mixture of two isomeric chlorides in approximately equal amounts.
   (a) Suggest reasonable structures for these two compounds.
   (b) Show the mechanism for their formation.

9. Suppose you need to prepare 4-methylpent-2-yne and discover that the only alkynes on hand are acetylene and propyne. You are also given methyl iodide, isopropyl bromide, and 1,1-dichloro-3-methylbutane. Which of these compounds would you choose in order to perform your synthesis, and how would you carry it out?

10. Compound **A** has a molecular formula $C_{14}H_{25}Br$ and was obtained by the reaction of sodium acetylide with 1,2-dibromododecane. On the treatment of compound **A**, with sodium amide, it was converted to compound **B** ($C_{14}H_{24}$). The ozonolysis of compound **B** gave the di-acid $HO_2C(CH_2)_{12}CO_2H$. The catalytic hydrogenation of compound **B** over Lindlar's catalyst gave compound **C** ($C_{14}H_{26}$), and the hydrogenation over platinum gave compound **D** ($C_{14}H_{28}$). A sodium–ammonia reduction of compound **B** gave compound **E** ($C_{14}H_{26}$). Both **C** and **E** yielded $O{=}CH(CH_2)_{12}CH{=}O$ on ozonolysis. Assign structures to compounds **A** through **E** so as to be consistent with the observed transformations.

11. Explain briefly the difference in bond lengths and bond strengths between the alkanes, alkenes, and alkynes with the same number of carbon atoms.

Chapter Three

Aromatic hydrocarbons

Introduction

Aromatic hydrocarbons are unsaturated chemical compounds characterised by one or more planar rings of atoms joined by covalent bonds of two different kinds (*sigma* and *pi*). Many aromatic compounds have a pleasant smell. However, not all compounds with pleasant smell are aromatic compounds. These compounds have a wide range of applications such as in the production of detergents, rubbers, nylons, pesticides, drugs, food preservatives, and artificial food flavour. In this chapter, you will learn about the conditions for aromaticity, sources, preparation, nomenclature, properties of aromatic hydrocarbons as well as uses and hazards.

3.1 Conditions for aromaticity

Aromaticity refers to an extra stability of a highly conjugated unsaturated molecule that exists as a planar ring with circular cloud of delocalised π -electrons, in which the stability is higher than the corresponding molecule with localised π-electrons.

For a molecule to be termed as aromatic, it must fulfil the following conditions:

(a) It must be cyclic (with ring structure).

Examples: Benzene is cyclic, while 1,3,5-hexatriene is not

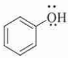
Cyclic
benzene

Acyclic
1,3,5-hexatriene

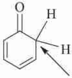
(b) It must be fully conjugated.

Every atom in the ring must consist of an alternating single and double bond in a molecule. This condition can also be expressed as every atom in the ring must have a *p*-orbital and be able to participate in the resonance. There must be no sp^3 hybridised atom in the ring.

Examples:



All ring atoms are conjugated



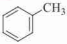
This carbon is not conjugated

(c) The molecule must fulfil the requirements for Hückel's rule.

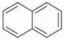
For a molecule to be aromatic, it must be cyclic and fully conjugated. However, not all cyclic conjugated molecules are aromatic. The cyclic conjugated molecule must obey the *Hückel's rule* which states that any planar cyclic conjugated system will be aromatic only if there are 4n + 2 delocalised π-electron system, where n is an integer (n = 1, 2, 3, 4….) and experiences unusual aromatic stabilisation. When n equals to 1, the number of π-electrons is 6 (for benzene, 4n + 2 = 6), when n equals to 2, 3, 4…, the number of π -electrons are 10, 14, 18, respectively. Therefore, from the Hückel's rule, a molecule with 4n π-electrons is non aromatic.

(d) The *p*-orbitals overlap and lie within the same plane, making the molecule flat (planar). An example of the most common aromatic compounds is benzene (C_6H_6) which meets all the above four conditions. Other examples of aromatic hydrocarbons include naphthalene, anthracene, toluene, (methyl benzene), phenanthrene, and biphenyl. Illustrations of the examples of aromatic hydrocarbons are shown in the following compounds:

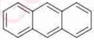
Benzene



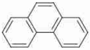
Toluene



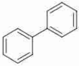
Naphthalene



Anthracene



Phenanthrene



Biphenyl

3.2 Sources of aromatic hydrocarbons

Aromatic hydrocarbons are largely obtained from destructive distillation of coal. Before the second World War (World War II), coal was the most important source of aromatic hydrocarbons. Due to an increase in the demand of aromatic hydrocarbons during and after the World War II, other sources of aromatic hydrocarbons such as petroleum and coal tar were found. Currently, benzene, toluene, and dimethylbenzene are mostly produced from petroleum. Coal tar which is the product of destructive distillation of coal, is a source of many aromatic compounds. The aromatic hydrocarbons are also found in minor but harmful quantities in cigarette smoke.

3.3 Special features of benzene

Benzene is the most common aromatic compound with molecular formula C_6H_6. The cyclic conjugated system of benzene consists of 6 *pi*-electrons, which is equivalent to n = 1 in the Hückel's rule (4 x 1 + 2 = 6). Each *pi*-bond consists of two electrons and benzene has three *pi*-bonds as shown in an orbital diagram below.

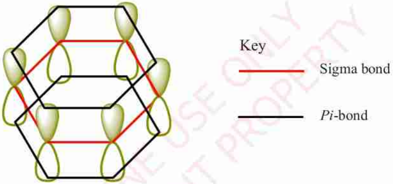
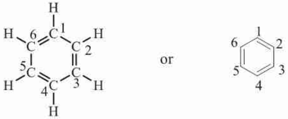


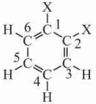
Figure 3.1 Benzene orbital diagram

Each carbon atom in benzene is sp^2 hybridised, and all the three sigma bonds lie in the common trigonal plane with a bond angle of 120° with each other. The structure of benzene was first recognised by a German chemist Friedrich August Kekulé (1829-1896), as a six-carbon compound with a cyclic planar structure having alternating single and double bonds. The molecular structure of benzene as proposed by Kekulé is shown as follows:

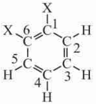


Structure of benzene

Each carbon atom in benzene is bonded to hydrogen in a C—H sigma bond. Some limitations to the Kekulé structure were later discovered. One of the limitations is that, if the structure was correct, then 1,2 and 1,6-disubstituted derivatives of benzene would create two different compounds that are isomers of each other.

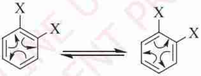


1,2-disubstituted derivative
of benzene



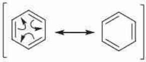
1,6-disubstituted derivative
of benzene

The two disubstituted carbons are connected by double bond in one structure of 1,2-disubstituted. Since the two isomers of that kind were found to be non-existent, Kekulé later suggested that the position of the double bond interconvert rapidly such that the two structural isomers cannot be isolated.



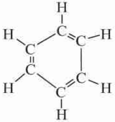
Rapid interconversion

Benzene was therefore said to have two equivalent resonance structures known as *Kekulé's structures.*



These are two equivalent structures of cyclohexatriene. If benzene existed as cyclohexatriene, the following observations would be expected to occur:

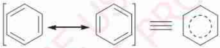
(a) The bond length would be different between the carbon-carbon single bond and the carbon-carbon double bonds, recalling that C=C are shorter than C—C as shown in the following structure.



However, the bond lengths between the carbon atoms are equivalent or identical and are intermediate between single and double bonds.

(b) Benzene would undergo addition reactions just like alkenes.

Benzene does not undergo addition reactions under normal condition, instead it undergoes substitution reactions which preserve the aromaticity. From the two equivalent resonance structures of benzene known as *Kekulé structures*, a hybrid structure was proposed and represented as a hexagon containing a circle inside. The hybrid structure of benzene indicates that the six-delocalised π-electrons are equivalently distributed throughout the six carbon atoms.



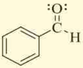
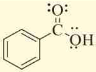
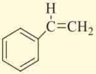
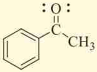
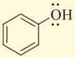
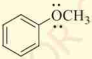
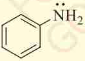
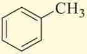
Kekulé resonance structure Resonance hybrid

Therefore, in benzene, unlike in other conjugated systems, the π-electrons are delocalised over a cyclic conjugated system. It is this cyclic conjugation that leads to a greater stabilisation in benzene than in the non-cyclic conjugated system.

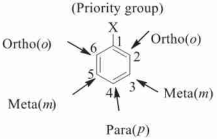
3.4 Nomenclature of substituted derivatives of benzene

Derivatives of benzene are compounds in which one or more of the six hydrogen atoms are replaced by other substituents. The substituted benzenes are also called *arenes*. Those which are substituted with only one substituent are called monosubstituted arenes. Thus, many monosubstituted arenes have IUPAC approved non-systematic names. The systematic and common names of some derivatives of benzene are shown in Table 3.1.

Table 3.1 Systematic and common names of some derivatives of benzene

Structure	Systematic name	Common name
	Benzene carbaldehyde	Benzaldehyde
	Benzene carboxylic acid	Benzoic acid
	Vinyl benzene	Styrene
	Methylphenyl ketone	Acetophenone
	Benzenol	Phenol
	Methoxybenzene	Anisole
	Benzenamine	Aniline
	Methylbenzene	Toluene

When there are two substituents on benzene ring, *ortho, meta,* and *para* are used to indicate the position of the second substituent relative to the first one. The general structure of the substituted benzene indicating the possible positions of the substituents is shown as follows:



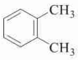
The *ortho*, *meta,* and *para* refer to 1, 2; 1, 3 and 1, 4 substitutions respectively. The position of the priority group is indicated as carbon number one in numbering. The concept of priority in naming is based on reactivity of functional group, alphabetical order, molecular weight of atoms and types of bond. Below is an example of the order of priority based on the functional groups.

$-CO(OH) > -SO_2OH > -CONH_2 > -CN > -CO(OR) > -CH(O) >$
$-COR > -OH > -NH_2 > R- > -X > -NO_2$

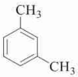
Example:

The amine and hydroxyl groups are in 1 and 4 positions (*para*) to each other. The parent structure is either aniline or phenol. The priority group in the parent structure is hydroxyl and therefore, the compound is named as 4-aminophenol.

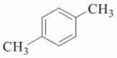
If the benzene ring is substituted with two methyl groups, the dimethyl derivatives are called xylenes, which exist in three isomers.



o-xylene
1,2-dimethylbenzene

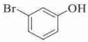


m-xylene
1,3-dimethylbenzene

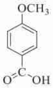


p-xylene
1,4-dimethylbenzene

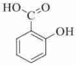
Other examples of disubstituted benzenes and their names are shown in the following compounds:



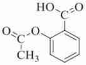
m-bromophenol
(3-bromophenol)



p-methoxybenzoic
acid



2-hydroxybenzoic
acid (salicylic acid)

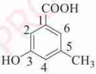


Acetylsalicylic acid
(Aspirin)

If there are three or more substituents on benzene ring, the prefixes *o, m,* and *p* are not used, instead numbers are used. The carbon bearing the dominant group should be given number one, proceeding either clockwise or anticlockwise in order to ensure the possible smallest ratio. The order of naming must be non-dominant group(s) which are named alphabetically followed by benzene ring and then a dominant group.

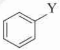
Examples:

2-bromo-6-methyl-4-nitrobenzenesulphonic acid

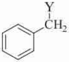


3-hydroxy-5-methylbenzenecarboxylic acid

The position of the first carbon is determined by the name of the benzene derivative. The word phenyl is used to indicate a benzene ring that is named as a substituent. The phenyl and benzyl groups are shown in the following structures.



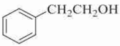
Phenyl group



Benzyl group

where Y is the dominant chain to which phenyl and benzyl groups are attached.

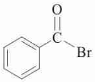
Example:



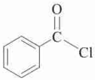
2-phenylethanol

A phenyl group which is bonded with –COR is called benzoyl.

Examples:



Benzoyl bromide



Benzoyl chloride

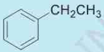
Exercise 3.1

1. Determine whether the following molecules are aromatic or not:

(a)

(b)

(c)



(d)

(e)

2. (a) What are the necessary conditions for any compound to be aromatic?

   (b) Explain why the following compounds are not aromatic:

(i)

(ii)

(iii)

3. (a) State the Hückel's rule.

   (b) How is the Hückel's rule applied in the identification of aromatic compounds?

4. Explain the shortcomings of the Kekulé's structure of benzene and how they were used to predict the modern structure of benzene.

5. The following structure representing a benzene molecule substituted with a number of different groups (A, B, C, D, E, and F):

State whether the following pairs of groups are *ortho, meta* or *para* to each other:

(a) B and D (b) F and B (c) F and C (d) B and C (e) E and F
(f) F and A (g) A and C (h) E and C (i) B and E.

6. Write the structures of the aromatic compounds with the following IUPAC names:

(a) 2,3-dibromo-5-chloronitrobenzene

(b) 2,3,4,5-tetrachlorophenol

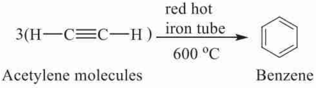
7. Explain why benzene is extra ordinary stable though it contains three double bonds.

3.5 Preparation of benzene

Benzene, as an example of aromatic hydrocarbons can be prepared by various laboratory and industrial techniques. Commercially, benzene is chiefly obtained by fractional distillation of coal. The following are some of the laboratory techniques used for the preparation of benzene.

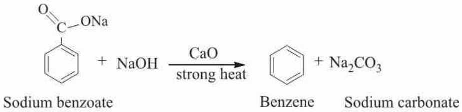
3.5.1 Cyclic polymerisation of ethyne/trimerisation of ethyne

Benzene is prepared by cyclic polymerisation of ethyne (acetylene). This process involves passing of three molecules of acetylene gas through a red-hot iron tube at a temperature of 600 °C. At this temperature, the acetylene molecules undergo a cyclic polymerisation to form a benzene ring.



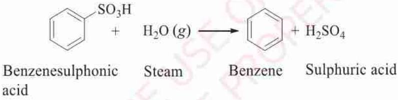
3.5.2 Decarboxylation of aromatic acid salts

This method involves the decarboxylation of sodium benzoate. The salt is heated with soda lime (mixture of NaOH and CaO) to produce benzene and sodium carbonate.



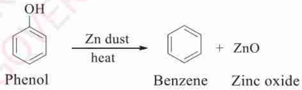
3.5.3 Hydrolysis of benzenesulphonic acid

The hydrolysis of benzene sulphonic acid is carried out by passing the acid into a super-heated steam. This process yields benzene and sulphuric acid.



3.5.4 Reduction of phenols

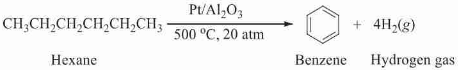
Benzene can be prepared by reducing phenols. This process involves the passing of phenol vapours over heated zinc dust. The phenols are reduced by zinc dust to form benzene and zinc oxide.

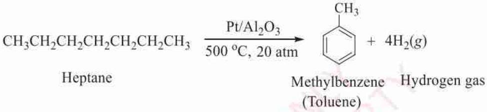


3.5.5 Catalytic reforming of hydrocarbons

The *catalytic reforming* is the rearrangement of straight chain hydrocarbons consisting of C_6 to C_8 to form compounds containing a benzene ring. The feedstock in this reaction is a mixture of the naphtha or gasoline fractions and hydrogen gas. The role of hydrogen gas is to prevent thermal decomposition of hydrocarbon into carbon dioxide and water.

The reaction is useful in the manufacture of arenes such as benzene and toluene, while hydrogen gas is produced as a by-product of reforming fractions from crude oil. Benzene is reformed from hexane and toluene from heptane in the presence of a catalyst, high temperature, and pressure.

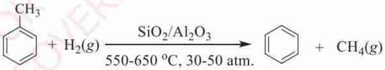




In these reactions, platinum catalyses the dehydrogenation process and Al_2O_3 catalyses the cyclisation process.

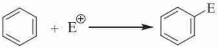
3.5.6 Dealkylation of toluene

Methyl group can be removed from toluene by a process known as *dealkylation*. In this process, toluene is mixed with hydrogen gas at a high temperature (550-650 °C) under a pressure range of 30-50 atm. The catalyst used is a mixture of silicon dioxide and aluminium oxide. The dealkylation of toluene yields benzene and methane.



3.6 Effects of substituent groups on benzene ring

Benzene does not undergo addition reactions easily, but it can undergo substitution reactions to form monosubstituted, disubstituted or simply polysubstituted products. Consider that benzene ring undergoes an electrophilic aromatic substitution reaction to form a monosubstituted product.

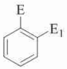


There are two phenomena that arise regarding the second substitution, which depend on the effect of the first substituent.

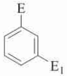
(a) The easiness with which the second substitution can be done relative to the first.

(b) The position on the benzene ring with which the second substituent attaches.

Note that, there are three possible positions for the second substituent (E_1) to attack: *ortho-, meta-*, and *para*-positions.



E_1 at *ortho* position



E_1 at *meta* position

E_1 at *para* position

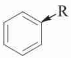
The first substituent that is attached to the benzene ring affects the rate at which the second substitution occurs as well as the position at which the second substituent group attacks. The factors that affect the reactivity of monosubstituted benzene ring towards the second and subsequent substitutions are divided into two main groups which are inductive and mesomeric effects.

3.6.1 Inductive effects

There are two types of inductive effects which are positive and negative inductive effects depending on the nature of a substituent group.

Positive inductive (+I) effect

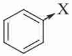
All alkyl groups have a +I effect and therefore release their bonding electrons into the benzene ring through sigma bonds. The positive inductive effect activate the ring, however the *ortho* and *para* positions are activated more than the *meta* position. Thus, alkyl groups are said to be *ortho-para* directors because of their positive inductive effects. The mechanism of stabilisation of *ortho-para* position will be illustrated when discussing the mesomeric effects.



Positive inductive effect

Negative inductive (-I) effect

When carbon atom is bonded to a more electronegative atom such as oxygen, nitrogen or halogen atom, it will experience a negative inductive effect. If a substituent group has only a –I effect, it would be a deactivating and *meta* directing group. However, most of the groups which have –I effect also show a positive mesomeric effect. Since mesomeric effects are stronger than inductive effects, the directing action of the most –I effect substituents is dominated by the accompanying mesomeric effect.



Negative inductive effect

3.6.2 Mesomeric effects (resonance effects)

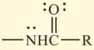
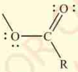
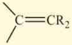
Mesomeric effects are also divided into two types, which are a positive mesomeric (+M) effect and a negative mesomeric (−M) effect.

Positive mesomeric (+M) effect

This is an electron donating effect, and mostly occurs in substituent groups which contain lone pairs. Generally, if the first substituent group is an electron donating group (EDG), it activates the benzene ring, but the activation occurs more on the *ortho* and *para* positions and less activation on the *meta* position of the ring. Therefore, the incoming second substituent will be directed and bonded to the *ortho* or *para* positions. Examples of electron donating groups are shown in Table 3.2.

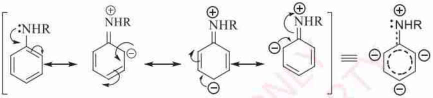
The hydrogen atom is used as a standard or reference group and is considered as having neither the activating effect nor the deactivating effect. One way of recognising the electron donating group is by checking whether the group consists of an atom that has lone pair and directly bonded to carbon atom of the benzene ring. Other electron donating groups which do not have lone pairs are alkyl (R), aryl (phenyl) and vinyl groups.

Table 3.2 The electron donating groups (EDG) and their activation effect on the benzene ring

EDG	Activation effect	Direction of incoming group
$-\ddot{O}^{\ominus}$	Strongly activating	Ortho-para position
$-\ddot{N}R_2$		
$-\ddot{N}H_2$		
$-\ddot{O}H$		
$-\ddot{O}R$		
 $-\ddot{N}H\overset{:O:}{\overset{\Vert}{C}}-R$	Moderately activating	
		
$-R$	Weakly activating	
		
		
$-H$	Reference group	

A mesomeric effect or a resonance effect occurs through the multiple bonds of the ring. The positive mesomeric effect or resonance effect is the effect in which *pi*-electrons or lone pairs are pushed towards the ring.

The electron donating group (EDG) activates the benzene ring by increasing the electron density on the ring through a resonance effect. However, not all positions of the ring are equally activated. By resonance, the extra electron density will be increased more at the *ortho* and *para* positions, making them more nucleophilic. The resonance stabilisation of the benzene ring by the electron donating groups is shown in the following mechanism:

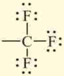
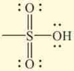
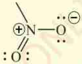
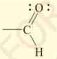
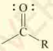
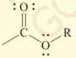
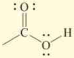
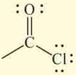


Because of the resonance effect, the incoming substituent which is an electrophile will be directed more to the *ortho-para* positions because they are more nucleophilic.

Negative mesomeric (-M) effect

If the first substituent group on benzene ring is an electron withdrawing group, it deactivates the ring. However, the deactivation occurs more at the *ortho* and *para* positions of the ring, making the positions less nucleophilic. Therefore, the incoming second substituent will be directed and bonded to the *meta* position which is less deactivated, because it is more nucleophilic. Examples of electron withdrawing groups are shown in Table 3.3.

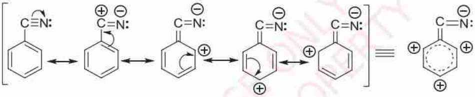
Table 3.3 The electron withdrawing groups (EWG) and their effects on the benzene ring

EWG	Deactivation effect	Direction of incoming group
 $-CF_3$	Strongly deactivating	Meta
$-C\equiv N:$		Meta
$-\overset{\oplus}{N}H_3$		
 $-SO_3H$		
$-\overset{\oplus}{N}R_3$		
 $-NO_2$		
   	Moderately deactivating	
		
$-\ddot{X}:$	Weakly deactivating	Ortho-para position

One way of recognising the EWG is to identify whether the atom attached directly to the benzene ring is itself bonded to another atom by a π–system or the atom attached to benzene ring is more electronegative.

Electron withdrawing resonance effect (negative mesomerism)

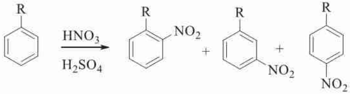
The electron withdrawing group (EWG) deactivates the benzene ring by decreasing the electron density on the ring through a resonance effect. However, not all positions of the ring are equally deactivated. By resonance, the electron density will be more decreased on the *ortho* and *para* positions, making them less nucleophilic (more electrophilic). The resonance deactivation of the benzene ring by the EWG is shown in the following illustration:



The partial positive charges at the *ortho* and *para* positions indicate that they are more electrophilic. Therefore, the incoming groups will be directed to the *meta* positions because they are more nucleophilic.

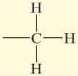
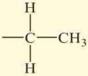
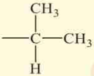
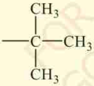
Except halogens, all the electron withdrawing groups are *meta* directors of the incoming substituents. Halogens are *ortho-para* directors despite being the electron withdrawing groups by the negative inductive effect. This is because halogens are also electron releasing groups by resonance due to the presence of lone pairs as discussed in chapter one. Normally, mesomerism is dominant over the inductive effect because mesomerism involves high electron density than inductive effect.

Apart from the inductive and resonance effects, which are electronic effects, the position of the incoming substituent group can also be influenced by a steric effect causing steric hindrance. *Steric hindrance* is defined as an inter-electronic repulsion force caused by closeness of the bulk groups of atoms in the same molecule due to spatial arrangement. At the *ortho* and *para* positions, whether the incoming group will be directed to either of these positions depends on the size (bulkness) of the first substituent to attack the ring. For example, the nitration of alkyl benzene produces a mixture of compounds at different percentages.



The percentage of the *ortho, para,* and *meta* product with an increase in the size of group -R are shown in Table 3.4.

Table 3.4 The products of nitration as a function of the size of alkyl group

Alkyl group(R)		% *Ortho*	% *Meta*	% *Para*
 $-\overset{H}{\underset{H}{C}}-H$	$-CH_3$	58	4	37
 $-\overset{H}{\underset{H}{C}}-CH_3$	$-CH_2CH_3$	45	6	49
 $-\overset{CH_3}{\underset{H}{C}}-CH_3$	$-CH(CH_3)_2$	30	8	61
 $-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	$-C(CH_3)_3$	16	11	73

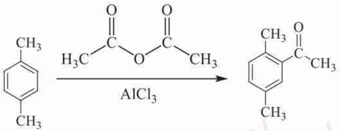
Note that, as the size of the alky group increases, the percentage of the product at the para position also increases significantly. This is accompanied with a significant decrease in the percentage of the *ortho* product due to steric hindrance.

3.6.3 Competing effects of different substituents on benzene ring

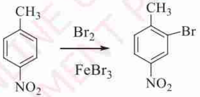
If a benzene ring consists of two different substituent groups, the position of the incoming third substituent will depend on the dominating activator or deactivator present on the ring.

Examples:

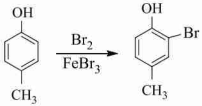
1. The two methyl groups are on the *para* positions with respect to each other and both are *ortho-para* directors. The *ortho* positions with respect to one methyl group are the *meta* positions with respect to the other. Therefore, all positions are equal and the incoming group will be bonded to any of the positions in the benzene ring.



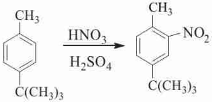
2. The benzene ring consists of a methyl group which is an *ortho-para* director and a nitro group which is a *meta* director. The *ortho* position with respect to a methyl group is the *meta* position with respect to a nitro group. Therefore, the incoming substituent will be bonded to this position because it is reinforced by two substituents.



3. The benzene ring consists of methyl and hydroxyl groups which are at the *para* positions with respect to each other. Both are activators and hence *ortho-para* directors. The *ortho* position with respect to hydroxyl group is the *meta* position with respect to methyl group. Under this situation, it is the stronger activator (–OH) that will control and direct the position of the incoming group. Therefore, the incoming group will be bonded to the *ortho* position with respect to hydroxyl group.



4. The two alkyl groups are on the *para* positions with respect to each other. They are activators and hence *ortho-para* directors. The *ortho* position with respect to one alkyl group is the *meta* position with respect to the other. Due to the steric hindrance of the large isobutyl group, the incoming group will be directed to the *ortho* position next to the methyl group which is small.



Exercise 3.2

1. By using chemical equations, explain how you would prepare benzene from ethanoic acid.
2. By using chemical equations, state the reagents and necessary conditions for preparation of benzene from:
   (a) Alkynes
   (b) Phenol
   (c) Benzene sulphonic acid
3. (a) In which nitration reaction will the product be formed faster? Give reasons.
   (i) Nitration of aniline.
   (ii) Nitration of nitrobenzene.
   (b) Classify these two groups as activating or deactivating groups:
   (i) Alcohol
   (i) Ester
4. (a) Discuss the effects of substituents on the reactivity of a benzene ring.
   (b) Explain the deactivating and *meta* directing nature of nitro group towards aromatic electrophilic substitution.
5. With the help of resonance structures, give an electronic interpretation of the *ortho-para* directing influence of amine group. Do the same for the influence of alkyl group.

6. Why is chlorine in chlorobenzene an *ortho-para* director although it has a negative inductive effect during electrophilic substitution in benzene ring?
7. Using the bromination of nitrotoluene as an example, explain the effect of substituent groups in disubstituted benzene on the position of the incoming third substituent.

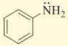
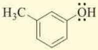
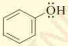
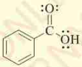
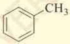
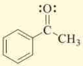
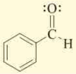
3.7 Properties of aromatic hydrocarbons

Aromatic hydrocarbons like aliphatic hydrocarbons exhibit both physical and chemical properties.

3.7.1 Physical properties of aromatic hydrocarbons

In general, aromatic hydrocarbons resemble closely to other hydrocarbons in their physical properties. Some aromatic hydrocarbons are liquids at room temperature while others are crystalline solids. Because of their symmetrical shapes, most aromatic hydrocarbons are non-polar. They are volatile carcinogenic compounds which are insoluble in water. Aromatic hydrocarbons have higher melting points compared to other hydrocarbons, because of their symmetrical shape and hence are packed better into crystals. Their boiling points are also higher than aliphatic hydrocarbons. They are denser than aliphatic hydrocarbons, but some are less dense than water while others are denser than water. The physical properties of some of aromatic hydrocarbons are shown in Table 3.5.

Table 3.5 Physical properties of some of aromatic compounds

S/N	Aromatic hydro carbon	Structural formula	Molecular formula	Boiling point (°C)	Melting point (°C)	Density (g/cm^3)
1.	Benzene		C_6H_6	80.1	5.5	0.878
2.	Aniline		$C_6H_5NH_2$	184.1	-6.3	1.02
3.	Cresol		C_7H_8O	*o*-cresol (191) *m*-cresol (202) *p*-cresol (201.9)	o-cresol (29.8) m-cresol (11.8) p-cresol (35.5)	o-cresol (1.05) m-cresol (1.03) p-cresol (1.02)
4.	Phenol		C_6H_6O	181	40.5	1.07
5.	Benzoic acid		$C_7H_6O_2$	249.2	122.4	1.270
6.	Toluene		C_7H_8	111	-95	0.867
7.	Aceto phenone		C_8H_8O	202	19-20	1.02
8.	Benzal dehyde		C_7H_6O	178.1	-57.12	1.044

3.7.2 Chemical properties of aromatic hydrocarbons

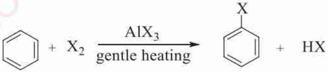
Although benzene with its 6 π- electrons is among the unsaturated hydrocarbons, it does not undergo addition reaction easily like other unsaturated hydrocarbons (alkenes and alkynes), since it is very stable towards strong acids, bases and oxidising agents. The stability of benzene is attributed to the delocalisation of π-electrons (resonance) which makes the electrons not available for the reaction. Therefore, they undergo electrophilic substitution reactions. The benzene ring in these reactions acts as a nucleophile and an electrophile attached on the ring forms a substituted product. Since the incoming electrophile substitutes only the hydrogen atom of the benzene ring, the product formed retains its stability and aromatic nature. Benzene being an aromatic compound, undergoes two types of organic reactions which are electrophilic substitution reactions and addition reactions.

Electrophilic aromatic substitution reaction

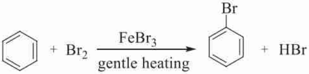
Electrophilic aromatic substitution is the type of substitution reaction in which a weak electrophile is substituted with strong electrophile. The electrophile is attacked by the aromatic ring and forms an intermediate which is stabilised by resonance. The electrophilic substitution reactions of benzene include; halogenation, alkylation, acylation, nitration, and sulphonation.

Halogenation of benzene

Benzene reacts with halogens in the presence of a halogen carrier, which acts as a catalyst. Suitable halogen carriers include aluminium or iron halides ($AlCl_3$ or $FeBr_3$). Such halides act as catalysts because they have empty orbitals into which the lone pairs from halogens are received, hence they are called Lewis acids, and for this reaction to proceed it requires gentle heating.



Example:

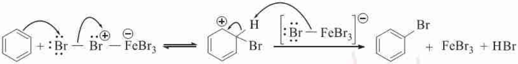


Mechanism

The catalyst ($FeBr_3$) reacts with bromine to form iron(III) complex acting as a halogen carrier in which the Br-Br bond is polarised.

iron(III) complex

This reaction is very important as it prepares an electrophile which then reacts with benzene (nucleophile) to form an intermediate arenium ion.



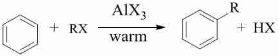
The Lewis acid-nucleophile complex attacks the proton of the arenium ion or sigma complex to regenerate the Lewis acid and aromatic ring. Then, the $FeBr_3$ can proceed polarising more bromine molecules for further halogenation.

Friedel-Crafts reactions

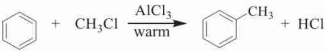
The *Friedel-Crafts reactions* are sets of chemical reactions used to insert an alkyl or acyl group into the aromatic ring (benzene). They were developed by two scientists in 1877: Charles Friedel (1832-1899), a French chemist and James Mason Crafts (1839-1917), an American chemist. A set of chemical reactions making up Friedel-Crafts reactions are alkylation and acylation.

Friedel-Crafts alkylation of benzene

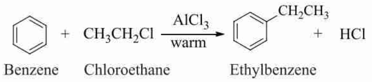
Alkylation of benzene is the transfer of an alkyl group from one molecule (alkyl halide) to benzene ring. In this reaction, a halogen carrier is required to generate a more reactive electrophile. Like in halogenation, the catalysts used are iron(III) chloride ($FeCl_3$) or aluminium chloride ($AlCl_3$) which are Lewis acids. The following reaction represent alkylation of benzene.



Examples:

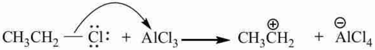


Benzene Chloromethane Methylbenzene



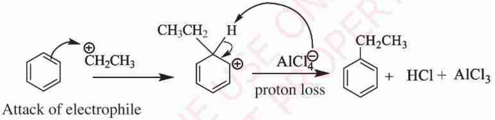
Mechanism

The $AlCl_3$ polarises the CH_3CH_2-Cl bond and generates a carbocation.

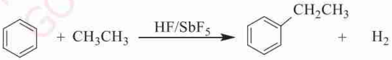


$$CH_3CH_2-\ddot{\underset{..}{Cl}}: + AlCl_3 \longrightarrow CH_3\overset{\oplus}{C}H_2 + \overset{\ominus}{A}lCl_4$$

The carbocation generated acts as a powerful electrophile which reacts with benzene (nucleophile), to form ethylbenzene and HCl, then $AlCl_3$ catalyst is regenerated.



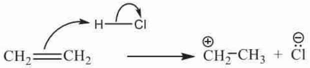
The $AlCl_3$ formed reacts with more chloroethane to facilitate further alkylation of benzene. The alkylation of benzene has a significant industrial importance such as the production of ethylbenzene which is essential in the polystyrene (polyphenylethene) synthesis. Benzene is industrially alkylated with ethane in the presence of HCl, $AlCl_3$ or HF/SbF_5 as catalysts. Ethane is used because it is cheaper and readily available than chloroethane.



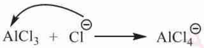
The alkylation of benzene can also be achieved by using an alkene in the presence of the same catalysts (HCl and $AlCl_3$) as shown in the following equation:

Mechanism

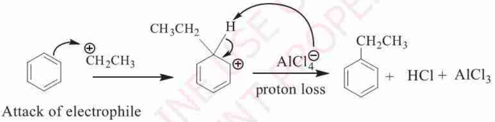
The ethene reacts with hydrochloric acid to form a carbocation, which is an active electrophile.



The $AlCl_3$ reacts with $Cl^{\ominus}$ to form $AlCl_4^{\ominus}$ as a means of preventing the formation of chloroethane to maintain the carbocation.



Then, benzene attacks the electrophile.

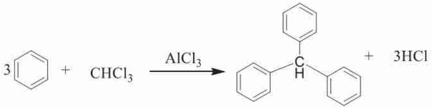


$$H^{\oplus} + AlCl_4^{\ominus} \longrightarrow HCl + AlCl_3$$

The HCl and $AlCl_3$ regenerated can further facilitate the alkylation of benzene.

Chemical test for arenes

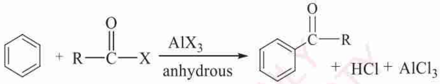
The Friedel-Crafts alkylation is used as a bench test for the presence of aromatic hydrocarbons (arenes). The test involves reacting the chloroform (alkyl halide) with an aromatic compound in the presence of aluminium chloride catalyst to give a bright coloured dye, triarylmethane.



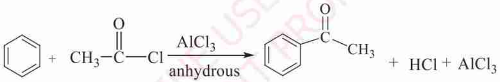
Triarylmethane

Friedel-Crafts acylation of benzene

Acylation of benzene is the transfer of an acyl group (RCO–) from one molecule (acylating agent) to a benzene ring. The reaction conditions for acylation are like the Friedel-Crafts alkylation discussed in the previous section. However, the acylation reaction is more advantageous than alkylation because the ketone produced is less reactive than the original molecule because of the electron withdrawing carbonyl group. As a result, there is no multiple acylation and carbocation rearrangement since the carbocation ion is stabilised by a resonance structure.

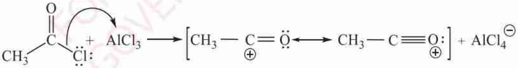


Example:

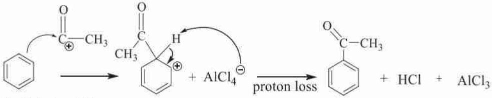


Mechanism

The $AlCl_3$ polarises the acylchloride (CH_3COCl) and generates carbocation (acyl cation).



The carbocation (acyl cation) reacts with benzene.



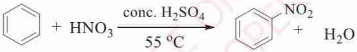
Attack of electrophile

$$H^{\oplus} + AlCl_4^{\ominus} \longrightarrow AlCl_3 + HCl$$

The aluminium chloride regenerated can react with more acyl chlorides to catalyse more acylation of benzene.

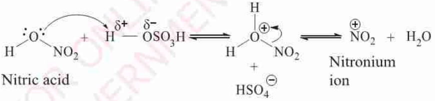
Nitration of benzene

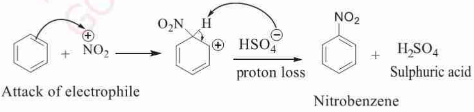
Nitration of benzene is the chemical reaction which involves the transfer of a nitro group from concentrated nitric acid to benzene ring in the presence of concentrated sulphuric acid. The reaction takes place at 55 °C and the conc. sulphuric acid acts as a catalyst. The nitration of arenes produces aromatic nitro compounds. The nitration products are important reagents for the synthesis of some products such as dyes, explosives and water is a by-product.



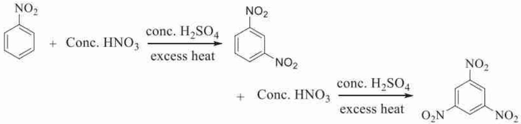
Mechanism

The concentrated sulphuric acid generates the nitronium ion ($NO_2^{\oplus}$) which acts as an active electrophile.



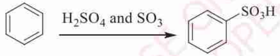


The proton captured by persulphate regenerates the sulphuric acid (H_2SO_4). Then, the H_2SO_4 molecule regenerated reacts with more nitric acid to form nitronium ion and hence facilitating further nitration of benzene. Although the average temperature required in the nitration of benzene is 50-55 °C, too much heating of the system may give further nitration of nitrobenzene to form 1,3-dinitrobenzene or 1,3,5-trinitrobenzene.



Sulphonation of benzene

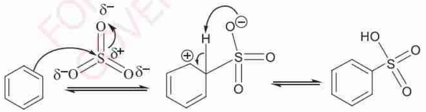
Sulphonation of benzene is a chemical reaction which involves the transfer of a sulphonyl group from sulphuric acid to a benzene ring. The reaction involves adding fuming sulphuric acid (a solution of sulphur trioxide and sulphuric acid) to form benzene sulphonic acid.



Benzene Benzene sulphonic acid

Mechanism

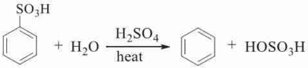
The sulphur in SO$_3$ is electrophilic because its electrons are pulled away by oxygen. The benzene attacks the electrophile and subsequently the proton is transferred to sulphonyl group to form benzene sulphonic acid.



Attack of electrophile

Benzene sulphonic acid

Sulphonation of benzene to form benzene sulphonic acid is a reversible reaction. Since sulphur trioxide readily reacts with water to produce sulphuric acid and heat, therefore by heating benzene sulphonic acid in dilute aqueous sulphuric acid, benzene is formed.

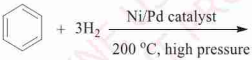


Addition reactions of benzene

Due to the resonance stabilisation of the conjugated double bond, benzene undergoes electrophilic substitution reactions because it is difficult to break the double bonds. However, under vigorous conditions, benzene exhibits some addition reactions. The typical addition reactions of benzene under suitable conditions include catalytic hydrogenation, ozonolysis, free radical addition and combustion.

Catalytic hydrogenation of benzene

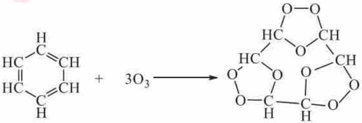
Hydrogenation of benzene is an addition reaction whereby hydrogen atoms are added directly to the benzene ring, forming cyclohexane. Benzene undergoes catalytic hydrogenation at a temperature between 200–230 °C using nickel or palladium catalyst to form cyclohexane.



Benzene Cyclohexane

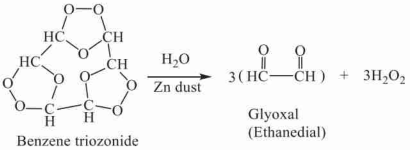
Ozonolysis of benzene

Ozonolysis of benzene is the cleavage of the carbon-carbon double bond of benzene with ozone (O_3) to form organic compounds in which the carbon-carbon double bond is replaced by two carbon oxygen bonds. First, the reaction forms benzene triozonide as an intermediate product.



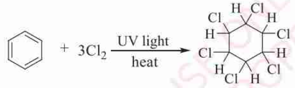
Benzene Benzene triozonide

In the presence of zinc dust, further hydrolysis of benzene triozonide forms ethanedial or glyoxal and hydrogen peroxide.



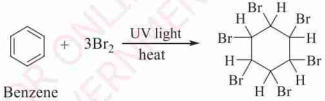
Free radical addition of benzene

In the presence of ultra violet light, chlorine reacts with benzene at its boiling point to form hexachlorocyclohexane.



Benzene 1,2,3,4,5,6-hexachlorocyclohexane

Similar reaction occurs when bromine reacts with benzene.



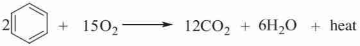
Benzene

1,2,3,4,5,6-hexabromocyclohexane

The reaction does not involve the use of a catalyst, and the delocalised *pi*-bonds are broken permanently.

Combustion

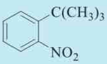
Just like other hydrocarbons, benzene burns in plenty supply of oxygen to produce carbon dioxide, water, and heat.



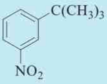
However, the combustion of benzene is difficult and hardly goes to completion especially if air is used instead of pure oxygen. This is because of the high proportion of carbon to hydrogen compared to other hydrocarbons. It means that, the reaction will require high proportion of oxygen to hydrocarbon for a complete combustion. If there is a limited supply of oxygen, hydrogen tends to acquire the available oxygen first, leaving behind carbon which may form carbon monoxide or just left as carbon black. Therefore, benzene burns in air with a smoky flame due to carbon particles.

Exercise 3.3

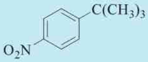
1. Using benzene and any other necessary organic or inorganic reagents, suggest efficient methods for the synthesis of:
   - (a) Isobutyl benzene, $C_6H_5CH_2CH(CH_3)_2$
   - (b) Neopentyl benzene, $C_6H_5CH_2C(CH_3)_3$
2. Draw the structures of the principal organic products obtained on nitration of each of the following:
   - (a) *p*-Methylbenzoic acid
   - (b) *p*-Methoxyacetophenone
   - (c) *m*-Dichlorobenzene
   - (d) *p*-Methylanisole
   - (e) *m*-Dinitrobenzene
   - (f) 2,6-dibromoanisole
3. Write chemical equations showing how you can prepare *m*-bromonitrobenzene as the principal organic product, starting with benzene and using any other necessary organic or inorganic reagents. How can you prepare *p*-bromonitrobenzene?
4. Arrange the following products according to the percentage (%) yield obtained from the nitration of *tert*-butylbenzene. Justify the order.



(a)

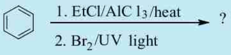


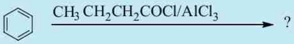
(b)



(c)

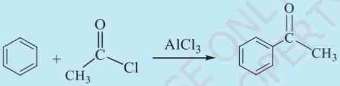
5. Give the major product(s) in the following reactions:

(a) 

(b) 

(c) 

6. Write complete mechanisms for the following reactions:

(a) 

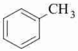
(b) 

7. Using benzene as a starting material, show how you can prepare each of the following:

(a) Tribromobenzene.
(b) Benzenehexachloride (an insecticide).
(c) Propylbenzene.
(d) Benzoic acid.

3.8 Substituted benzene (methylbenzene)

Toluene is a benzene derivative with a methyl group in place of hydrogen atom of the benzene ring. In this section, you will learn about the various preparation reactions of methyl benzene, chemical properties of methyl benzene, effects of the substituent groups on the rate and orientation, directive influence in disubstituted benzene and uses of aromatic hydrocarbons.



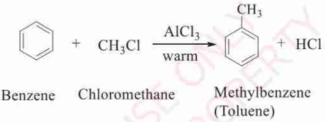
Toluene

3.8.1 Preparation of methylbenzene (toluene)

Toluene as an example of aromatic hydrocarbons is cheaply produced industrially, although it could be prepared in the laboratory by a variety of methods. The following are some of the methods used to prepare toluene.

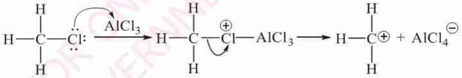
Friedel-Crafts alkylation of benzene

Friedel-Crafts alkylation is a chemical reaction involving the introduction of an alkyl group into benzene ring. In the preparation of toluene, benzene is treated with a haloalkane in the presence of a Lewis acid such as aluminium chloride or iron(III) chloride.

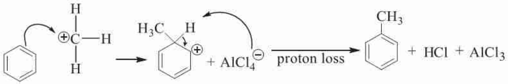


Mechanism

The $AlCl_3$ polarises Cl–CH_3 bond and generates a carbocation.



Then, the carbocation generated acts as a powerful electrophile which reacts with benzene.



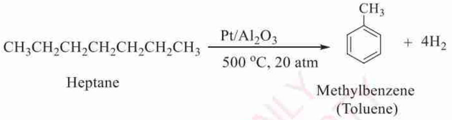
Attack of electrophile

Attack of the proton (H^+) by $AlCl_4^{\ominus}$ regenerates the catalyst and forms HCl.

The $AlCl_3$ can further react with more chloromethane to facilitate further alkylation of benzene to form toluene.

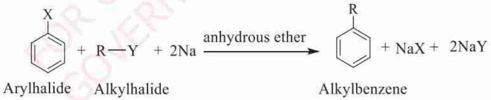
The catalytic reforming of hydrocarbons

Catalytic reforming of hydrocarbons involves the rearrangement of straight chain hydrocarbons consisting of C_6 to C_8 to form aromatic hydrocarbons containing benzene ring. The rearrangement of fractions containing C_7 (heptane) produces toluene and hydrogen gas.

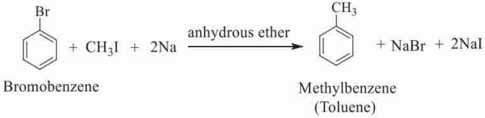


Wurtz-Fittig reaction

The *Wurtz-Fittig* reaction is the chemical reaction of aryl halides with alkyl halides and sodium metal in the presence of anhydrous ether to form substituted aromatic hydrocarbons. This reaction is an extension of Wurtz synthetic reaction which is used for the preparation of symmetrical alkanes. The reaction is named after Wilhelm Rudolph Fittig (1835-1910) a German chemist who invented it in 1855. He discovered that, even aryl halides can undergo Wurtz reaction to form alkylated aromatic hydrocarbons. The general form of Wurtz-Fittig reaction is:

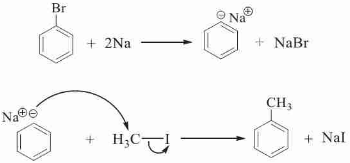


Example:



Mechanism

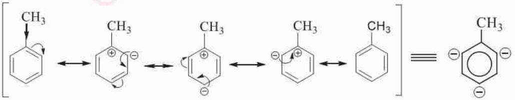
The mechanism of Wurtz-Fittig reaction is given in the following equations:



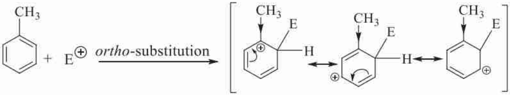
3.8.2 Chemical properties of methylbenzene

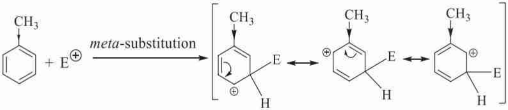
Methylbenzene is commonly known as *toluene*. It is a benzene derivative in which one hydrogen of benzene is replaced by a methyl group. The structure of toluene is shown in the following structure:

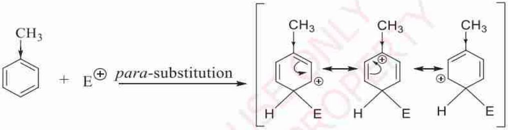
While all the carbon atoms in benzene ring are sp^2 hybridised, the carbon atom of the methyl group is sp^3 hybridised. The methyl group on benzene is an activator, hence an *ortho-para* director, due to a positive inductive effect. The activation effect of the methyl group in toluene is shown in the following resonance structures:



The previous given structures show the incoming group can attack either the *ortho*-(2-) position or *para*-(4-) position. The possibility of substitutions at different positions is shown in the following mechanism:







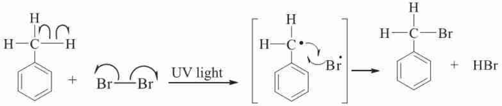
The +I effect of the methyl group can only provide the direct stabilising effect to the carbocation formed by *ortho* and *para* attack of the electrophile. Therefore, only ortho and para substituted methyl benzene can be formed. The chemical reactions of toluene can either be side chain or electrophilic substitution on the benzene ring.

Side chain reaction

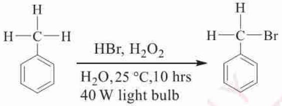
Side chain reaction is a type of the reaction which occurs on the substituent groups of benzene. The reactions that involve side chains are halogenation and oxidation.

Halogenation reaction

Bromination reaction will be used to discuss halogenation in haloalkanes. The bromination occurs through a free radical mechanism, resulting into the formation of benzyl bromide. The reaction takes place in the presence of UV light or bromine water with carbon tetrachloride.

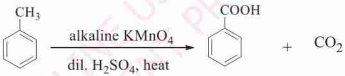


The side chain bromination can also occur in the presence of hydrogen bromide with hydrogen peroxide and light bulb.

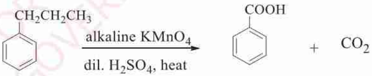


Oxidation

When toluene is treated with alkaline potassium permanganate and dilute sulphuric acid and heated, it becomes oxidised to benzoic acid and carbon dioxide.



Any alkyl group attached to the ring is oxidised to carboxylic acid and carbon dioxide, irrespective of the number of carbon atoms in the alkyl group.

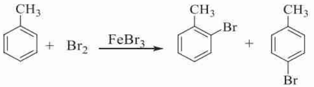


Electrophilic substitution on aromatic ring

Methylbenzene (toluene) and benzene undergo similar reactions which involve electrophilic substitution. However, toluene is more reactive than benzene due to the presence of the methyl group. The following section discusses the electrophilic substitution reactions of toluene.

Halogenation of toluene

The reaction occurs in the presence of Lewis acid catalyst such as ferric bromide ($FeBr_3$).

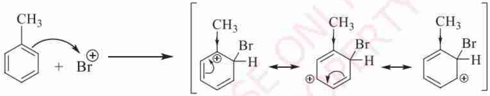


Mechanism

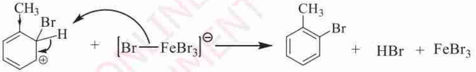
The reaction of a catalyst with bromine form a brominium ion which is an electrophile.

$Br-Br + FeBr_3 \longrightarrow Br^{\oplus} + [Br-FeBr_3]^{\ominus}$

The attack of brominium ion on toluene



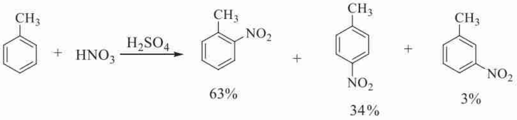
The loss of proton to restore the aromaticity



All three isomers are formed in this reaction, but the products are dominated by *ortho* and *para* isomers.

Nitration of toluene

Nitration of toluene is the introduction of a nitro group in toluene using nitrating reagent. The nitro group attacks at the *ortho* or *para* positions and the reaction occurs in the presence of sulphuric acid.

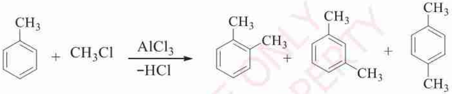


The high yields of *ortho* and *para* products can be explained by drawing the corresponding resonance structures of the arenium ions.

Friedel-Craft's alkylation of toluene

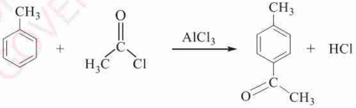
Friedel-Crafts alkylation is an electrophilic aromatic substitution reaction in which a hydrogen atom bonded to an aromatic ring is replaced by an alkyl group. The reaction in toluene occurs in the same way as in benzene, only that in toluene the product is directed to a certain specific carbon atom due to the activating effect of the methyl group.

The reaction involves the use of alkyl halide in the presence of aluminium trihalide as a catalyst.



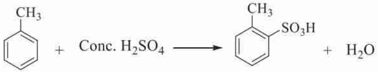
Friedel-Crafts acylation of toluene

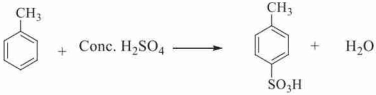
An acyl group is an alkyl group that is bonded to a carbon containing a carbon-oxygen double bond. It has the form $R-\overset{\oplus}{C}=O$, where R is an alkyl group. One of the common sources of an acyl group is an acyl chloride R—CO—Cl, for example ethanoyl chloride (CH_3COCl). Just like in alkylation, the acylation of toluene occurs in the same way as in benzene, only that the methyl group directs the position of the incoming acyl group. Due to steric effect, the major product of acylation of toluene occurs at the *para* position.



Sulphonation of toluene

Sulphonation is the substitution reaction in which one hydrogen atom of an aromatic ring is replaced with a sulphonic acid group ($-SO_3H$). Methylbenzene reacts with concentrated sulphuric acid under reflux for five minutes to form toluene sulphonic acid. A mixture of *ortho* and *para* products are mainly formed with only about 5−10% *meta* product. The main reactions are:





3.9 Uses and hazards of aromatic hydrocarbons (arenes)

Arenes like aliphatic hydrocarbons have a wide application in industrial, health, and agricultural sectors.

(a) In industry, benzene for example is widely used as a raw material in the manufacturing of daily used products such as detergents, rubber and plastics. It is also used in the manufacture of other organic compounds of industrial importance including styrene which is used in making plastics, cumene which is used in making resins and adhesives; and cyclohexane which is used in the production of nylon. Due to its high-octane number, benzene is used as fuel and additive in gasoline to increase engine efficiency. Benzoic acid is applied as a food preservative and as artificial food flavour.

Toluene, a methyl substituted benzene, colourless, and water insoluble liquid is used as a solvent in paints, paint thinners, rubber, printing, leather tanning and lacquers. Toluene and picric acid are used in the production of explosives such as trinitrotoluene (TNT).

Anthracene and aniline derivatives are well known as dye stuffs or artificially produced dyes. Xylene, a dimethyl benzene, is used as a solvent as well as in printing, leather tanning, and as a cleaning agent. It is also used as a thinner for varnishes and paints.

(b) In agriculture, arenes such as *p*-dichlorobenzene, naphthalene, anthracene, and xylene play a big role in wood preservation, production of pesticides and disinfectants. Mothball for example, is a small pellet of a pungent substance made from naphthalene or *p*-dichlorobenzene, put among stored clothes or books to keep away moths.

(c) In medical and health matters, arenes are used in the manufacture of many medicines. Paracetamol and acetylsalicylic acid (ASA) are drugs which are used for alleviating pains.

Despite their useful applications in daily life, arenes are well known for their carcinogenic effects. Apart from its carcinogenic effects benzene for example has both chronic and acute effects when ingested by man, inhaled or contacted through skin. You are therefore advised not to be exposed to high levels of benzenes such as cigarette smoke, sites of petroleum refining, pharmaceutical plants, petrochemical manufacturing facilities, rubber tyre manufacturing, shoe making and other areas where arenes are highly utilised.

Exercise 3.4

1. Briefly describe the reactions of methylbenzene which are:
   (a) Typical of benzene
   (b) Not shared by benzene
2. (a) How is toluene prepared from the following compounds?
   (i) Benzene.
   (ii) Chlorobenzene.
   (b) How does toluene react with chlorine gas in the presence of:
   (i) Sunlight?
   (ii) FeCl3?
3. Suggest an efficient synthesis of *m*-nitrobenzoic acid from toluene.
4. Explain what happens when chlorine gas is bubbled through a boiling toluene.
5. Discuss the uses and hazards of arenes.
6. Why can halogenations of methylbenzene take place on the methyl group or on the benzene ring?
7. Outline the mechanism for the formation of 4-nitromethylbenzene from methylbenzene using $NO_2^{\oplus}$ as the electrophile.
8. Which one is more reactive in an electrophilic aromatic substitution reaction, toluene or nitromethylbenzene? Explain.

Revision exercise 3

1. (a) Write the mechanism of chlorination of benzene and methylbenzene:
   - (i) In the presence of carrier catalyst
   - (ii) In the presence of ultra violet light

   (b) Give the differences and similarities in the mechanism of the two reactions (i) and (ii) in (a).

2. (a) Starting with benzene, write equations to show how you can prepare the following compounds:
   (i) Methylbenzene (ii) Benzenecarboxylic acid

   (b) In each case show how the compounds formed in (a) can be reconverted back into benzene.

3. Write equations to show how you would prepare each of the following compounds starting with benzene and any other inorganic and organic reagents:
   - (a) Bromobenzene
   - (b) Benzoic acid
   - (c) Ethylbenzene
   - (d) Nitrobenzene
   - (e) Benzenesulphonic acid
   - (f) Phenylethanone

4. Alkoxy group (—OR) is *ortho-para* directing even though oxygen is more electronegative than carbon. Explain.

5. Write the structural formulas for the cyclohexadienyl cations formed from aniline ($C_6H_5NH_2$) during:
   - (a) ortho bromination.
   - (b) meta bromination.
   - (c) para bromination.

6. Give the mechanism for the Friedel-Crafts alkylation to form ethylbenzene.

7. Using examples, explain the role(s) of catalysts used in Friedel-Crafts alkylation and acylation reactions.

8. Arrange the following haloalkanes in the order of increasing reactivity in the Friedel-Crafts alkylation of benzene. Give reasons for your answer.

   (a) Chlorobutane

   (b) 2-chloro-2-methylpropane

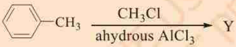
   (c) 1-chloro-2-methylpropane

   (d) 2-chlorobutane.

9. Identify compounds X and Y in the following reactions:

(a)

(b)



10. (a) Give two reactions in which benzene and ethene react in a similar way.

   (b) By using molecular orbital diagrams show how the structure of benzene is related to the structure of ethene.

   (c) Write down two reactions in which benzene and ethene react in different ways.

11. Two isomeric hydrocarbons **P** and **Q** have the molecular formula C_9H_{12}. On oxidation, **P** gives a monocarboxylic acid which when heated with excess soda lime yields benzene. **Q** is oxidised to give a tricarboxylic acid, which can then undergo nitration to give a mono-nitro derivative.

   (a) Deduce the structural formula of **P** and **Q**.

   (b) Write chemical equations to show the reactions which have been described.

Chapter Four

Halogen derivatives of hydrocarbons

Introduction

The halogen derivatives of hydrocarbons are also called halohydrocarbons. These organic compounds contain carbon, hydrogen, and at least one carbon-halogen bond (C—X) where X represent halogens. These compounds are used in refrigerators, fire extinguishers, and as solvents in laboratories and industries. Thus, this chapter takes you through the structures, nomenclature, preparation, properties, uses and hazards of halogen derivatives of hydrocarbons.

4.1 Structures and nomenclature of halohydrocarbons

The general formula for the halogen derivatives of hydrocarbons is R—X, where R represents any alkyl or aryl hydrocarbon group. These include alkyl halides (haloalkanes) and aryl halides.

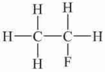
The structures of halohydrocarbons are very useful in the IUPAC naming system for these compounds. Their isomers show variety of properties that differ from one isomer to another. In this section, you will learn about the structures, isomers, and IUPAC nomenclature of halohydrocarbons.

4.1.1 Structure of halohydrocarbons

There are different ways in which halohydrocarbons can be classified. These include the classification based on the types of halogen atoms or functional groups, the number of halogen atoms, the degree of alkyl substitution on carbon bearing the halogen, and the type of hydrocarbyl to which the halide is attached.

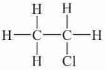
Types of halogen atoms or functional groups

The classes of halohydrocarbons based on the types of halogen atoms attached to carbon atom are fluorohydrocarbon, chlorohydrocarbon, bromohydrocarbon, and iodohydrocarbon. Examples of the halohydrocarbon are shown below.



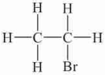
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & F & \end{array}$$

Fluoroethane



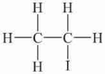
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & Cl & \end{array}$$

Chloroethane



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & Br & \end{array}$$

Bromoethane

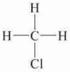


$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & I & \end{array}$$

Iodoethane

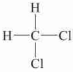
Number of halogen atoms

Halohydrocarbons can be classified based on the number of halogen atoms attached to the carbon atom. Carbon atom can be bonded with up to four halogen atoms as shown in the following compounds:



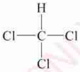
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & Cl & \end{array}$$

Chloromethane
(one halogen atom)



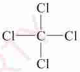
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -Cl \\ & | & \\ & Cl & \end{array}$$

Dichloromethane
(two halogen atoms)



$$\begin{array}{ccc} & H & \\ & | & \\ Cl- & C & -Cl \\ & | & \\ & Cl & \end{array}$$

Trichloromethane
(three halogen atoms)



$$\begin{array}{ccc} & Cl & \\ & | & \\ Cl- & C & -Cl \\ & | & \\ & Cl & \end{array}$$

Tetrachloromethane
(four halogen atoms)

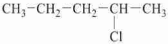
Degree of alkyl substitution on carbon bearing the halogen

Halohydrocarbons are classified as primary, secondary or tertiary based on the degree of alkyl substitution on the carbon atom that is bonded with the halide functional group. Primary (1°) alkyl halides consist of only one alkyl group that is bonded to the carbon bearing the halide functional group. Secondary (2°) and tertiary (3°) alkyl halides consist of two and three alkyl groups, respectively that are, bonded to the carbon bearing the halide functional group.

Examples:

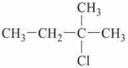
$CH_3-CH_2-CH_2-CH_2-CH_2Cl$

1-chloropentane
(1° alkylhalide)



$$\begin{array}{c} CH_3-CH_2-CH_2-CH-CH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad Cl \end{array}$$

2-chloropentane
(2° alkylhalide)

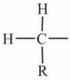


$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3-CH_2- & C & -CH_3 \\ & | & \\ & Cl & \end{array}$$

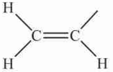
2-chloro-2-methylbutane
(3°alkylhalide)

Type of hydrocarbyl to which the halide is attached

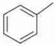
Hydrocarbyl is a group formed when one hydrogen atom is removed from a hydrocarbon. For example, an alkane forms an alkyl group when hydrogen is removed, benzene or arene forms an aryl group and an alkene such as ethene forms a vinyl group. Others are benzylic and allylic groups. The groups are shown in the following examples:



Alkyl group



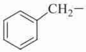
Vinyl group



Aryl group

$CH_3-CH=CH-CH_2-$

Allylic group



Benzylic group

These classes of halohydrocarbons show remarkable differences in their chemical reactivity/properties.

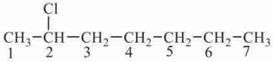
4.1.2 Nomenclature of halohydrocarbons

The general rules of nomenclature were discussed in chapter one. Many of the rules that are applied in naming hydrocarbons are also useful in naming halohydrocarbons with some specific additional rules for halohydrocarbons:

1. The halogen functional group is presented in a short form as halo-. Examples in halohydrocarbons R—F, R—Cl, R—Br, and R—I, the fluoride (F), chloride (Cl), bromide (Br), and iodide (I), are named as fluoro-, chloro-, bromo-, and iodo-, respectively.

2. The naming is done by considering the longest carbon chain that bears a functional group. The numbering of the carbon atoms in the chain is done by starting from the nearest end to the functional group.

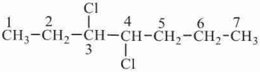
   Example:



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{Cl}{|}}{CH}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

2-chloroheptane

3. If more than one of the same type of halogen is present, the naming is done by using the prefix *di*, *tri,* and *tetra*. For example,

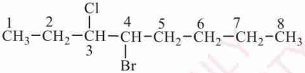


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{3}{\overset{Cl}{CH}}-\underset{Cl}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

3,4-dichloroheptane

4. If different types of halogens are present in the halohydrocarbon, naming is done by following the alphabetical order and the position of the halogens is indicated by numbers.

Example:

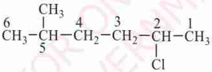


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{3}{\overset{Cl}{CH}}-\underset{Br}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

4-bromo-3-chlorooctane

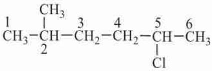
5. If two substituent groups (example alkyl and halide) are at the same distance from the opposite ends of the chain, the numbering is done by beginning from the side that is nearer to the substituent that appears first in the alphabetic order.

Example:



$$\overset{6}{CH_3}-\underset{5}{\overset{CH_3}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{Cl}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2-chloro-5-methylhexane
(Correct naming)



$$\overset{1}{CH_3}-\underset{2}{\overset{CH_3}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\underset{Cl}{\overset{5}{CH}}-\overset{6}{CH_3}$$

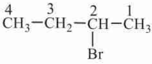
5-chloro-2-methylhexane
(Incorrect naming)

4.1.3 Isomers of haloalkanes

Haloalkanes exhibit chain and position isomerism. A chain isomerism exists in haloalkanes with four or more carbon atoms. In this type of isomerism, the isomers differ in the length of the parent chain of the carbon atoms. The presence of halogen as a functional group results into positional isomers in which the isomers differ in the position of the halogen atom. Examples of chain and positional isomers of bromobutane (C_4H_9Br) are shown in the following compounds:

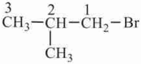
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$

1-bromobutane



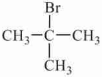
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(Br)-\overset{1}{C}H_3$

2-bromobutane



$\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}H_2-Br$

1-bromo-2-methylpropane



$CH_3-C(Br)(CH_3)-CH_3$

2-bromo-2-methylpropane

4.2 Preparation of halohydrocarbons

Using various methods, halohydrocarbons can be prepared in small and large quantities in the laboratory and industries. In this section, you will learn about the different methods of preparing haloalkanes.

4.2.1 Preparation of haloalkanes

The haloalkanes can be prepared by the following general methods: halogenation of aliphatic hydrocarbons, hydrohalogenation of unsaturated hydrocarbons, and halogenation of alcohols.

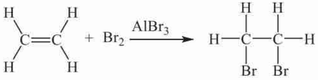
Halogenation of aliphatic hydrocarbons

Halogenation of either alkanes, alkenes or alkynes can result into the formation of alkyl halides. This reaction can be achieved through electrophilic addition (halogen addition) and free radical substitution (halogen substitution).

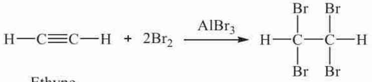
Electrophilic addition (halogen addition) reaction

This type of halogenation reaction involves the addition of a halogen across a carbon-carbon double or triple bond. The halogenation of an alkene yields a dihalogenated alkane while the halogenation of an alkyne yields a tetrahalogenated alkane.

Examples:



Ethene 1,2-dibromoethane



$$H-C\equiv C-H + 2Br_2 \xrightarrow{AlBr_3} CHBr_2-CHBr_2$$

Ethyne

1,1,2,2-tetrabromoethane

Free radical substitution (halogen substitution) reaction

This is the type of halogenation in which a hydrogen atom is substituted by a halogen atom in the presence of ultra-violet light or high temperature to form a haloalkane. Methane as an example undergoes halogen substitution reaction as shown in the following equations:

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

Chloromethane

$$CH_3Cl + Cl_2 \xrightarrow{\text{UV light}} CH_2Cl_2 + HCl$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{\text{UV light}} CHCl_3 + HCl$$

Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow{\text{UV light}} CCl_4 + HCl$$

Tetrachloromethane

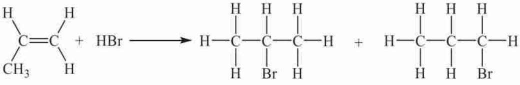
The halogen substitution reaction under the influence of ultraviolet light produces polysubstituted halides that are difficult to separate. Higher alkanes (alkanes with large number of carbons) produce a mixture of isomeric products even when they undergo a halogen monosubstitution reaction.

Hydrohalogenation of unsaturated hydrocarbons

Hydrohalogenation is the addition of hydrogen halides such as HBr and HCl to the unsaturated hydrocarbons (alkene and alkynes) to form alkyl halides. In this reaction, alkenes and alkynes react with hydrogen halides (HX) to form corresponding alkyl halides, depending on the number of HX equivalents being added.

Hydrohalogenation of alkenes

The addition of HX to asymmetrical alkenes follows the Markovnikov's Rule: when an asymmetrical alkene undergoes addition with E–Nu, then electrophile, E, adds to the carbon of alkene that has the greater number of hydrogen and the nucleophile, Nu, adds to the carbon with fewer hydrogen. The addition of hydrogen bromide in prop-1-ene yields a mixture of products which are 2-bromopropane (major product) and 1-bromopropane (minor product).



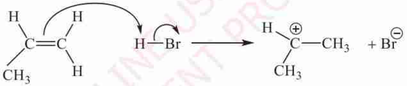
Prop-1-ene

2-bromopropane
(major product)

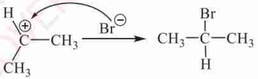
1-bromopropane
(minor product)

Mechanism

The π-electron pair acts as a Lewis base. The prop-1-ene is protonated to form the more stable carbocation.



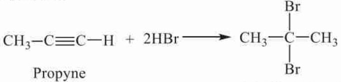
Then, the bromide ion (acting as a nucleophile) attacks on the electrophilic carbocation to form propyl bromide (bromopropane).



2-bromopropane

Hydrohalogenation of alkynes

The addition of excess hydrogen bromide in a propyne produces a germinal 2,2-dibromopropane.



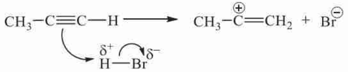
$$CH_3-C\equiv C-H + 2HBr \longrightarrow CH_3-\underset{Br}{\overset{Br}{C}}-CH_3$$

Propyne

2,2-dibromopropane

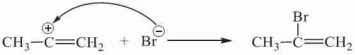
Mechanism

The π-electron pairs act as Lewis bases. The hydrogen bromide dissociates to form proton and bromide ions. The propyne is protonated to form a carbocation.



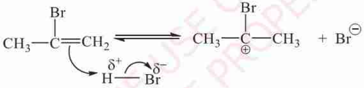
$$CH_3-C\equiv C-H + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow CH_3-\overset{\oplus}{C}=CH_2 + Br^{\ominus}$$

The carbocation intermediate reacts with bromide to form bromopropene.



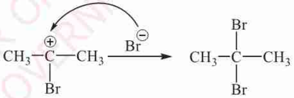
$$CH_3-\overset{\oplus}{C}=CH_2 + Br^{\ominus} \longrightarrow CH_3-\overset{Br}{C}=CH_2$$

In the excess of hydrogen bromide, a second protonation will occur to form a more stable carbocation.



$$CH_3-\overset{Br}{C}=CH_2 + \overset{\delta+}{H}-\overset{\delta-}{Br} \rightleftharpoons CH_3-\underset{\oplus}{\overset{Br}{C}}-CH_3 + Br^{\ominus}$$

The nucleophilic bromide ion attacks on the electrophilic carbocation to form a germinal 2,2-dibromopropane.



$$CH_3-\underset{Br}{\overset{\oplus}{C}}-CH_3 \xrightarrow{Br^{\ominus}} CH_3-\underset{Br}{\overset{Br}{C}}-CH_3$$

2,2-dibromopropane

The hydrohalogenation of unsaturated hydrocarbons is a type of electrophilic addition reaction which follows the Markovnikov's Rule. However, the addition of HBr to asymmetrical double bond in the presence of organic peroxides makes the reaction take place against Markovnikov's Rule. This is called anti-Markovnikov's addition also known as peroxide effect. In the addition of hydrogen bromide (HBr) to but-1-ene for example, bromine radical attacks the carbon atom carrying more hydrogen atoms while the hydrogen goes to the carbon atom containing fewer number of hydrogen atoms.

$$CH_3CH_2\mathbf{CH}{=}\mathbf{CH_2} + HBr \xrightarrow[\text{peroxide}]{\text{organic}} CH_3CH_2CH_2CH_2Br$$

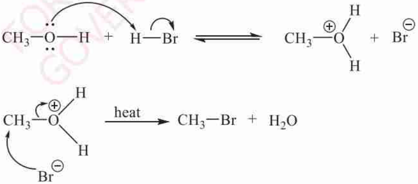
1-bromobutane

Halogenation of alcohols

Halogenation of alcohols is the chemical reaction that replaces the hydroxyl group of an alcohol by a halogen. This replacement occurs when an alcohol is treated with concentrated halogen acids like phosphorus halides (PX_3 or PX_5), thionyl chloride ($SOCl_2$), and sulphonyl chloride ($R{-}SO_2Cl$). The replacement of the hydroxyl group of an alcohol by a halogen is a type of nucleophilic substitution reaction. But alcohols have a strong basic hydroxyl group (OH) which is a poor leaving group and therefore, it cannot undergo a nucleophilic substitution reaction. However, if a strong base (poor leaving group) is converted into a weaker base (a better leaving group), a nucleophilic substitution reaction can occur.

Reactions of alcohols with concentrated halogen acid to form alkyl halides

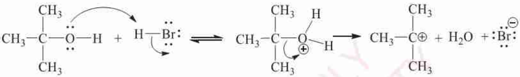
Alcohols cannot undergo nucleophilic substitution reactions because of their strong basic characters. Hence, they need to be converted to weaker bases (better leaving groups). The protonation by adding acid to the reaction mixtures converts a strong base $OH^{\ominus}$ group to a weaker base (H_2O) which is a better leaving group. When protonated, $OH^{\ominus}$ changes to H_2O, it can be easily displaced by nucleophiles which are basically weak ($I^{\ominus}$, $Br^{\ominus}$, $Cl^{\ominus}$). The strong basic nucleophiles such as NH_3, RNH_2 and $RCH_2O^{\ominus}$ are not suitable because they can be protonated in the acidic solution.



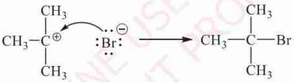
Primary, secondary, and tertiary alcohols undergo nucleophilic substitution reactions with halogen acids (HX) to form alkyl halides. The mechanism of the substitution reaction depends much on the type of the alcohol. The secondary and tertiary alcohols undergo S_N1 mechanism while primary alcohols undergo only S_N2 mechanism. This is because primary carbocations are very unstable. The stability of carbocations follows this order: 3° > 2° > 1° and the reactivity of halogen acids follows this order: HI > HBr > HCl > HF.

Mechanism for the S_N1 reaction of an alcohol

The acid protonates the OH group to form a better leaving group which leave as the weaker base (H_2O), forming a methylpropyl carbocation.



The carbocation (electrophile) is then attacked by $Br^{\ominus}$ nucleophile to form the bromoalkane.

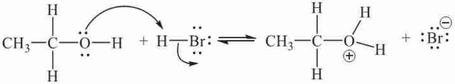


Methylpropyl carbocation 2-bromo-2-methylpropane

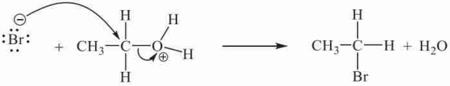
The nucleophilic substitution in tertiary alcohols with hydrogen halide are very fast and proceed at room temperature, but nucleophilic substitution reaction in secondary alcohols with hydrogen halide needs heating to speed up the reaction.

Mechanisms for the S_N2 reaction of an alcohol

The acid protonates the OH group of an alcohol to form a better leaving group.



Then, the nucleophile ($Br^{\ominus}$) attacks the back side of the carbon carrying the leaving group and displaces the water as a leaving group.



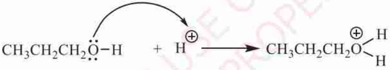
$$:\ddot{Br}:^{\ominus} + CH_3-CH_2-\overset{\oplus}{O}H_2 \longrightarrow CH_3-CH_2Br + H_2O$$

When the less reactive halogen acid like HCl is used, the S_N2 reaction occurs very slowly because the $Cl^{\ominus}$ is a weaker nucleophile than $Br^{\ominus}$ and $I^{\ominus}$. However, the use of $ZnCl_2$ as a catalyst increases the rate of reaction.

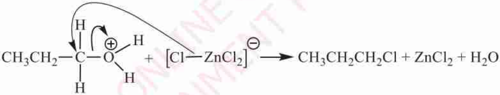
$$\underset{\text{Propan-1-ol}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}OH} + HCl \xrightarrow[\text{heat}]{ZnCl_2} \underset{\text{1-chloropropane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl} + H_2O$$

The reaction occurs in the following steps:

$$ZnCl_2 + HCl \longrightarrow ZnCl_3^{\ominus} + H^{\oplus}$$



$$CH_3CH_2CH_2\ddot{O}-H + H^{\oplus} \longrightarrow CH_3CH_2CH_2\overset{\oplus}{O}H_2$$



$$CH_3CH_2-CH_2-\overset{\oplus}{O}H_2 + [Cl-ZnCl_2]^{\ominus} \longrightarrow CH_3CH_2CH_2Cl + ZnCl_2 + H_2O$$

Reactions of alcohols with phosphorus halides

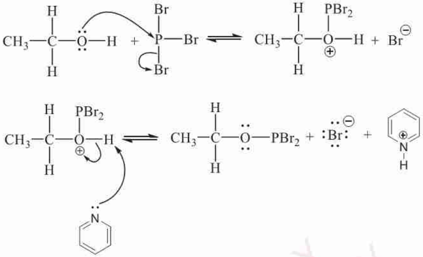
An alcohol reacts with phosphorus halides in the presence of pyridine to form an alkyl halide, phosphoric or hydrogen halide. The reaction shown below show products when phosphorus trihalide react with alcohols where there is no carbocation rearrangement.

$$3CH_3CH_2OH + PBr_3 \xrightarrow{\text{pyridine}} 3CH_3CH_2Br + H_3PO_3$$

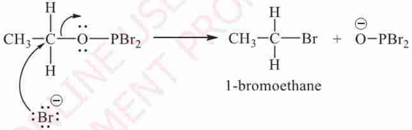
$$3CH_3CH_2OH + PCl_3 \xrightarrow{\text{pyridine}} 3CH_3CH_2Cl + H_3PO_3$$

Mechanism

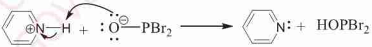
Step 1: The reaction is initiated by activation of oxygen. The lone pair electrons in oxygen of hydroxyl group attacks the phosphorus atom to form oxygen-phosphorous (O–P) bond at bromophosphite group (a good leaving group). This is immediately followed by hydrogen uptake by the pyridine to neutralise the positive charge on oxygen.



Step 2: The displaced bromine ion from the first step attacks the electrophilic carbon via the back side attack to displace a weaker base which is the bromophosphite group (good leaving group).



The $\overset{\ominus}{O}-PBr_2$ can combine with protonated pyridine to regenerate the pyridine and $HOPBr_2$



The by-product formed ($HOPBr_2$) undergoes further S_N2 reaction with more alcohol molecules until all bromides from bromophosphite are substituted by hydrogen and oxygen to form H_3PO_3.

Reactions of alcohols with thionyl chloride

Alcohols react with thionyl chloride (sulphur dichloride oxides) in the presence of triethyl amine or pyridine to form alkyl halides, sulphur dioxide, and hydrogen chloride gases.

$$R—OH + SOCl_2 \xrightarrow{\text{pyridine}} R—Cl + SO_2 + HCl$$

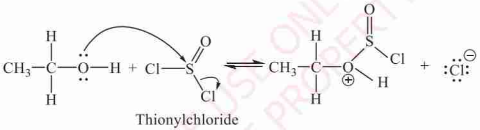
Example:

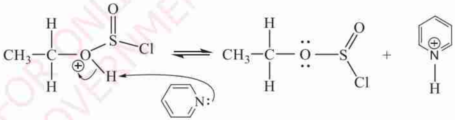
$$CH_3{-}CH_2{-}OH + SOCl_2 \xrightarrow{\text{pyridine}} CH_3{-}CH_2{-}Cl + SO_2 + HCl$$

Mechanism

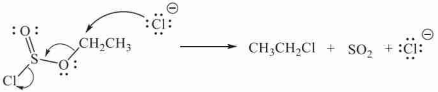
Step 1: The attack of oxygen lone pair electrons on the sulphur of thionyl chloride.

This reaction displaces $Cl^{\ominus}$ ion. The pyridine picks a proton from an intermediate complex to form another intermediate complex and a chlorosulphite group. Pyridine removes a proton from the intermediate product preventing it from reverting to starting materials.

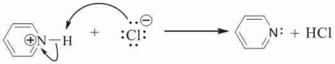




Step 2: The chlorosulphite group is a weaker base than a chloride ion. The $Cl^{\ominus}$ ion attacks on the carbon, displacing the leaving group, which release SO_2 and $Cl^{\ominus}$.

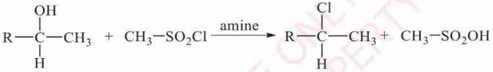


Then, the released second $Cl^{\ominus}$ ion will combine with the protonated pyridine to regenerate the pyridine and HCl.



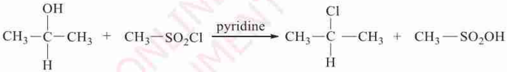
Reactions of alcohols with sulphonyl chlorides to form alkyl halides

Alcohols react with sulphonyl chlorides in the presence of amine (example pyridine) to form alkyl sulphonates (sulphonate esters) which are good leaving groups. The sulphonate group can be displaced easily by the corresponding halide ion to form alkyl halide. The most commonly used reagents are methane sulphonyl chloride (mesyl chloride) and *p*-toluene sulphonyl chloride (tosyl chloride).



$$R-\underset{H}{\overset{OH}{C}}-CH_3 + CH_3-SO_2Cl \xrightarrow{\text{amine}} R-\underset{H}{\overset{Cl}{C}}-CH_3 + CH_3-SO_2OH$$

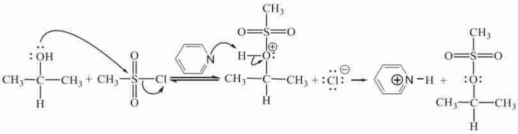
Example:



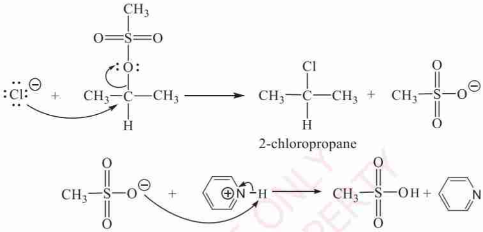
$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 + CH_3-SO_2Cl \xrightarrow{\text{pyridine}} CH_3-\underset{H}{\overset{Cl}{C}}-CH_3 + CH_3-SO_2OH$$

Mechanism

Step 1: The lone pair electrons in oxygen of hydroxyl group attack the sulphur atom of mesyl chloride to form an O—S bond (sulphonate ester). The role of pyridine is to prevent the intermediate product to revert to the starting materials by removing the proton.



Step 2: The displaced chloride ion from the sulphur attacks electrophilic carbon through the backside attack, forming C–Cl bond and breaking the C–O bond. The new propyl chloride is formed and $CH_3–SO_3H$ detaches as a leaving group



The substitution of the sulphonate group by a halide ion proceeds via S_N2 reaction mechanism and this applies to primary and secondary alcohols only.

Exercise 4.1

1. Write the structures of the following compounds:
   (a) 2-chloro-3-methylpentane
   (b) 1-chloro-4-ethylcyclohexane
   (c) 4-*tert*-butyl-3-iodoheptane
   (d) 1,4-dibromobut-2-ene
   (e) 1-bromo-4-sec-butyl-2-methylbenzene.
2. Identify one isomer from alkanes with molecular formula C_5H_{12} which on photochemical chlorination yields;
   (a) A single monochloride
   (b) Three isomeric monochlorides
   (c) Four isomeric monochlorides
3. Write all the structural isomers of a compound having a molecular formula C_4H_9Cl and name the structures according to the IUPAC system.

4. Using reaction equations, explain the products formed when but-1-ene reacts with hydrogen halide;

   (a) In the presence of organic peroxides

   (b) In the absence of organic peroxides

5. Write the structure of the main product obtained by treating 1-propanol with excess of hydrogen chloride in the presence of anhydrous zinc chloride.

6. By using reaction mechanisms, show how you can prepare alkyl halides from the following reagents:

   (a) Primary alcohol

   (b) Tertiary alcohol

7. What will be the product when 1-propanol is treated with thionyl chloride?

4.3 Properties of haloalkanes

Haloalkanes like any other organic compounds exhibit both physical and chemical properties. In this section, you will learn about the physical and chemical properties of haloalkanes.

4.3.1 Physical properties of haloalkanes

The physical properties of haloalkanes depend largely on the molecular masses of the compounds (number of carbons) and the type of intermolecular or intramolecular forces of attraction. The common physical properties of haloalkanes such as physical state, boiling point, melting point, solubility, and density are discussed in the following sections:

Physical appearance

Haloalkanes are colourless compounds when in pure forms. However, when iodoalkanes and bromoalkanes are exposed to light, they develop some colours. Some volatile haloalkanes have sweet smell.

Boiling points

The boiling points of haloalkanes increase with an increase in the number of carbon atoms. The boiling points of haloalkanes as a function of the number of carbons are shown in Figure 4.1. There are two types of intermolecular forces that account for the boiling points of haloalkanes: London (dispersion) forces and dipole-dipole forces. London dispersion forces increase with an increase in the molecular mass and molecular sizes. As the number of carbons increase, the molecular mass as well as the size increases, hence the boiling points increase due to the increase of intermolecular forces. Comparing haloalkanes to normal alkanes with the same number of carbons, haloalkanes exhibit a larger surface area than alkanes because of the substitution of hydrogen with halogen. The increase in the surface area increases the dispersion forces that results into higher boiling points.

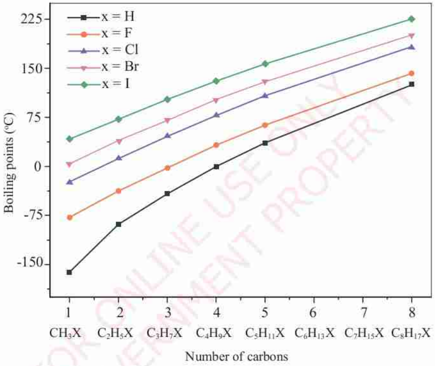


Figure 4.1 The boiling points of haloalkanes as a function of number of carbon atoms

The second type of intermolecular forces that contribute to an increase in boiling points is dipole-dipole interactions. These interactions exist in haloalkanes due to the differences in electronegativity between carbon and halogens. Therefore, dipole-dipole forces also account for the higher boiling points of haloalkanes compared to the alkanes.

Note that, the boiling points of haloalkanes increase in the following order:

R–F < R–Cl < R–Br < R–I,

where R is an alkyl group. This trend is caused by an increase in the size and mass of the halogen atoms which cause an increase in the London dispersion forces. The atomic size increases in the same order (down the group in halogens): F < Cl < Br < I. For isomers of haloalkanes, the boiling points decrease with an increase in the degree of branching because branching decreases the contact surface area of the molecules and therefore, reducing the strengths of the attractive forces.

Melting points

Melting points of haloalkanes depend on the strengths of their lattice structures. The trend in the melting points of haloalkanes is like that of the boiling points.

Solubility

Haloalkanes are highly soluble in organic solvents but slightly soluble in water. This is because, in order for haloalkanes to dissolve in water they need to break the strong hydrogen bonds which is difficult. Haloalkanes dissolve easily in organic solvents due to the types of intermolecular forces that dominate in the haloalkanes, which are covalent nonpolar.

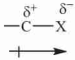
Density

The densities of haloalkanes increase with the increase in the number of carbon and halogen atoms. Haloalkanes are denser than alkanes with the same number of carbon atoms. The density of alkyl bromides and iodides are higher than that of water while the densities of alkyl chlorides are lower than that of water.

4.3.2 Chemical properties of haloalkanes

Haloalkanes are more reactive than their corresponding alkanes. Their reactivity is attributed to the partially polarised nature of the carbon-halogen bond caused by the electronegativity difference. Halogens are more electronegative than the carbon atom. This results in a carbon-halogen bond that is largely polarised with carbon atom acquiring a partial positive charge and the halogen a partial negative charge.

The polar C—X bond



$$-\overset{\delta^+}{C}-\overset{\delta^-}{X}$$

Of the four halogens, fluorine is the most electronegative and iodine the least. It implies that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. The electronegativity of halogens is shown in the following general trend:

$$\xrightarrow[\text{decrease in the electronegativity}]{\text{Flourine, Chlorine, Bromine, Iodine}}$$

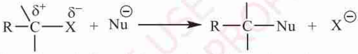
The reactivity of haloalkanes is governed by the strengths of the bonds which have to be broken during the reactions. It is very difficult to break a carbon-fluorine bond, but easy to break a carbon-iodine one. Therefore, the reactivity of haloalkanes obeys the following trend:

$$\xrightarrow[\text{decrease in reactivity}]{\text{Iodine, Bromine, Chlorine, Flourine}}$$

Haloalkanes will be used to discuss the chemical properties of halohydrocarbons. The chemical reactions of haloalkanes can be divided into four main types, which are nucleophilic substitution, elimination reactions, reactions with metals and interconvertibility reactions.

Nucleophilic substitution reactions of haloalkanes

These are the reactions in which nucleophiles react with haloalkanes and the halogen atoms leave the haloalkanes as halogen ions.



$$R-\overset{\delta^+}{C}-\overset{\delta^-}{X} + \overset{\ominus}{Nu} \longrightarrow R-C-Nu + X^{\ominus}$$

For the halide to be substituted, the nucleophile needs to be stronger than the halide itself. The typical reagents which undergo nucleophilic substitutions, and the corresponding substituted product are shown in Table 4.1.

Table 4.1 Reagents, nucleophiles and products of nucleophilic substitution of alkyl halide

Reagent	Nucleophile	Substitution product
NaOH/KOH	$OH^{\ominus}$	ROH
H_2O	H_2O	ROH
NaOR	$RO^{\ominus}$	ROR'
NaI	$I^{\ominus}$	RI
NH_3	NH_3	$R-NH_2$
$R-NH_2$	$R-NH_2$	$R-NHR$
KCN	${}^{\ominus}C\equiv N$	RCN
KNO_2	$O=N-O^{\ominus}$	$R-O-N=O$
$LiAlH_4$	$H^{\ominus}$	$R-H$
$R^{\ominus}-M^{\oplus}$	$R^{\ominus}$	$R-R'$

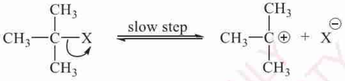
Mechanisms of nucleophilic substitution reaction

The nucleophilic substitution reaction can occur through two different mechanisms which are unimolecular and bimolecular substitutions reactions.

Unimolecular nucleophilic substitution (S_N1) reaction

This is also called the first order nucleophilic substitution. In this reaction, the rate of reaction depends on the concentration of one reactant (alkyl halide) in the rate determining step. The reaction occurs in two steps. The first step is the formation of carbocation intermediate.

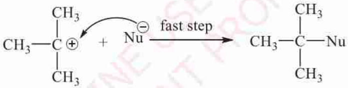
Step 1:



Carbocation

The second step occurs when a nucleophile attacks the carbocation.

Step 2:



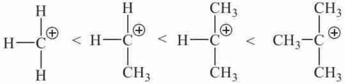
The slowest step of S_N1 mechanism is the first step which is also reversible. Since the nucleophile is not involved in the rate determining step, the rate of reaction depends on the concentration of alkyl halide, hence the first order reaction.

$$Rate = k\left[alkyl\ halide\right]$$

The energy involved in the breaking of the C—Br bond is obtained from the solvation of the halide ion with proton of protic solvent. The reaction is also enhanced by the stability of the carbocation. S_N1 reaction is therefore, faster for tertiary (3°) alkyl halides because of the formation of a highly stable 3° carbocation than 2° alkaly halide.

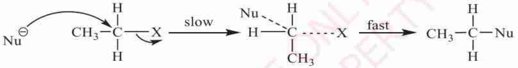
Generally, the rate of S_N1 reaction increases with an increase in the number of alkyl groups on the substituted carbon. The order of reactivity occurs in the following trend:

$$\xrightarrow[\text{Increase in reactivity}]{\text{methyl} < 1^{o}\text{ alkyl halide} < 2^{o}\text{ alkyl halide} < 3^{o}\text{ alkyl halide}}$$



Bimolecular nucleophilic substitution (S_N2) reaction

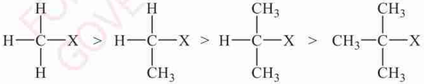
This is also called second order nucleophilic substitution. The rate of reaction depends on the concentrations of both reactants (alkyl halide and the nucleophile) in the rate determining step. This reaction occurs in one step which involves the formation of a transition state instead of a carbocation intermediate. The attack of a nucleophile to the haloalkane and the removal of the halogen occur simultaneously.



In S_N2 reactions, both reactants are involved in the reaction, the rate of reaction depends on the concentration of both the alkyl halide and the nucleophile, hence it is a second order reaction.

$$Rate = k\left[alkyl\ halide\right]\left[nucleophile\right]$$

The S_N2 mechanism generally occurs in haloalkanes without bulky alkyl groups that would otherwise cause steric effect. Therefore, unlike the S_N1 mechanism, the order of reactivity in S_N2 mechanism is as shown in the following equation.



methyl > 1^oalkyl halide > 2^o alkyl halide > 3^o alkyl halide

The typical nucleophilic substitution reactions of alkyl halides are discussed in the section that follows:

(a) *Alcohol formation (hydrolysis of haloalkanes)*

Haloalkanes react with aqueous alkalis such as an aqueous solution of KOH to give alcohols.

$$\mathrm{R{-}X + OH^{\ominus} \xrightarrow[\text{heat}]{H_2O} R{-}OH + X^{\ominus}}$$

Example:

$$\underset{\text{Chloroethane}}{\mathrm{CH_3CH_2Cl}} + \mathrm{K^{\oplus}OH^{\ominus}} \xrightarrow[\text{heat}]{\mathrm{H_2O}} \underset{\text{Ethanol}}{\mathrm{CH_3CH_2OH}} + \mathrm{KCl}$$

(b) *Formation of ether (Williamson ether synthesis)*

This is the reaction in which haloalkanes react with alkoxides (RONa) to form ethers. The reaction was developed in 1850 by an English chemist Alexander William Williamson (1824 –1904). It is a very useful reaction in the preparation of ethers.

$$\mathrm{R{-}X + NaOR} \longrightarrow \underset{\text{Ether}}{\mathrm{R{-}O{-}R}} + \mathrm{NaX}$$

Example:

$$\underset{\text{Bromoethane}}{\mathrm{CH_3CH_2Br}} + \mathrm{NaOCH_3} \xrightarrow[\text{alcohol}]{\text{heat}} \underset{\substack{\text{Methoxyethane}\\ \text{(Methyl ethyl ether)}}}{\mathrm{CH_3CH_2OCH_3}} + \mathrm{NaBr}$$

(c) *Formation of amine (substitution by amino group)*

When a haloalkane is heated with alcoholic ammonia solution, a primary amine is formed. The reaction occurs in a sealed tube at about 110 °C, and the halogen gets substituted by $-NH_2$ group.

$$\mathrm{R{-}X + H{-}\ddot{N}H_2} \xrightarrow[\text{alcohol}]{\text{heat}} \underset{\text{alkylamine}}{\mathrm{R{-}NH_2}} + \mathrm{HX}$$

Example:

$$\underset{\text{Bromoethane}}{\mathrm{CH_3CH_2Br}} + \mathrm{H{-}\ddot{N}H_2} \xrightarrow[\text{alcohol}]{\text{heat}} \underset{\text{Ethylamine}}{\mathrm{CH_3CH_2NH_2}} + \mathrm{HBr}$$

When the haloalkane is present in excess, a mixture of primary, secondary, and tertiary amines is formed. This is because more than one hydrogen atoms of the primary amine can be replaced by the alkyl groups.

$$CH_3CH_2Br + CH_3CH_2NH_2 \xrightarrow[\text{alcohol}]{\text{heat}} (CH_3CH_2)_2\ddot{N}H + HBr$$

diethylamine
(N-ethylaminoethane)

$$CH_3CH_2Br + (CH_3CH_2)_2\ddot{N}H \xrightarrow[\text{alcohol}]{\text{heat}} (CH_3CH_2)_3\ddot{N} + HBr$$

Triethylamine
N,N-diethylaminoethane

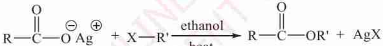
The addition of one alkyl group to the tertiary amine results into the formation of quartenary ammonium salt.

$$CH_3CH_2Br + (CH_3CH_2)_3N\colon \xrightarrow[\text{alcohol}]{\text{heat}} \left[(CH_3CH_2)_4\overset{\oplus}{N}\right]\overset{\ominus}{Br}$$

Tetraethylammonium bromide

(d) Formation of esters (Substitution by carboxyl group)

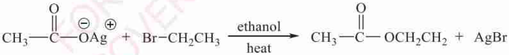
An ester is formed when a haloalkane is heated with silver carboxylate salt under alcoholic condition.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Ag} + X-R' \xrightarrow[\text{heat}]{\text{ethanol}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + AgX$$

Ester

Example:

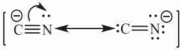


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Ag} + Br-CH_2CH_3 \xrightarrow[\text{heat}]{\text{ethanol}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2 + AgBr$$

Ethyl ethanoate

(e) Formation of alkyl cyanide

Cyanide ion (nucleophile) from potassium cyanide can act as a nucleophile in two different ways.



When the cyanide nucleophile links with carbon through its carbon atom, it forms an alkyl cyanide and when it links through nitrogen atom it forms an isocyanide. Generally, haloalkanes react with alcoholic solution of potassium cyanide (KCN) to form alkyl cyanide as a major product and alkyl isocyanide as the minor product.

$$R{-}X + KCN \xrightarrow{\text{alcohol}} R{-}C{\equiv}N + KX$$

Alkyl halide

Alkane nitrile
Alkyl cyanide

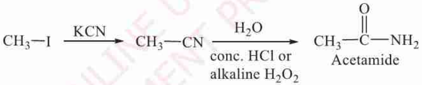
The formation of alkyl cyanide

$$CH_3CH_2{-}Br + K^{\oplus}CN^{\ominus} \xrightarrow{\text{alcohol}} CH_3CH_2C{\equiv}N + KBr$$

Ethyl bromide

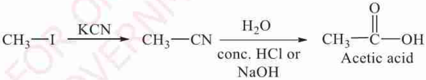
Propane nitrile
(Ethyl cyanide)

Under different conditions, the resulting alkyl cyanides can be further converted to primary amines, carboxylic acids and acid amides which have α -hydrogen atom.



$$CH_3{-}I \xrightarrow{KCN} CH_3{-}CN \xrightarrow[\text{conc. HCl or alkaline } H_2O_2]{H_2O} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}NH_2$$

Acetamide



$$CH_3{-}I \xrightarrow{KCN} CH_3{-}CN \xrightarrow[\text{conc. HCl or NaOH}]{H_2O} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH$$

Acetic acid

$$CH_3{-}I \xrightarrow{KCN} CH_3{-}CN \xrightarrow[\text{Na, } C_2H_5OH \text{ or } LiAlH_4]{\text{reduction}} CH_3CH_2NH_2$$

Ethyl amine

(f) *Formation of isocyanide*

Isocyanide is obtained by reacting haloalkane with alcoholic silver cyanide (AgCN).

$$CH_3CH_2{-}Br + AgCN \xrightarrow{\text{alcohol}} CH_3CH_2{-}NC + AgBr$$

Ethyl bromide

Ethyl isocyanide

When reduced with sodium in alcohol alkyl isocyanide forms a secondary amine.

$$CH_3CH_2NC + [4H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethyl methylamine}}{CH_3CH_2NHCH_3}$$

(g) *Formation of nitroalkanes*

When a haloalkane is treated with metal nitrite like KNO_2, it gives nitroalkanes. In this reaction, the halogen of haloalkane is replaced by a nitro group.

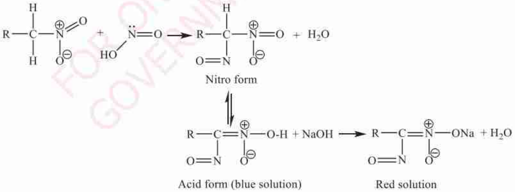
Further reaction of the nitroalkane with nitrous acid gives different coloured complexes depending on whether the nitroalkane was primary, secondary or tertiary.

$$R\text{-}X + KNO_2 \longrightarrow \underset{\text{Alkyl nitrite}}{R\text{-}NO_2} + KX$$

Example:

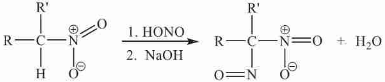
$$CH_3CH_2Br + KNO_2 \xrightarrow{\text{heat}} \underset{\text{Ethyl nitrite}}{CH_3CH_2NO_2} + KBr$$

When a primary nitroalkane reacts with nitrous acid it forms blue coloured nitroso-nitroalkane which dissolves in NaOH to produce a red solution.



$$\underset{1^{\circ}\text{ alkyl halide}}{R{-}CH_2{-}X} + AgNO_2 \xrightarrow[C_2H_5OH]{\text{reflux}} RCH_2{-}NO_2 \xrightarrow[2.\ NaOH]{1.\ HONO} \text{Red complex}$$

Secondary nitroalkanes react with nitrous acid to give blue coloured nitroso-nitroalkanes which no longer dissolve in NaOH due to the absence of a replaceable α-hydrogen atom.



Blue solution (Insoluble in NaOH)

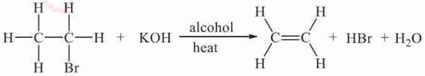
Tertiary nitroalkanes do not react with nitrous acid because they have no α-hydrogen.

$$\underset{3^{o}\text{ alkyl halide}}{R_3C{-}X} + AgNO_2 \xrightarrow[C_2H_5OH]{\text{reflux}} R_3C{-}NO_2 \xrightarrow{HONO(aq)} \text{Colourless solution}$$

These reactions can therefore, be used to distinguish primary (1°), secondary (2°), and tertiary (3°) haloalkanes.

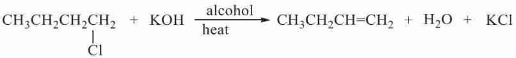
Elimination reactions of haloalkanes

The *elimination reaction* is the type of reaction which decreases the number of atoms attached to the adjacent reacting carbon atoms, forming multiple bonds. When haloalkanes are boiled with alcoholic solution of potassium hydroxide, a hydrogen halide molecule (HX) is eliminated and a double bond is formed. Note that, the carbon atom that is bonded with the halogen substituent is called alpha (α) carbon and the carbon adjacent to the α-carbon is called a beta (β)-carbon. During the elimination, the double bond forms between α- and β- carbon atoms.



Bromoethane

Ethene

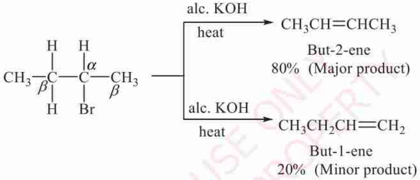


$$\underset{\text{Cl}}{CH_3CH_2CH_2CH_2} + KOH \xrightarrow[\text{heat}]{\text{alcohol}} CH_3CH_2CH{=}CH_2 + H_2O + KCl$$

Chlorobutane

But-1-ene

If there are two possible positions at which the double bond can be formed, then the major product of alkyl halide elimination will be the one in which the carbon atoms which are joined by double bonds have a larger number of alkyl groups. This is the *Zaitsev (Saytzeff) rule* which states that *the base induced elimination of haloalkanes will result into the formation of double bond that contains the most alkyl substituents.* This means that, the alkene which is most favoured during elimination is the one which removes hydrogen from the β carbon that contains less number of hydrogen atom(s). The rule applies to haloalkanes with more than one beta carbons.



Reactions of haloalkanes with metals

Haloalkanes react with metals and other organic substances through various reaction mechanisms to form different useful reagents and products.

Reactions of haloalkanes with magnesium

The reaction results into the formation of what is known as Grignard reagents. In this reaction, haloalkanes react with magnesium in dry ether to form alkyl magnesium halides.

$$\text{R–X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R–Mg–X}$$

Alkyl magnesium halide

Example:

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Ethylmagnesium bromide

The Grignard reagents are very useful in the preparation of many other organic compounds.

Reaction of haloalkane with sodium

The reactions of haloalkanes with metallic sodium is also called *Wurtz reaction***.** In this reaction, two molecules of alkyl halides that are either the same or different react with metallic sodium in the presence of dry ether to form alkanes.

$$2R{-}X + 2Na \xrightarrow{\text{dry ether}} R{-}R + 2NaX$$

$$2CH_3CH_2Cl + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3 + 2NaCl$$

The above reaction is used in the preparation of symmetrical alkanes (even numbered alkanes).

Reduction to alkanes

Haloalkanes can be reduced to alkanes by using various reagents.

Reduction with hydrogen and metal catalyst such as nickel, platinum, or palladium.

$$CH_3CH_2Br + H_2 \xrightarrow[250\ ^{o}C]{\text{Ni or Pd,}} CH_3CH_3 + HBr$$

Reduction with zinc/copper couple in ethyl alcohol

$$CH_3CH_2Br + 2[H] \xrightarrow[C_2H_5OH]{Zn/Cu} CH_3CH_3 + HBr$$

Reduction with lithium aluminium tetrahydride ($LiAlH_4$).

$$CH_3CH_2Cl \xrightarrow{LiAlH_4} CH_3CH_3$$

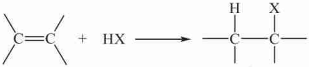
Interconvertibility reactions

Alkanes, alkenes and alkynes can be converted to haloalkanes and similarly haloalkanes can be converted to the above-mentioned hydrocarbons. Alkanes can be obtained from haloalkanes by the reaction between haloalkanes and sodium (Na) in dry ether, with zinc/copper couple in alcohol and by the reduction with lithium aluminium hydride ($LiAlH_4$). Haloalkanes can also be obtained directly from alkanes. This is done by a direct halogenation of alkanes using ultra violet (UV) light. For example,

$$R{-}CH_3 + Cl_2 \xrightarrow{\text{UV light}} R{-}CH_2Cl + HCl$$

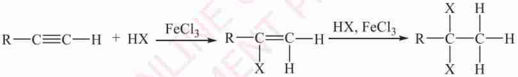
Interconvertibility between alkenes and haloalkanes

Alkenes can be obtained from haloalkanes by a reaction called dehydro halogenation. This is done through the treatment of haloalkane with alcoholic potassium hydroxide under heating. Similarly, haloalkanes can be obtained from alkenes by electrophilic addition of hydrogen halide.



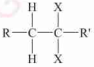
Interconvertibility between alkynes and haloalkanes

Alkynes can be converted directly to haloalkanes which can also be converted back to alkynes. Alkyne can be converted to haloalkane by direct addition of hydrogen halide. However, when this method is applied to alkynes, two steps are involved for a complete reaction and the resulting haloalkane will have two halide atoms bonded to the same carbon.

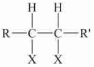


$$R{-}C{\equiv}C{-}H + HX \xrightarrow{FeCl_3} R{-}C(X){=}C(H){-}H \xrightarrow{HX,\ FeCl_3} R{-}CX_2{-}CH_2{-}H$$

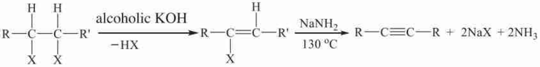
Similarly, alkynes can be obtained from vicinal dihaloalkanes when treated with alcoholic potassium hydroxide followed by a reaction with sodium amide. *Vicinal dihaloalkanes* are derivatives of alkanes with halogens attached to adjacent carbon atoms while in *germinal dihaloalkanes*, the halogens are attached to the same carbon atoms.



Germinal dihaloalkane



Vicinal dihaloalkane



$$R{-}CH(X){-}CH(X){-}R' \xrightarrow[-HX]{\text{alcoholic KOH}} R{-}C(X){=}CH{-}R' \xrightarrow[130\ ^{o}C]{NaNH_2} R{-}C{\equiv}C{-}R + 2NaX + 2NH_3$$

4.4 Uses and hazards of halogen derivatives of hydrocarbons

The halogen derivatives of hydrocarbon are very useful for domestic and industrial purposes. These compounds are used as solvents, propellants, refrigerants and fire extinguishers. Also they are largely applied in synthesis of polymers, testing other organic compounds and as raw materials in laboratories and industries. Some of the halogen derivatives have harmful environmental effects. In this section, you will learn about the uses and hazards of haloalkanes.

Solvents

Haloalkanes have been widely used as solvents. For example, dichloromethane (CH_2Cl_2), trichloromethane or chloroform ($CHCl_3$) and trichloroethylene are used as solvents and degreasing agents. However, due to their harmful environmental effects and toxicity, their uses have been largely restricted.

Propellants

Chlorofluorocarbons (CFCs) have been widely used as propellants in aerosol inhalers in the treatment of asthma. However, it was later discovered that CFCs, have some environmental effects such as being responsible for destroying the ozone layer. At high atmosphere, the carbon chlorine bond ($C—Cl$) breaks, giving free chlorine radicals. These free radicals are responsible for destroying the ozone layer, hence causing global warming. CFCs have therefore been replaced by environmentally friendly compounds such as hydrochlorofluorocarbons (HCFCs). The HCFCs have a shorter lifespan in the atmosphere than CFCs and they get destroyed at lower atmosphere, hence they do not reach the ozone layer. The effect of HCFCs is about one-twentieth that of CFCs. Butane which is not a haloalkane can also be used as aerosol propellant.

Refrigerants

A refrigerant is a fluid that is used in a heat pump (moving heat from lower to higher temperatures). Chlorofluorocarbons (CFCs) had been used as fluids for refrigerants for a long time in the 20th century. However, their applications have been replaced by other compounds due to their ozone depletion effects.

Fire extinguishers

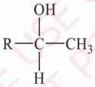
Bromochlorodifluoromethane and bromotrifluoromethane are used as fire extinguishers. However, these compounds have high potential for depletion of the ozone layer. Therefore, they are used for critical applications such as in aviation (fire extinguishing on a burning aircrafts) and in military.

Testing of other organic compounds

Chloroform is used in isocyanide test for the detection of primary amines. The process involves heating of a mixture of amine and chloroform in alcoholic NaOH. The unpleasant smell of isocyanide is obtained.

$$CH_3CH_2NH_2 + CHCl_3 + 3NaOH \xrightarrow{\text{alcohol}} CH_3CH_2NC + 3NaCl + 3H_2O$$

When carbonyl compounds are treated with iodide and sodium hydroxide, triodomethane (iodoform) is formed as yellow crystals and are recognised with a characteristic smell. The formed iodoform is used as a test for carbonyl compounds and alcohols that consist of terminal CH_3, H, and OH on the same carbon, in the so called iodoform test. Example of an alcohol that shows a positive iodoform test is,



$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3$$

where R can be hydrogen or any alkyl group.

Synthesis of plastics (Polymers)

Chloroethene ($CH_2{=}CHCl$), also called vinyl chloride is used as a monomer to make polychloroethene also called poly(vinyl chloride) (PVC) which has many household and industrial applications.

Tetrafluoroethene ($F_2C{=}CF_2$) is used as a monomer to make polytetrafluoro ethylene (PTFE) which is used as non-stick coating for pans and other cooking utensils.

Laboratory and industrial raw materials

Because halohydrocarbons react with many other organic compounds, they are highly used as laboratory reagents for the synthesis of other organic chemicals. The reactions have been discussed in the chemical properties of haloalkanes.

Exercise 4.2

1. 2-bromo-2-methylpropane reacts with aqueous alkalis via S_N1 mechanism.
   (a) Write the chemical equations to show how the reactions occur according to this mechanism
   (b) Identify the rate determining step
   (c) Explain why it is referred to as S_N1.

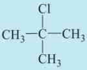
2. Predict the mono-substituted halogenated product(s) of chlorine gas reacting with 2-methylbutane in the presence of sunlight.

3. When 3-bromo-2,3-dimethylpentane reacts with aqueous potassium hydroxide, an alcohol is formed.
   (a) Name the type of reaction that takes place and give the role of the reagent
   (b) Outline the mechanism for the reaction, showing clearly the structure of the alcohol formed

4. If 3-bromo-2,3-dimethylpentane reacts with ethanolic potassium hydroxide, three structural isomeric alkenes are formed
   (a) Name the type of reaction that takes place and give the role of the reagent
   (b) One of the reaction products is 2,3-dimethylpent-2-ene
      (i) Give the structure of this alkene
      (ii) Show the mechanism for its formation.

5. Describe how you would prepare the following compounds:
   (a) Butan-2-ol from 2-iodobutane
   (b) Propane from 1-chloropropane
   (c) Butane from bromoethane
   (d) 1-iodopropane from 1-bromopropane.

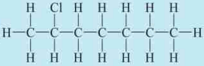
6. In the following pairs of alkyl halides, which one undergoes faster S_N1 reaction?

(a) 

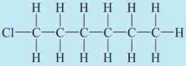
$$\begin{array}{ccccc} & & Cl & & \\ & & | & & \\ CH_3 & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

and 

$$\begin{array}{ccccccccccccc} & & H & & H & & Cl & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

(b) 

$$\begin{array}{ccccccccccccccccc} & & H & & Cl & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & H & & \end{array}$$

and 

$$\begin{array}{ccccccccccccccc} & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & \\ Cl & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & \end{array}$$

7. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

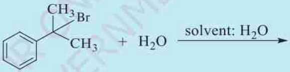
   (a) $CH_3CH_2CH_2Br$ or $CH_3CH_2CH(Br)CH_3$

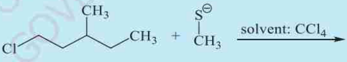
   (b) $CH_3CH_2CH(Br)CH_3$ or $CH_3CBr(CH_3)_2$

   (c) $CH_3CH(CH_3)CH_2CH_2Br$ or $CH_3CH_2CH(CH_3)CH_2Br$

8. Predict whether the following reactions will undergo S_N2 or S_N1 mechanism and give reason(s):

   (a) 

   (b) 

   (c) 

Revision exercise 4

1. Draw condensed molecular structures for the following haloalkanes:

   (a) 1,1-dichloro-2,2,3,3,3-pentafluoropropane

   (b) 3-bromo-2-chloro-2-methylpentane

2. Explain how the boiling points of haloalkanes vary;

   (a) with the substituted halogen atom.

   (b) with the alkyl group.

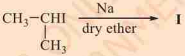
3. Complete the following reactions by giving major product(s) represented by letters A to I.

   (a) $CH_3CH_2COOAg \xrightarrow{Br_2} \mathbf{A} \xrightarrow{\text{alcoholic KOH}} \mathbf{B}$

   (b) $\mathbf{C} \xrightarrow{PBr_3} CH_3CH(Br)CH_3 \xrightarrow{\text{alcoholic KOH}} \mathbf{D} \xrightarrow[\text{peroxides}]{HBr} \mathbf{E}$

   (c) $CH_3CH_2CH_2Cl + CH_3C{\equiv}CNa \longrightarrow \mathbf{F}$

   (d) $CH_3I + (C_2H_5)_2NH \longrightarrow \mathbf{G}$

   (e) 

   $CH_3{-}\underset{\underset{CH_3}{|}}{CHI} \xrightarrow[\text{dry ether}]{Na} \mathbf{I}$

4. A chloro derivative of hydrocarbon **J** when treated with zinc copper couple gives a hydrocarbon with five carbon atoms. When **J** is dissolved in ether and treated with sodium, a compound **K** (2,2,5,5-tetramethyl hexane) is formed. What is the formula of compound **J**?

5. When 2-bromo-2-methylpropane reacts with aqueous NaOH at 25 °C, the two products formed are an alcohol and an alkene. Giving balanced equations answer the following questions:

   (a) Explain the type of the reaction that leads to the formation of alcohol and give the mechanism for the reaction.

   (b) Give the name and structural formula for the alcohol that is produced.

(c) Explain the type of reaction that leads to the formation of the alkene and show the mechanism for the reaction.

(d) Give the name and structural formula of the alkene which is produced.

(e) What conditions will favour the formation of the:

(i) Alcohol?

(ii) Alkene?

6. Although haloalkanes are polar in nature, they are immiscible in water. Explain.

7. Give products that will be obtained when 2-bromobutane reacts with;

(a) Aqueous KOH

(b) Alcoholic KOH

8. Explain the following:

(a) Alcohols cannot undergo nucleophilic substitution reactions under strong basic condition.

(b) Nucleophilic substitution reaction in primary alcohols with HBr is faster than with HCl.

(c) Primary alcohols undergo S_N2 mechanism and not S_N1 while tertiary alcohols undergo S_N1 mechanism and not S_N2 mechanism.

9. Explain how you can convert the following alcohols into the corresponding alkyl halides using any of the provided reagents: thionyl chloride, sulphonyl chloride, and hydrogen halide acid and phosphorus halides:

(a) Butan-1-ol

(b) Butan-2-ol

(c) 2-Methylpropan-2-ol

10. What are the major products for each of the following reactions?

(a) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{organic}}$

(b) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\quad}$

(c) $CH_3CH_2CH(OH)CH_3 + HBr \xrightarrow{heat}$

(d) $CH_3CH(CH_3)CH(OH)CH_3 + HBr \xrightarrow{heat}$

(e) $CH_3CH_2C(CH_3)_2CH_2OH + HCl \xrightarrow{ZnCl_2,\ heat}$

Chapter Five

Alcohols and Phenols

Introduction

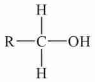
Alcohols and phenols are organic compounds that contain a hydroxyl (−OH) as the functional group. These compounds are formed when a hydrogen atom in aliphatic or aromatic hydrocarbon is replaced by a hydroxyl group. Alcohols and phenols are highly applied in industry as solvents, fuels, disinfectants, and starting material in the synthesis of other organic compounds such as haloalkanes and carbonyl compounds. Ethanol, an alcohols is used in many alcoholic drinks. In this chapter, you will learn about structures, nomenclature, preparation, properties, uses and hazards of alcohols and phenols.

5.1 Alcohols

Alcohols are organic compounds which contain one or more hydroxyl groups bonded to sp^3 hybridised carbon atoms of aliphatic hydrocarbons. In this section, you will learn about the structures, nomenclature, preparations, properties, uses and hazards of alcohols.

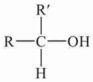
5.1.1 Structure of alcohols

Alcohols can be classified according to the degree of substitution at the carbon that bears the functional group and the number of hydroxyl groups (–OH) present in the compound. In terms of degree of substitution at the carbon that bears the functional group, alcohols are classified into primary (1°), secondary (2°), and tertiary (3°) alcohols. The following are structures of the primary, secondary, and tertiary alcohols:



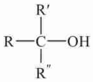
$R-\underset{H}{\overset{H}{C}}-OH$

Primary (1°) alcohol



$R-\underset{H}{\overset{R'}{C}}-OH$

Secondary (2°) alcohol

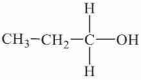


$R-\underset{R''}{\overset{R'}{C}}-OH$

Tertiary (3°) alcohol

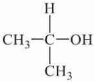
A primary alcohol is an alcohol which contain a hydroxyl group that is bonded to a primary carbon atom (carbon containing only one alkyl group). In the secondary and tertiary alcohols, the hydroxyl groups are bonded to carbon atom connected to two and three alkyl group, respectively.

Example:



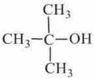
CH_3-CH_2-C-OH

Primary (1°) alcohol
(Propan-1-ol)



CH_3-C-OH

Secondary (2°) alcohol
(Propan-2-ol)



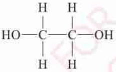
CH_3-C-OH

Tertiary (3°) alcohol
(2-methylpropan-2-ol)

In terms of the number of hydroxyl (OH) groups, alcohols can be classified into *monohydric, dihydric,* and *polyhydric* alcohols. A monohydric alcohol is an alcohol which contains only one hydroxyl group. The following are examples of monohydric alcohols

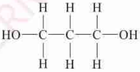
CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$
Methanol	Ethan-1-ol	Propan-1-ol

A dihydric alcohol is an alcohol which contains two hydroxyl groups. Examples of dihydric alcohols are 1,2-ethanediol (ethylene glycol), 1,3-propanediol, and 1,4-butanediol (tetramethylene glycol).



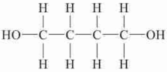
$HO-C-C-OH$

Ethane-1,2-diol
(Ethylene glycol)



$HO-C-C-C-OH$

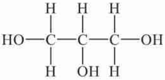
Propane-1,3-diol



$HO-C-C-C-C-OH$

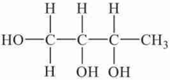
Butane-1,4-diol
(Tetramethylene glycol)

A trihydric alcohol is an alcohol which contains three hydroxyl groups. The following are examples of trihydric alcohols.



$HO-C-C-C-OH$

Propane-1,2,3-triol
(Glycerol)



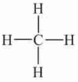
$HO-C-C-C-CH_3$

Butane-1,2,3-triol

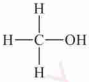
Generally, a polyhydric alcohol is an alcohol which contains three or more hydroxyl groups.

5.1.2 Nomenclature of alcohols

The IUPAC rules of naming alkanes are also applied in naming alcohols, but alcohols are named by replacing the suffix *e* of alkane with *ol* as shown in the following examples:



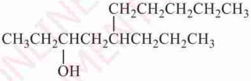
Methane



Methanol

The following are the basic IUPAC rules for naming alcohols:

1. The longest carbon chain that contains the hydroxyl group is considered as the parent chain. In the example below, the longest chain consists of ten carbon atoms (C_{10}).

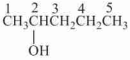


$$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2\overset{\overset{CH_2CH_2CH_2CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$$

5-propyldecan-3-ol

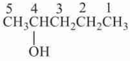
2. Numbering of the parent chain begins at the end nearest to the hydroxyl group and in the naming of alcohols, the appropriate number is used to indicate the position of the hydroxyl group.

Examples:



$$\overset{1}{C}H_3\underset{\underset{OH}{|}}{\overset{2}{C}}H\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$$

Pentan-2-ol
(Correct)

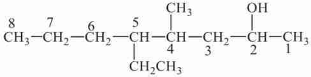


$$\overset{5}{C}H_3\underset{\underset{OH}{|}}{\overset{4}{C}}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$

Pentan-4-ol
(Incorrect)

3. The substituents are numbered according to their positions in the chain and named by listing them in an alphabetical order.

Example:



$$\overset{8}{CH_3}-\overset{7}{CH_2}-\overset{6}{CH_2}-\underset{CH_2CH_3}{\overset{5}{CH}}-\underset{4}{\overset{CH_3}{CH}}-\underset{3}{CH_2}-\underset{2}{\overset{OH}{CH}}-\underset{1}{CH_3}$$

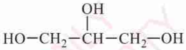
5-ethyl-4-methyloctan-2-ol

4. If the alcohol contains more than one hydroxyl groups, the suffixes such as *diol* and *triol* are used. However, the suffix *e* of alkane is retained.

Examples:

$HO-CH_2-CH_2-OH$

Ethane-1,2-diol

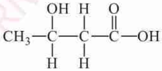


$$HO-CH_2-\overset{OH}{CH}-CH_2-OH$$

Propane-1,2,3-triol

5. If the hydroxyl functional group appears on a structure with a functional group of higher priority, the –OH group is named as "hydroxyl" where it is considered as the substituent group. This also applies when the structure is too difficult to name as a simple alcohol.

Example:



$$CH_3-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

3-hydroxylbutanoic acid

5.1.3 Laboratory preparation of alcohols

Alcohols can be prepared in the laboratory by various methods. These methods involve chemical reactions which convert organic reagents to alcohols. The organic reagents which can be converted to alcohols include; unsaturated hydrocarbons, alkyl halides, carbonyl compounds, carboxylic acids, esters, epoxides, and amines.

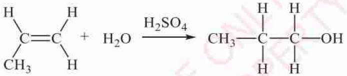
Conversion of unsaturated hydrocarbons to alcohols

Alkene is one of the unsaturated hydrocarbons that can be converted directly to alcohols through various chemical reactions. Chemical reactions which are used to convert alkenes to alcohols include: hydration, hydroboration-oxidation, and oxymercuration-demercuration of alkenes.

Hydration of alkenes

Hydration is a chemical reaction which involves the addition of water molecule to alkenes in the presence of aqueous acid to form alcohols. The common acid used is H_2SO_4.

Example:

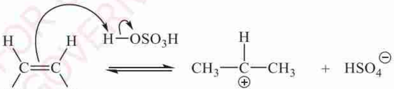


This is an electrophilic addition reaction, which proceeds via the protonation of the alkene to give a more stable carbocation intermediate.

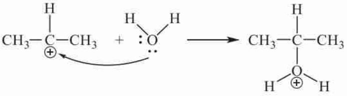
The mechanism for this reaction involves three steps:

Step 1: Protonation of the alkene by an acid to form a more stable carbocation.

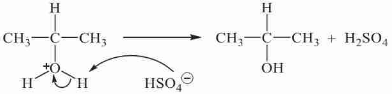
The π-electron pair acts as a Lewis base.



Step 2: The nucleophile which is a water molecule attack on the electrophilic carbocation to form an oxonium ion.



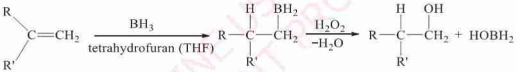
Step 3: The generated hydrogen sulphate group $HSO_4^{\ominus}$ acts as a base and deprotonates the oxonium ion to form the alcohol and regenerate the acid catalyst.

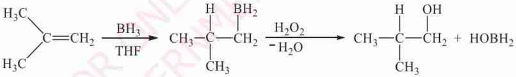


Hydroboration-oxidation of alkenes

Hydroboration-oxidation reaction of alkene is a two-step chemical reaction that involves the net addition of water molecule across the double bond of an alkene to form alcohol. Hydroboration-oxidation of alkene is an anti Markownikov's reaction, with the hydroxyl group (–OH) attaching to the less substituted carbon and hydrogen ion ($H^{\oplus}$) add to the more substituted carbon.

Examples:



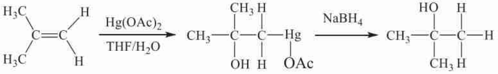


This reaction obeys anti-Markovnikov's rule because in BH_3, the boron is less electronegative than hydrogen (H). The hydrogen atom has a partial negative charge, hence it exhibits a nucleophilic character unlike in hydrogen halides where the hydrogen atom exhibits an electrophilic character. Boron has an empty *p*-orbital making it a Lewis acid which can accept electron from the π–bond of the alkene.

Oxymercuration-demercuration of alkenes

The oxymercuration-demercuration of alkene is an alternative method which hydrates alkenes to alcohols. The process involves treating the alkene with mercury acetate in aqueous tetrahydrofuran (THF). The demercuration of the complex formed (mercurinium ion) is effected by treating the complex with sodium borohydride ($NaBH_4$).

Example:



2-methylprop-1-ene

2-methylpropan-1-ol

Conversion of alkyl halides to alcohols

The hydrolysis of alkyl halides using water or hydroxides forms alcohols. The type of reaction is nucleophilic substitution where water or hydroxides act as nucleophiles.

The hydrolysis of alkyl halides to alcohols is useful in the reactions in which the reagents do not undergo E_2 elimination reaction easily.

$$\mathrm{R{-}X} \xrightarrow{\mathrm{H_2O\ or\ HO^{\ominus}}} \mathrm{R{-}OH} + \mathrm{HX}$$

Example:

$$CH_3CH_2Cl + KOH(aq) \longrightarrow CH_3CH_2OH + KCl$$

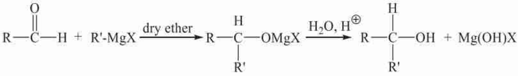
Since alkyl halides are prepared from alcohols, the reaction is very rarely used for the synthesis of alcohols. However, the use of moist Ag_2O or aqueous K_2CO_3 produces better yields.

Conversion of carbonyl compounds to alcohols

The carbonyl compounds such as aldehydes and ketones can be converted to alcohols by treating them with Grignard reagents, organolithium or through reduction reactions.

By using Grignard reagents

When carbonyl compounds are treated with Grignard reagents in the presence of organic solvent followed by H_2O and $H^{\oplus}$, they form the corresponding alcohols. The reaction is shown in the following general equation.

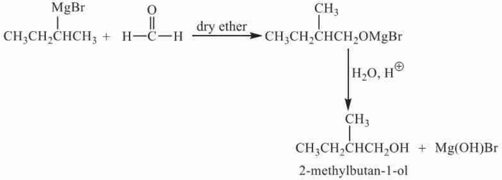


$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + \mathrm{R'{-}MgX} \xrightarrow{\text{dry ether}} \mathrm{R{-}\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle H}{}}{C}}{-}OMgX} \xrightarrow{\mathrm{H_2O,\ H^{\oplus}}} \mathrm{R{-}\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}OH} + \mathrm{Mg(OH)X}$$

Alcohol

The type of alcohol formed by adding Grignard reagent depends on the type of carbonyl compound used. Formaldehyde (HCOH) yields primary alcohols, other aldehydes (RCOH) yield secondary alcohols and ketones (RCOR’) yield tertiary alcohols.

Example:

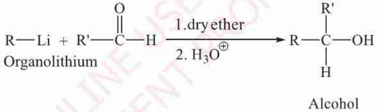


$$CH_3CH_2\overset{MgBr}{\overset{|}{C}}HCH_3 + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dry ether}} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OMgBr \xrightarrow{H_2O,\ H^{\oplus}} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH + Mg(OH)Br$$

2-methylbutan-1-ol

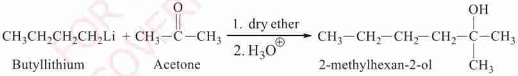
By using organolithium compounds

Organolithium compounds are the types of organometallic compounds that contain carbon-lithium bonds. They reduce aldehydes and ketones to the corresponding alcohols in a similar manner as Grignard reagents do in the presence of dry ether or tetrahydrofuran followed by $H_3O^{\oplus}$ as shown in the following equation:



$$\underset{\text{Organolithium}}{R-Li} + R'-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{2. } H_3O^{\oplus}]{\text{1. dry ether}} \underset{\text{Alcohol}}{R-\overset{R'}{\overset{|}{\underset{\underset{H}{|}}{C}}}-OH}$$

Example:



$$\underset{\text{Butyllithium}}{CH_3CH_2CH_2CH_2Li} + \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[\text{2. } H_3O^{\oplus}]{\text{1. dry ether}} \underset{\text{2-methylhexan-2-ol}}{CH_3-CH_2-CH_2-CH_2-\overset{OH}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3}$$

By using reducing agents ($LiAlH_4$ and $NaBH_4$)

The reduction of carbonyl compounds to alcohols also depends on the types of carbonyl compounds used. Formaldehyde (HCOH) is reduced to methanol, other aldehydes (RCOH) are reduced to primary alcohols, and ketones (RCOR) to secondary alcohols. Aldehydes and ketones are reduced to the corresponding alcohols when treated with metal hydrides like lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). The reaction of $LiAlH_4$ with water and alcohol is very explosive, hence the preparation of alcohol by using $LiAlH_4$ must use anhydrous diethyl ether or THF as a solvent.

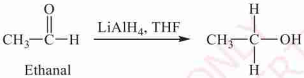
Examples:

$$\mathrm{H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{LiAlH_4,\ THF} H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH}$$

Formaldehyde Methanol

$$\mathrm{R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{LiAlH_4,\ THF} R-\overset{\overset{OH}{|}}{CH_2}}$$

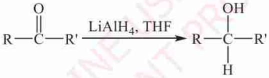
Aldehyde Primary alcohol



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{LiAlH_4,\ THF} CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH}$$

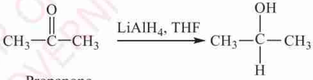
Ethanal

Ethanol



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{LiAlH_4,\ THF} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-R'}$$

Ketone Secondary alcohol



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4,\ THF} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

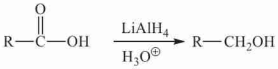
Propanone

Propan-2-ol

Both lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) react with carbonyl compounds in a similar way. They act in the same way as Grignard reagents do with the exception that they donate hydride rather than generating a carbanion.

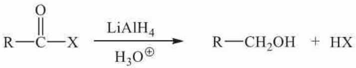
Conversion of carboxylic acids and their derivatives to alcohols

Carboxylic acids and acid halides can be converted to alcohols by using strong reducing agents such as lithium aluminium hydride ($LiAlH_4$) or diborane (B_2H_6). The reduction of carboxylic acids and acid halides mostly yields primary alcohols. The general reactions are shown in the following equations:



$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_3O^{\oplus}]{LiAlH_4} R-CH_2OH$$

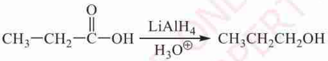
Carboxylic acid Primary alcohol



$$R-\overset{O}{\overset{\|}{C}}-X \xrightarrow[H_3O^{\oplus}]{LiAlH_4} R-CH_2OH + HX$$

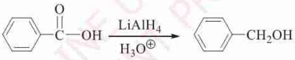
Acid halide Primary alcohol

Examples:

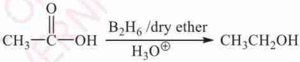


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3CH_2CH_2OH$$

Propanoic acid Propan-1-ol

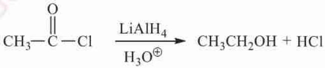


Benzoic acid Benzyl alcohol



$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_3O^{\oplus}]{B_2H_6\ /dry\ ether} CH_3CH_2OH$$

Acetic acid Ethanol



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3CH_2OH + HCl$$

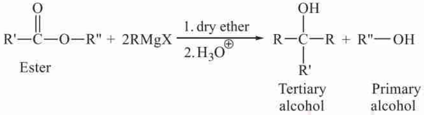
Acetyl chloride Ethanol

Conversion of esters to alcohols

Esters can be converted to alcohols when reacted with Grignard reagents or organolithium compounds followed by hydrolysis of the alkoxides.

Reaction of organolithium (RLi) or Grignard reagents (RMgX) with esters

Organolithium and Grignard reagents react with esters in the same manner similar to that of conversion of carbonyl compounds to alcohols. The esters (R—COOR) react with two equivalents of RLi or RMgX to give tertiary and primary alcohols as the major and minor products, respectively.



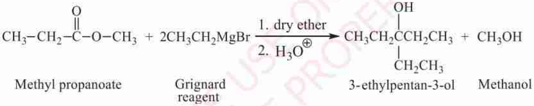
$$R'-\overset{\overset{\Large O}{\|}}{C}-O-R'' + 2RMgX \xrightarrow[2.\,H_3O^{\oplus}]{1.\text{ dry ether}} R-\underset{\underset{\Large R'}{|}}{\overset{\overset{\Large OH}{|}}{C}}-R + R''-OH$$

Ester

Tertiary alcohol

Primary alcohol

Example:



$$CH_3-CH_2-\overset{\overset{\Large O}{\|}}{C}-O-CH_3 + 2CH_3CH_2MgBr \xrightarrow[2.\;H_3O^{\oplus}]{1.\text{ dry ether}} CH_3CH_2\underset{\underset{\Large CH_2CH_3}{|}}{\overset{\overset{\Large OH}{|}}{C}}CH_2CH_3 + CH_3OH$$

Methyl propanoate

Grignard reagent

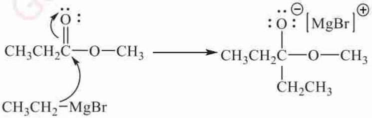
3-ethylpentan-3-ol

Methanol

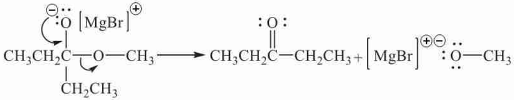
Mechanism

Step 1: The nucleophilic attack

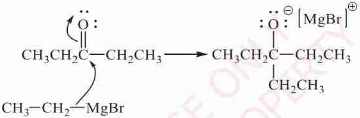
The nucleophilic carbon in the organometallic reagent attacks the electrophilic carbon in the polar carbonyl group. The electrons from C=O move to a more electronegative oxygen atom, hence creating metal alkoxide intermediate.



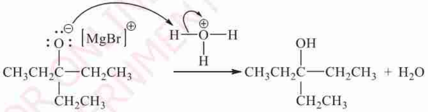
Step 2: The electrons move back from oxygen atom to carbon atom resulting into the removal of a leaving group and creating a ketone group.



Step 3: The nucleophilic carbon in the organometallic reagent attacks the electrophilic carbon in the polar ketone group and electrons move to a more electronegative oxygen atom creating a metal alkoxide intermediate.

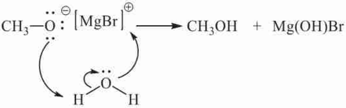


Step 4: The alkoxide complex is then protonated by hydrogen ion ($H^{\oplus}$) from hydroxonium ($H_3O^{\oplus}$) ion to form the alcohol and water.



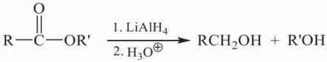
3-ethylpentan-3-ol

Step 5: The removed leaving group $\left(CH_3{-}O^{\ominus}[MgBr]^{\oplus}\right)$ can be protonated by hydrogen ion ($H^{\oplus}$) from water to form primary alcohol and magnesium hydroxide bromide Mg(OH)Br.



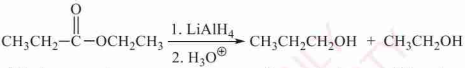
Reduction of esters to alcohols

Esters can be reduced by a strong reducing agent such as lithium aluminium hydride ($LiAlH_4$) to form primary alcohols.



$$R-\overset{O}{\overset{\parallel}{C}}-OR' \xrightarrow[2.\ H_3O^{\oplus}]{1.\ LiAlH_4} RCH_2OH + R'OH$$

Esters are more readily reduced by $LiAlH_4$ than carboxylic acids to form two primary alcohols. For example, ethyl propanoate can be reduced by $LiAlH_4$ followed by the treatment with $H_3O^{\oplus}$ to form ethanol and propanol.



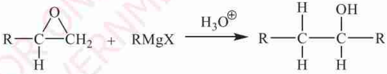
$$CH_3CH_2-\overset{O}{\overset{\parallel}{C}}-OCH_2CH_3 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ LiAlH_4} CH_3CH_2CH_2OH + CH_3CH_2OH$$

Ethyl propanoate Propan-1-ol Ethanol

The sodium borohydride reduces esters, but the reaction is very slow because $NaBH_4$ is less reactive than $LiAlH_4$.

Conversion of epoxides to alcohols

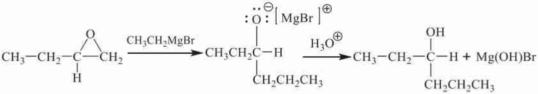
The organolithium and Grignard reagents all containing carbon nucleophiles react with epoxides in an S_N2 mechanism to give alcohols. The epoxides are more reactive than ethers due to the presence of a ring strain.



Epoxide Grignard reagent Alcohol

The negatively charged nucleophiles which are either Grignard reagents or organolithium compounds attack at the least substituted carbon of the epoxide.

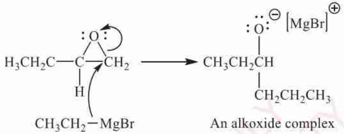
Example:



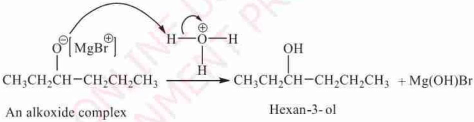
Hexan-3-ol

Mechanism

Step 1: The pair of electrons in carbon–magnesium (C—Mg) bond within the nucleophile of Grignard reagent attacks the least hindered electrophilic carbon of the epoxide to form a new C—C bond. Consequently, the carbon-oxygen (C—O) bond breaks and forms an alkoxide intermediate complex.

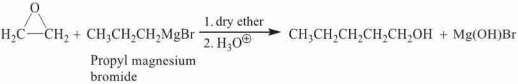


Step 2: The protonation of alkoxide complex generates oxygen–hydrogen bond (O—H) by adding an acid source ($H^{\oplus}$). The $MgBr^{\oplus}$ leaves the complex and combine with hydroxide group to form Mg(OH)Br.



The ethylene oxides react with Grignard reagents or organolithium compounds in the presence of dry ether followed by $H_3O^{\oplus}$ to form primary alcohols. The alcohols formed contain two or more carbon atoms than that of organolithium or Grignard reagents.

Example:



Conversion of primary amines to alcohols

When primary amines are treated with nitrous acid, they yield primary alcohols, water, and nitrogen gas. For example, if propan-1-amine is treated with nitrous acid, it yields propan-1-ol, water, and nitrogen gas.

Example:

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + H_2O + N_2(g)$$

Since, nitrous acid is a weak unstable acid it is always prepared *in-situ* by treating $NaNO_2/KNO_2$ with a strong aqueous acid solution

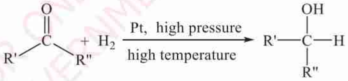
5.1.4 Industrial preparation of alcohols

Alcohols can be prepared in a large scale in industry. There are several methods which are used to prepare alcohols, these include; catalytic hydrogenation of carbonyl compounds, hydration of alkenes, and fermentation of carbohydrates.

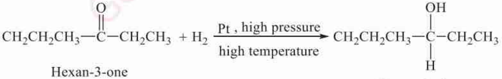
Catalytic hydrogenation of carbonyl compounds

Alkenes can be hydrogenated to alkanes by reacting with hydrogen in the presence of either nickel (Ni), palladium (Pd) or platinum (Pt) catalysts. The catalytic hydrogenation reaction occurs at room temperature and 1 atmosphere of hydrogen gas. In the same way, π-bonds of aldehydes and ketones can be hydrogenated to alcohols in the presence of catalysts such as Pt, Ni or Pd. Since the π-bonds of carbonyl compounds are much more stable than that of alkenes, the hydrogenation of a carbonyl group needs extreme conditions such as high pressures and elevated temperatures.

Generally, the catalytic hydrogenation over metal catalysts focuses on effectively attaining the controlled transformation of organic compounds.



Example:



$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3 + H_2 \xrightarrow[\text{high temperature}]{\text{Pt , high pressure}} CH_3CH_2CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2CH_3$$

Hexan-3-one

Hexan-3-ol

The catalytic hydrogenation of polyunsaturated esters is called *hydrogenolysis.* The hydrogenolysis of esters to form alcohols involves the breaking of a carbon-oxygen (C—O) bond which is adjacent to a carbonyl group. The methyl esters of vegetable oil such as linseed, sunflower, and soyabean can be catalytically hydrogenated to valuable organic compounds.

Hydration of alkenes

The alkenes can be converted to alcohols through hydration in the following two methods: the direct addition of water molecules in the presence of acid as a catalyst and the indirect method of hydration. Ethanol is one of the alcohols which is manufactured in the industry by reacting ethene with steam at 60-70 atm and 300 °C in the presence of phosphoric acid catalyst.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2O(g) \underset{300\,^{\circ}C,\ 60\text{-}70\ \text{atm}}{\overset{H_3PO_4}{\rightleftharpoons}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

The reaction is reversible and each pass of ethene to the reactor yields 5% of ethanol. Hence, by removing ethanol from the equilibrium mixture and recycling ethene, the yield of ethanol reaches 95%. The reaction scheme of ethene and steam is shown in Figure 5.1.

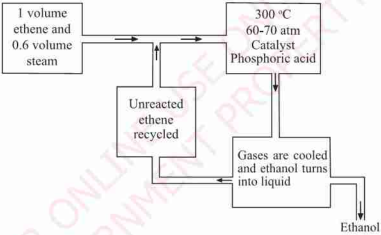


Figure 5.1 The reaction scheme of ethene and steam to form ethanol

Preparation of methanol

Methanol is prepared in a large scale from a mixture of carbon monoxide and hydrogen. When the gaseous mixture is passed over a heated catalyst mixture of ZnO and Cr_2O_3 at a pressure of 200 atm and 400 °C temperature, methanol vapours are produced which are then condensed to liquid methanol.

$$CO(g) + 2H_2(g) \xrightarrow[400-450\,^{\circ}C,\ 200\ \text{atm}]{ZnO + Cr_2O_3} CH_3OH(l)$$

Preparation of ethanol by fermentation of starch

Fermentation is a metabolic process that breaks down sugars in the absence of oxygen to form organic acids, gases or alcohols. The process is catalysed by enzymes, which commonly occurs in yeast, bacteria, and muscle cells of animals that have oxygen deficiency as in the case of lactic acid fermentation.

The fermentation of starchy rich materials such as wheat, rice, barley, maize, potatoes, and millet follow the following steps: conversion of starch to maltose, alcoholic fermentation, distillation, and rectification.

Conversion of starch to maltose

The conversion of starchy materials to maltose or *saccharification* process is done by the following processes: malting, mashing, hydrolysis, and alcoholic fermentation.

Malting

Malting is a process that converts raw grains into malt which is used for brewing. The malt is normally germinated cereal grains that have been dried. The malting process involves allowing moist cereals to germinate in the dark at 17 °C. The germinated cereal is then heated to 57 °C to dry and stop further germination. The dried malt is then crushed and extracted with water. The malt extract usually contains *diastase* enzyme.

Mashing

The mashing process involves reacting the starch containing grain with superheated steam which breaks the cell walls and exposes the starch, forming a paste-like mass called mash.

Hydrolysis

The mash and malt extracts are then mixed up together at a temperature of 47-57 °C for about half an hour to form maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{in malt extract}]{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Alcoholic fermentation

The maltose is then fermented to alcohol (ethanol) in the presence of maltase and zymase enzymes in yeast cell. Carbon dioxide gas is released as a by-product.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{in yeast cell}]{\text{maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{yeast cell}]{\text{zymase in}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2(g)$$

The produced fermented liquor is not pure, it is then distilled and purified.

Activity 5.1 Preparation of alcohol from cassava

Requirements: Cassava tubers, fungamyl enzyme, termamyl enzyme, water, bakery yeast, calcium chloride ($CaCl_2$), knife, motor and pestle, sieve, beakers, thermometer, source of heat, condenser, conical flask, and round bottom flask.

Procedure

1. Peel five cassava tubers and grind them.
2. Extract the starch content of cassava with water and filter them with a sieve. Allow the solution to stay for about 30-40 minutes, followed by decantation of the solution to get starch slurry which is about 35% starch.
3. Mix the resultant slurry with about 0.15% of termamyl enzyme and add $CaCl_2$ salt.
4. Keep the reaction mixture at 95-97 °C for four hours then add 0.15% fungamyl enzyme to obtain hydroxylate. To obtain glucose from maltose by hydrolysis, the hydroxylate is maintained at 55-65 °C for 20 hours.
5. Add 1 gram of bakery yeast to the mixture of the glucose solution to get wort and then ferment it for four days. The fermented liquor is then distilled in a distillation column as shown in Figure 5.2

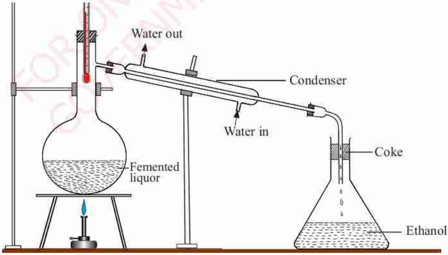


Figure 5.2: Distillation of cassava fermented liquor to obtain ethanol

Questions

(a) Explain the role of yeast, termamyl enzyme, fungamyl enzyme and $CaCl_2$ in this experiment.

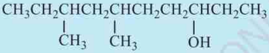
(b) Name and define the process investigated in this experiment.

(c) Write down two chemical reactions that occur during the experiment.

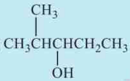
(d) Explain the importance of ethanol in daily life.

Exercise 5.1

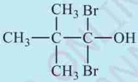
1. Give the IUPAC names of the following compounds and for each, state whether it is a primary, secondary or tertiary alcohol:

(a) 

$$\mathrm{CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}CH_2\underset{\substack{|\\ CH_3}}{CH}CH_2CH_2\underset{\substack{|\\ OH}}{CH}CH_2CH_3}$$

(b) 

$$\mathrm{CH_3\overset{\substack{CH_3\\ |}}{C}H\underset{\substack{|\\ OH}}{CH}CH_2CH_3}$$

(c) 

$$\mathrm{CH_3{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{-}\overset{\substack{Br\\ |}}{\underset{\substack{|\\ Br}}{C}}{-}OH}$$

2. Draw structures for the compounds with the following names:

(a) Hexan-2-ol

(b) 3-methylpentan-2-ol

3. Explain using chemical equations, the preparation of propan-2-ol from:

(a) Alkene

(b) Grignard reagent

4. Write chemical equations, showing all the necessary reagents, for the preparation of butan-1-ol using each of the following methods:

(a) Hydroboration-oxidation of an alkene

(b) The use of a Grignard reagent

(c) The use of an organolithium reagent

(d) Reduction of a carboxylic acid

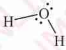
(e) Reduction of a butyl ester
(f) Hydrogenation of an aldehyde
(g) Reduction with sodium borohydride

5. Write chemical equations, showing all the necessary reagents and mechanisms for the preparation of tert-butyl alcohol by:
   (a) The reaction between Grignard reagent and a ketone.
   (b) The reaction between Grignard reagent and an ester.

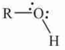
6. Which of the isomeric alcohols with molecular formula $C_5H_{12}O$ can be prepared by lithium aluminium hydride reduction of:
   (a) An aldehyde
   (b) A carboxylic acid
   (c) A ketone
   (d) An ester of the type $RCOOCH_3$

5.1.5 Physical properties of alcohols

The physical properties of organic compounds are largely determined by the types of intermolecular forces and the sizes of the molecules. Alcohols can be considered as the derivatives of water in which one hydrogen of water is replaced by an alkyl group.



Water



Alcohol

The types of intermolecular forces that exist in alcohols are governed by the hydroxyl group. However, the presence of an alkyl group in alcohol relative to hydrogen in water makes a large difference in terms of intermolecular forces and hence the physical properties.

Physical state of alcohols

Lower alcohols up to four carbon atoms are colourless liquids. Alcohols from C_5 to C_{11} are oily liquids and members from C_{12} and higher are waxy solids.

Boiling point

Generally, alcohols have higher boiling points compared to hydrocarbons (alkanes) of relatively the same molar mass. Figure 13.3 is a plot of the boiling points of alcohols as a function of molar masses. The boiling points of alkanes and water are included for comparison.

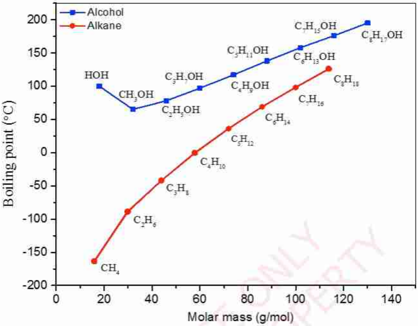
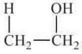


Figure 5.3 Boiling points of alcohols versus molar masses

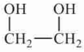
The plot shows a large difference in the boiling points between ethane with a molecular mass of 30 and methanol with a molecular mass of 32. The high boiling points of alcohols are caused by the presence of hydrogen bonding between oxygen atoms of hydroxyl groups in one molecule and the hydrogen of the hydroxyl groups of the neighbouring molecules. The strength of hydrogen bonds between water, methanol and ethanol can be used to explain the observed trend in the boiling points. The plots also show that within alcohols themselves, the boiling points increase with an increase in the number of carbons (molar mass). This is because the bigger the size of the molecules the stronger the van der Waals forces. The boiling points also increase with an increase in the number of hydroxyl (–OH) groups, because of the increase in the number of hydrogen bonds. Thus, ethylene glycol has a higher boiling point than ethanol as shown in the following structures.



$$\underset{\text{H}}{\overset{|}{}}\text{CH}_2\text{—}\text{CH}_2\text{OH}\quad \begin{array}{cc}\text{H} & \text{OH}\\ | & | \\ \text{CH}_2\text{—} & \text{CH}_2\end{array}$$

Ethanol

b.p. = 78 °C



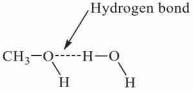
$$\begin{array}{cc}\text{OH} & \text{OH}\\ | & | \\ \text{CH}_2\text{—} & \text{CH}_2\end{array}$$

Ethylene glycol

b.p. = 197 °C

Solubility

Alcohols are soluble in water because of their ability to form intermolecular hydrogen bonds with water molecules as illustrated by the following compounds:



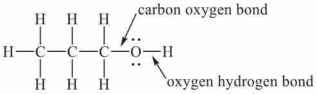
However, the solubility of alcohols in water decreases with an increase in hydrocarbon chain. This is because of the increase of non-polar hydrocarbon chain which is hydrophobic in nature. The solubility of alcohols in water with an increase in the number of carbons is shown in Table 5.1.

Table 5.1 Solubility of alcohols in water

Formula	Name	Solubility in water (g/100 mL water)
CH_3OH	Methanol	Infinitely soluble
CH_3CH_2OH	Ethanol	Infinitely soluble
$CH_3CH_2CH_2OH$	Propanol	Infinitely soluble
$CH_3CH_2CH_2CH_2OH$	Butanol	9
$CH_3CH_2CH_2CH_2CH_2OH$	Pentanol	2.7
$CH_3CH_2CH_2CH_2CH_2CH_2OH$	Hexanol	0.6
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	Heptanol	0.18
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	Octanol	0.054
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	Nonanol	Insoluble in water
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	Decanol	Insoluble in water

5.1.6 Chemical properties of alcohols

Alcohols consist of alkyl groups bonded with hydroxyl groups. Consider the following structure of propanol:



The hydroxyl group of alcohol consists of two reactive covalent bonds, the carbon-oxygen bond and the oxygen-hydrogen bond. As a result, alcohols can undergo several types of reactions, either by breaking the carbon-oxygen (—C—O) bond or the oxygen-hydrogen (O—H) bond. As seen from the structure of the alcohol, the O—H bond consists of a more electronegative atom (O) and less electronegative atom (H) making the bond electron pair to be more displaced towards oxygen and depriving hydrogen. Thus, this makes oxygen to have a partial negative charge and hydrogen to have a partial positive charge, making the bond to be polar. This hydrogen is called acidic hydrogen as it can be released in the solution because it is weakly bonded to oxygen. Consequently, the chemical reactions of alcohols can be divided into two main types: the reactions which involve the use of acidic hydrogen and the reactions which involve the hydroxyl functional group.

Reactions which involve breaking of the O-H bond

The following are the chemical reactions of alcohols that involve the breaking of the oxygen-hydrogen (O-H) bond while leaving the carbon-oxygen bond intact:

Reaction with sodium metal

Alcohols react with sodium metal to form salts (sodium alkoxide) and hydrogen gas.

Example:

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$

Ethanol Sodium Sodium ethoxide Hydrogen

The reaction occurs in the same way as the reaction between water and sodium, forming sodium hydroxide. However, the reaction of sodium with alcohol is much slower than that of water. The sodium alkoxide can also be formed by reacting alcohol with sodium amide.

$$C_2H_5OH + \overset{\oplus}{Na}\overset{\ominus}{NH_2} \rightleftharpoons C_2H_5\overset{\ominus}{O}\overset{\oplus}{Na} + NH_3$$

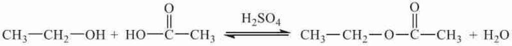
Ethanol Sodium amide Sodium ethoxide Ammonia

Reaction with carboxylic acids (esterification)

Alcohols react with carboxylic acids in the presence of concentrated sulphuric acid to form esters.

$$R—OH + HO—\overset{\overset{\displaystyle O}{\|}}{C}—R' \xrightleftharpoons{H_2SO_4} R—O—\overset{\overset{\displaystyle O}{\|}}{C}—R' + H_2O$$

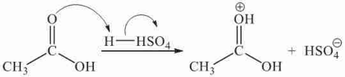
Example:



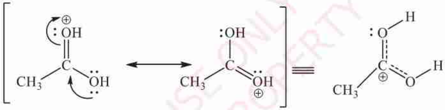
$$CH_3-CH_2-OH + HO-\overset{\overset{O}{\|}}{C}-CH_3 \xrightleftharpoons{H_2SO_4} CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

Mechanism

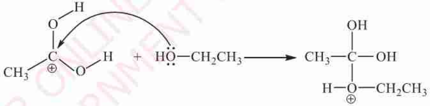
Step 1: Protonation of the carboxylic acid



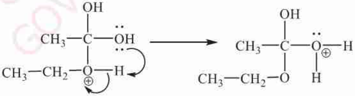
The positive charge is delocalised over the whole carboxyl group.



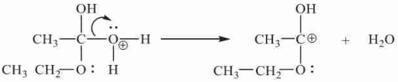
Step 2: The attack on the positively charged carbon by a lone pair from ethanol



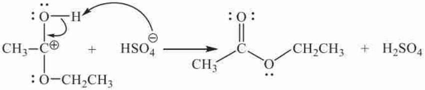
Step 3: Proton transfer



Step 4: Loss of water molecule

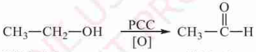


Step 5: Removal of hydrogen by the reaction with $HSO_4^{\ominus}$



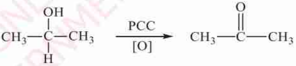
Reaction with oxidising agents (oxidation)

Alcohols react with oxidising agents, breaking the carbon-hydrogen (C—H) bond, forming the carbon-oxygen (C—O) bond on the same carbon. If a weak oxidant such as pyridinium chlorochromate (PCC) is used, a primary alcohol (R—OH) is oxidised to aldehyde and the reaction stops. This kind of oxidation reaction can also be achieved by using chromic acid (H_2CrO_4) in pyridine. In the absence of pyridine, it is hard to stop the reaction, as soon as the aldehyde is formed it is further oxidised to carboxylic acid and the secondary alcohol is converted to a ketone.



$$CH_3-CH_2-OH \xrightarrow[[O]]{PCC} CH_3-\overset{\overset{O}{\|}}{C}-H$$

1° Alcohol Aldehyde

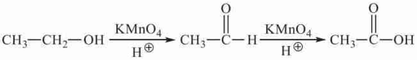


$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[[O]]{PCC} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

2° Alcohol Ketone

If a strong oxidising agent such as potassium permanganate ($KMnO_4$) is used, a primary alcohol is oxidised to aldehyde which is further oxidised to carboxylic acid.

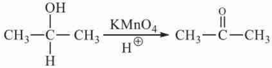
Example:



$$CH_3-CH_2-OH \xrightarrow[H^{\oplus}]{KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H^{\oplus}]{KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Oxidation of a secondary alcohol with a strong oxidising agent forms a ketone which cannot be further oxidised.

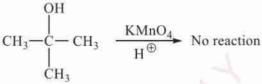
Example:



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 \xrightarrow[H^{\oplus}]{KMnO_4} CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$$

Tertiary alcohols are never oxidised, even with a strong oxidising agent because they lack hydrogen on the carbinol carbon.

Example:



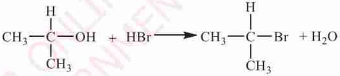
$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow[H^{\oplus}]{KMnO_4} \text{No reaction}$$

Reactions which involve the breaking of the C−O bond

In these reactions, the whole –OH group is removed which involves the breaking of the carbon-oxygen (C−O) bond.

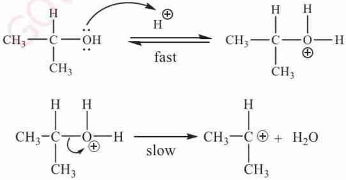
Reaction with hydrogen halides

Alcohols undergo nucleophilic substitution reactions with hydrogen halides such as HBr and HCl to form alkyl halides and water.



$$CH_3-\underset{CH_3}{\overset{H}{C}}-OH + HBr \longrightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-Br + H_2O$$

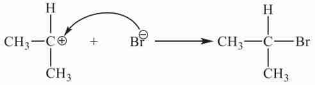
The reactions occur by S_N1 mechanism, which involve the formation of an intermediate carbocation.



$$CH_3-\underset{CH_3}{\overset{H}{C}}-\ddot{O}H \underset{\text{fast}}{\overset{H^{\oplus}}{\rightleftharpoons}} CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{\oplus}{\overset{H}{O}}-H$$

$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{\oplus}{\overset{H}{O}}-H \xrightarrow{\text{slow}} CH_3-\underset{CH_3}{\overset{H}{C}}{}^{\oplus} + H_2O$$

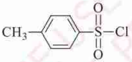
Intermediate carbocation



Since the reaction involves the formation of carbocation, the order of reactivity of alcohols follows the trend: tertiary (3°) > secondary (2°) > primary (1°) > methyl. The reactions involving methanol and other primary alcohols occur through S_N2 mechanism to avoid the formation of highly unfavourable carbocation.

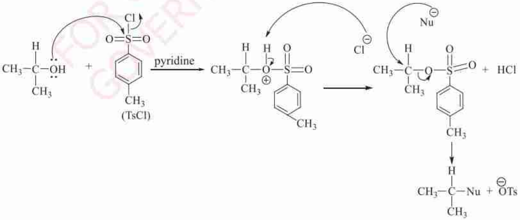
Reaction with tosyl chloride followed by nucleophile

The reaction mechanism of alcohol and halogen acid involves the protonation of the –OH group to make it a good leaving group. However, some nucleophiles cannot be used under acidic conditions, an alternative approach of making a good leaving group can be used, that involves converting alcohols into tosylate which is a better leaving group. In this reaction, *p*-toluene sulphonyl chloride or tosyl chloride is used.



p-toluene sulphonyl chloride
(Tosyl chloride, TsCl)

Mechanism



First, the hydroxyl (–OH) group of the alcohol reacts as a nucleophile and attacks the electrophilic centre of tosylate and displaces the chloride ($Cl^{\ominus}$). The tosylate reacts with nucleophile ($Nu^{\ominus}$) in the same way as alkyl halide.

Reaction of alcohol with $SOCl_2$, PCl_3 or PCl_5

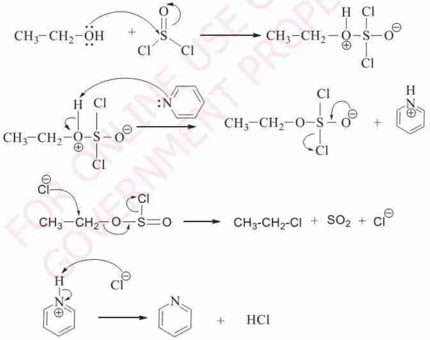
Alcohols can also be converted to alkyl halides by nucleophilic substitution using thionyl chloride ($SOCl_2$), phosphorus trichloride (PCl_3) or phosphorus pentachloride (PCl_5). The reaction occurs mostly by S_N2 mechanism on primary (1°) or secondary (2°) alcohols. A base such as triethylamine $(CH_3CH_2)_3N$ or pyridine (C_5H_6N) is used as a catalyst. Hydroxyl group (–OH) is not removed directly, but it is first converted to a better leaving group. This reaction is advantageous because it occurs in less acidic conditions.

Examples:

$$CH_3-CH_2-OH + SOCl_2 \xrightarrow[\text{or pyridine}]{\text{triethylamine}} CH_3-CH_2-Cl + SO_2 + HCl$$

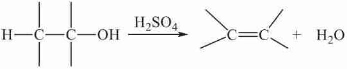
$$3CH_3-CH_2-OH + PCl_3 \xrightarrow[\text{or pyridine}]{\text{triethylamine}} 3CH_3-CH_2-Cl + H_3PO_3$$

Mechanism

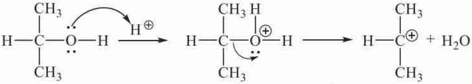


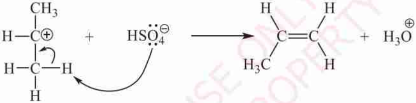
Acid catalysed elimination (dehydration) of alcohols

When alcohols are heated with strong acids such as sulphuric acid (H_2SO_4) or phosphoric acid (H_3PO_4), they undergo 1,2– elimination reactions to give alkenes. The reaction is also called dehydration because it involves the removal of water molecules. The elimination reaction follows Saytzeff's rule and therefore, the major product will be the one which is highly substituted with alkyl groups. General equation,



E_1 mechanism in secondary alcohols



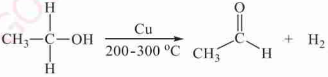


Other reactions which distinguish 1°, 2° and 3° alcohols

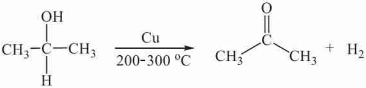
Oxidation of alcohols by using either weak or strong oxidising agents gives different products such as aldehydes, ketones, and carboxylic acids depending on the nature of the alcohol. There are other reactions that can be used to determine whether the alcohol is primary, secondary, or tertiary.

Reaction of alcohols with copper

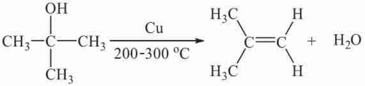
When vapours of alcohols are passed over hot reduced copper at 200-300 °C, primary alcohols form aldehyde, secondary alcohol forms ketone, and tertiary alcohols form alkenes as shown in the following examples.



Primary alcohol



Secondary alcohol



Tertiary alcohol

The chemical test for the respective products can then be conducted. The test for distinguishing aldehydes from ketones can be done using Tollen's reagent (Tollen's test).

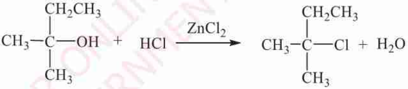
Reaction with Lucas' reagent (Lucas test)

Lucas' reagent is a solution of anhydrous zinc chloride and concentrated hydrochloric acid in an equimolar amounts. The aim of zinc chloride is to increase the ionisation of HCl.

$$ZnCl_2 + HCl \longrightarrow ZnCl_3^{\ominus} + H^{\oplus}$$

When an alcohol is treated with Lucas reagent, cloudy appearance is observed in the reaction mixture, indicating that alcohol is converted to alkyl chloride.
Tertiary alcohols react immediately, therefore the cloudy appearance is observed immediately.

Example:



$$CH_3-\underset{CH_3}{\overset{CH_2CH_3}{\underset{|}{\overset{|}{C}}}}-OH + HCl \xrightarrow{ZnCl_2} CH_3-\underset{CH_3}{\overset{CH_2CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + H_2O$$

2-methylbutan-2-ol

2-chloro-2-methylbutane

Secondary alcohols react within five minutes while primary alcohols do not react appreciably at room temperatures, therefore no cloudy appearance is observed.

Reaction with hydrogen iodide and silver nitrate

Alcohols react with hydrogen iodide to form iodoalkanes as shown in the following example

$$-\underset{OH}{\underset{|}{\overset{|}{C}}}-H + H-I \longrightarrow -\underset{H}{\underset{|}{\overset{|}{C}}}-I + H_2O$$

Alcohol Hydrogen iodide iodoalkane

$$CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH + HI \longrightarrow CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-I + H_2O$$

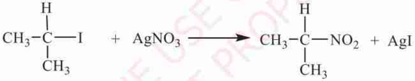
Propan-2-ol 2-iodopropane

Reaction of iodoalkane with silver nitrate gives nitroalkane. The formed nitroalkane when reacted with nitrous acid form complexes with different colours based on the type of the nitroalkane.

$$-\overset{|}{\underset{|}{C}}-I + Ag-NO_3 \longrightarrow -\overset{|}{\underset{|}{C}}-NO_2 + AgI$$

Iodoalkane Silver nitrate Nitroalkane

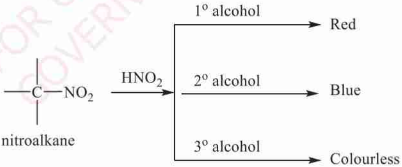
Example:



$$CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-I + AgNO_3 \longrightarrow CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-NO_2 + AgI$$

2-iodopropane 2-nitropropane

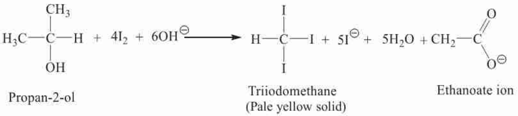
The following is the generalised summary of the distinguishing tests for the three types of alcohols.



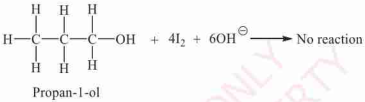
Iodoform test (triiodomethane test)

Iodoform test is used to distinguish primary alcohols such as methanol from secondary alcohols containing a methyl group. The secondary alcohol will react with alkaline solutions of iodine to form triiodomethane (iodoform, CHI_3) which is a pale-yellow solid with a characteristic smell.

Positive iodoform test:



Negative iodoform test:



Activity 5.2 Investigation of the chemical properties of ethanol

Requirements: One watch glass, two measuring cylinders of 10 mL, two test tubes, two sources of heat, match box, glacial ethanoic acid, concentrated sulphuric acid, and cold water.

Procedure

1. Put some few drops of ethanol in a watch glass and ignite. Observe.
2. Put 2 mL of glacial ethanoic acid in a dry test tube and add 2 mL of ethanol in the same test tube. Carefully add 1 mL of concentrated sulphuric acid drop wise to the test tube and gently shake the contents. Observe each step.
3. Place the test tube in a beaker of cold water, warm the beaker while shaking gently the contents in the test tube. Do not allow the mixture in the test tube to boil. Pour the test tube contents in the small beaker containing water at room temperature. Observe.

Questions

(a) Explain the observation of experiments done in procedure number 1, 2, and 3.

(b) State the aim of experiments done in procedure number 1, 2, and 3.

(c) Write down the chemical equations for the reactions that occurred in procedures 1-3.

(d) What is the economic importance of the reaction between ethanol and ethanoic acid?

5.1.7 Uses and hazards of alcohols

Alcohols are well known for their valuable uses in daily life, however some detrimental effects have been associated with the use of alcohols. In this sub-topic you will learn about the uses and hazards of alcohols.

Uses of alcohols

Ingredients in alcoholic drinks

In alcoholic drinks, the word *alcohol* refers to ethanol (CH_3CH_2OH). Ethanol is a key ingredient in alcoholic drinks such as whisky, champagne, wine, and beer.

Production of methylated spirit

Industrial methylated spirit is an ethanol with a small quantity of methanol and possibly some additive colour. The methylated spirit is unfit for consumption because the methanol that is added is poisonous. Being combustible, methylated spirit can be used in lamps and stoves.

Combustion of alcohols gives carbon dioxide, water, and energy

Alcohols such as methanol and ethanol can be used as petrol additives to improve combustion. The use of alcohol as fuels contributes much less to pollution. Fuel alcohols can also be obtained as biofuel (fuel derived from biological sources). For example, ethanol can be obtained from sugars such as sucrose from sugarcane, through fermentation and distillation. When blended with petrol, they are used as fuel in motor vehicles.

Alcohols as solvents

Methanol, ethanol, and propanol are widely used as solvents. They are especially used to dissolve organic compounds which are insoluble in water. They are also used as solvents for varnishes and paints. They are also used in the removal of ink from surfaces such as metals and plastics as well as components of household cleaning products such as glass cleaners. Moreover, ethanol has antiseptic properties as it slows or stops the growth of micro-organisms (germs), therefore it is used as disinfectants and toiletries such as after shave lotions, used in cosmetics such as perfumes.

Alcohols as industrial feedstocks

Alcohols are used as a raw materials (feedstocks) in the synthesis of other organic compounds such as aldehydes, ketones, amines, haloalkanes, esters, ethers, and carboxylic acids.

Hazards of alcohols

Despite the useful applications, alcohols have some hazardous effects to human beings. Though ethanol is the key ingredient in alcoholic drinks, when taken excessively, it can cause several diseases or abnormal conditions. These include anaemia, increased cancer risks, cardiovascular diseases, and cirrhosis. Excessive drinking of alcohols can also cause epilepsy and trigger seizures even in people who do not have epilepsy. Gout, high blood pressure, suppressed body immunity, nerve damage and pancreatitis are other effects that can be caused by excessive drinking of alcohols.

Methanol (CH_3OH) is highly toxic to humans when it enters the body, by ingestion, inhalation or absorption through the skin; it gets metabolised to formic acid via formaldehyde. This process is initiated by the enzyme alcohol *dehydrogenase* in the liver. The resulting formic acid is toxic because it inhibits mitochondrial cytochrome C *oxidase*. This inhibition causes some parts of the body to be deprived of oxygen at the cellular level, a condition known as *hypoxia*. It can also cause metabolic acidosis, that is, the body produces excessive acid or kidney not removing enough acid.

Exercise 5.2

1. Why are the lower members of alcohols soluble in water while higher members are not?
2. Explain the following phenomena:
   (a) Alcohols have higher boiling points than alkyl halides or alkanes of comparable molecular weight.
   (b) The boiling points of alcohols increase with an increase in the number of hydroxyl (–OH) groups.
3. Explain the following phenomena:
   (a) Ethanol is more soluble in water than hexan-1-ol.
   (b) Butan-1-ol has a lower boiling point than hexan-1-ol.
4. (a) Arrange the following alcohols in the order of increasing boiling points: ethanol, methanol, and propan-1-ol.

(b) Arrange the following alcohols in the order of increasing solubility in water: butan-1-ol, methanol, and octan-1-ol.

5. Show by using a series of chemical equations, how 3-methylpentane can be obtained from ethanol and any necessary inorganic reagents.

6. Why are alcohols considered as weak acids?

7. Show the trend in acidity of methanol, primary alcohol, secondary alcohol and tertiary alcohol, and explain the observed trend.

8. Write the structure of the major organic products formed in the reaction of propan-1-ol with each of the following reagents:
   - (a) Sulphuric acid (catalytic amount), heat at 140 °C
   - (b) Sulphuric acid (catalytic amount), heat at 200 °C
   - (c) Nitric acid (H_2SO_4 catalyst)
   - (d) Pyridinium chlorochromate (PCC) in dichloromethane
   - (e) Potassium dichromate ($K_2Cr_2O_7$) in aqueous sulphuric acid followed by heating
   - (f) Sodium amide ($NaNH_2$)
   - (g) Acetic acid in the presence of dissolved hydrogen chloride

9. Write chemical equations for the reactions between alcohols and;
   - (a) halogen acids
   - (b) thionyl chloride
   - (c) phosphorus halide

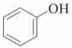
5.2 Phenols

Phenols are organic compounds containing at least one hydroxyl (–OH) group bonded to an aromatic ring. Both alcohols and phenols have –OH as their characteristic functional group, however, their chemistry is very different. In this sub-topic you will learn about the structures, nomenclature, preparations, properties, uses and hazards of phenols.

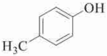
5.2.1 Structure of phenols

Generally, phenols are organic compounds which contain one or more hydroxyl groups bonded to sp^2 hybridised carbon atoms of aromatic hydrocarbons. The general formula for phenol is given as Ar–OH, where Ar- is a phenyl group, a substituted phenyl or some other aryl groups such as naphthyl and phenanthryl.

In phenol, the hydroxyl group is directly attached to the benzene ring. Phenol is therefore a specific name for hydroxyl benzene, and a general name for the derivatives of hydroxybenzene.

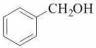


Hydroxybenzene
(Phenol)



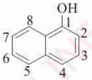
4-methylphenol
(Substituted phenol)

When the hydroxyl group is bonded to an sp^3 hybridised carbon of the side chain, Ar-CH_2-OH, the compound is called an aromatic alcohol.

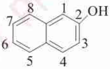


An aromatic alcohol

When the hydroxyl group is attached to a polycyclic benzenoid ring, the compounds are chemically similar to phenols, but they are called naphthols and phenanthrols.



1-Naphthol
(α-Naphthol)



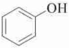
2-Naphthol
(β-Naphthol)

Like alcohols, classification of phenols depend on the number of hydroxyl groups attached to the aromatic ring. For example phenols can be classified as monohydric, dihydric, and trihydric.

5.2.2 IUPAC nomenclature of phenols

The following are the rules of naming phenols:

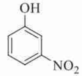
1. Phenol or hydroxybenzene is the parent or base name. It is also called benzenol.



Phenol or hydroxybenzene
(Benzenol)

2. Substituted phenols are generally named as derivatives of the simplest member of the family, which is phenol or hydroxybenzene.

4-chlorophenol

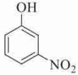


3-nitrophenol

2-bromophenol

3. If phenol contains only one additional substituent, the relative position is indicated by letters *o*-(for 1, 2), *m*-(for 1,3), and *p*-(for 1,4). The letters *o*-, *m*-, and *p*-stands for ortho, meta and para positions, respectively.

4-chlorophenol
(*p*-Chlorophenol)

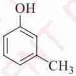


3-nitrophenol
(*m*-Nitrophenol)

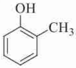
2-bromophenol
(*o*-Bromophenol)

4. Methylphenols are commonly known as *cresols*

4-methylphenol
(*p*-Cresol)

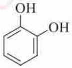


3-methylphenol
(*m*-Cresol)

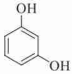


2-methylphenol
(*o*-Cresol)

5. Phenols that consist of two hydroxyl groups (–OH) are also named by using common names as shown in the following structures:



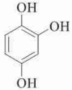
Benzene-1,2-diol
(Catechol)



Benzene-1,3-diol
(Resorcinol)

Benzene-1,4-diol
(Hydroquinone)

6. If more than one hydroxyl groups are attached to the benzene ring, the number of hydroxyl groups is indicated by using the prefixes such as *di*, *tri*, and tetra.



Benzene-1,2,4-triol

7. If more than two substituents are present on benzene ring, numbers are used to indicate the relative positions of the substituents but the carbon bearing the hydroxyl group is assigned number one to the direction which gives the lowest number for the sum of substituents.

2-bromo-6-methyl-4-nitrolphenol

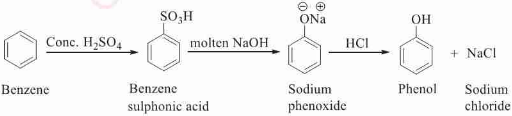
2,4,6-trinitrophenol

5.2.3 Preparation of phenols

Phenols to a large extent are produced in industries because of their reaction requirements. The methods which are used to produce phenols in industries include: sulphonation of benzene, hydrolysis of benzene diazonium salts, hydrolysis of haloarenes (Dow's process), oxidation of cumene (cumene process), and fractional distillation of coal tar.

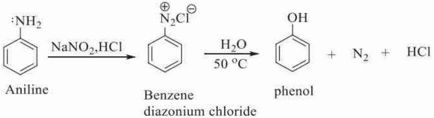
Sulphonation of benzene

The benzene sulphonic acid is obtained from benzene by reacting benzene with concentrated sulphuric acid. Then, the formed benzene sulphonic acid is treated with a strong molten alkali such as NaOH at a temperature range of 297-347 °C to yield sodium phenoxide. The sodium phenoxide on acidification gives phenols.

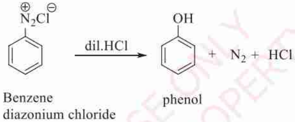


Hydrolysis of benzene diazonium salts

The benzene diazonium salts are formed when aromatic primary amines such as aniline are treated with a mixture of sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl) at a very low temperature of 0-5 °C. Since benzene diazonium salts are very reactive, they can easily undergo hydrolysis when warmed with water at 50 °C to form phenol.

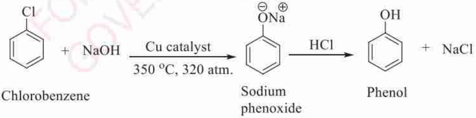


The treatment of benzene diazonium salt with dilute acid also yields phenol.



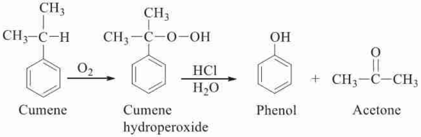
Hydrolysis of haloarenes (Dow's process)

The Dow's process is named after Herbert Henry Dow (1866-1930), an American chemical industrialist who discovered the process of extracting bromine from brine. The same process is applied in the hydrolysis of chlorobenzene in the manufacturing of phenol. When chlorobenzene is treated with 10% NaOH at 350 °C and 320 atmospheric pressure in the presence of copper catalyst it forms sodium phenoxide as an intermediate product. The acidification of sodium phenoxide with hydrochloric acid yields phenol.



Oxidation of Cumene (Cumene process)

The Cumene process involves the industrial process that forms phenol and acetone from benzene and propylene. The Cumene (isopropyl benzene) is an intermediate material which is produced when benzene reacts with propylene through Friedel-Crafts alkylation. The oxidation of Cumene in the presence of oxygen forms Cumene hydroperoxide which produces phenol and acetone when treated with dilute acid.



The Cumene process is the most worldwide used method for the production of phenol. It is the economical process because the starting raw materials, benzene and propylene, are cheaper and yields two most valuable organic compounds (phenol and acetone).

Fractional distillation of coal tar

Coal tar is a product of destructive distillation of coal. Other products of destructive distillation of coal are ammoniacal liquor and coal gas. The coal tar is an immiscible viscous black liquid containing about 10,000 organic compounds of different types. Out of these, about 300 are mostly aromatic hydrocarbons. On fractional distillation, coal tar yields benzene, toluene and xylene as light oil (2.25%); phenol, cresol and naphthalene as middle oil (7.5%); heavy oil (cresote) largely consisting of cresol, naphthalene and naphthols with a total of 16.5%; anthracene oil (12%), and 56% of all content remains as carbon residue. The fractional distillation of coal tar is as shown in Figure 5.4.

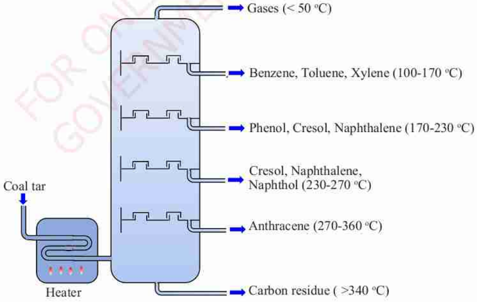


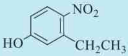
Figure 5.4: Fractional distillation of coal tar

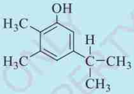
Exercise 5.3

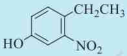
1. (a) What is phenol?
   (b) Explain the different classes of phenols.

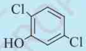
2. Write down the structures of the following derivatives of phenol:
   (a) p-cresol
   (b) Resorcinol
   (c) Hydroquinone
   (d) Benzene-1,2,4-triol

3. Name each of the following compounds by using the IUPAC system:

(a)


(b)


(c)


(d)


4. Draw structures corresponding to the following names:
   (a) 6-chloro-2,3-dimethylphenol
   (b) 3,5-diethylphenol
   (c) 2,4-dinitrophenol
   (d) 4-methylphenol
   (e) 2,4,6-tribromophenol

5. Using reaction equations, explain how phenol can be prepared from aniline.

5.2.4 Physical properties of phenol

The physical properties of phenols are due to the presence of hydroxyl group (–OH), which accounts for the intermolecular forces. Some physical properties of phenols are boiling points, melting points, and solubility in water as summarised in Table 5.2.

Table 5.2: The boiling points, melting points and solubilities of phenols in water

Common name	Systematic name	m.p. °C	b.p. °C	Solubility (g/100 g of water)
Phenol	Benzenol	43	182	9.3
o–Cresol	2–methylbenzenol	31	191	2.5
m–Cresol	3–methtylbenzenol	11	202	2.6
p–Cresol	4–methylbenzenol	35	202	2.3
Pyrocatechol	Benzene –1,2–diol	105	245	30
Resorcinol	Benzene –1,3,–diol	111	280	52
Hydroquinone	Benzene–1,4,–diol	171	286	6.7
n–Hexylresorcinol	4-hexylresorcinol	69	334	0.05
Methyl salicylate	Methyl 1–2–hydroxybenzoate	–9	223	0.7
Vanillin	4–hydroxy–3–methoxybenzoldehyde	81	285	10
Bugenol	4–ally–2–methoxyphenol	–9	255	–
Thymol	5–methyl–2–methoxyphenol	51	233	9.1
Picric acid	2,4,6–trinitrophenol	122	–	1.4
o–Bromophenol	2–bromophenol	5	194	–
p–Hydroxy benzoic acid	4–hydroxybenzoic acid	214	–	8

Boiling points

Generally, phenols have higher boiling points compared to other hydrocarbons of relatively equal molar masses. This is because of the existence of intermolecular hydrogen bonding between the hydroxyl groups of phenol molecules. Like in other organic compounds, the boiling points of phenols increase with an increase in the number of carbon atoms. Phenols have stronger hydrogen bonds than alcohols; therefore, they have higher boiling points compared to alcohols. The strength of intermolecular hydrogen bonding and hence the boiling points, are affected by the position of substituent groups from each other. For example, the boiling points of catechol, resorcinol and hydroquinone are 245 °C, 280 °C, and 286 °C, respectively.

Melting points

In addition to the types of intermolecular forces, melting points are largely contributed by the shapes of molecules on the packed structure. The positions of the substituent groups in phenols, and hence packing of the molecules affect the melting points. Generally, molecules with stronger intermolecular forces and good packing of molecules on each other have higher melting points.

Solubility

Solubility of some phenols in water are shown in Table 5.2. The solubility is largely determined by the types of intermolecular forces. Since water has a strong hydrogen bonding, the solubility of phenols in water is high for the molecules with high strength of hydrogen bonding. However, the aryl group that is attached to the hydroxyl group is hydrophobic in nature. Therefore, as the size of the aryl group increases, the solubility of phenol in water decreases.

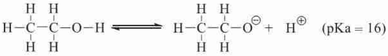
Acidity of alcohols and phenols

When an acid loses a proton, it becomes a conjugate base, and when a base gain a proton it becomes a conjugate acid. The conjugate base of an alcohol is called an alkoxide, and the conjugate acid of an alcohol is called an oxonium ion. Acidity is measured in terms of pKa which is defined as the negative logarithm of Ka (pKa = −log Ka). The higher the pKa the less the acidity, and the lower the pKa means the more the acidity. Usually, weaker acids give a stronger conjugate base and stronger acids give a weaker conjugate base.

Consider the acid-base reaction of alcohol in which ethanol reacts with an amide.

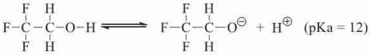
$$\underset{\text{Acid}}{CH_3{-}CH_2{-}OH} + \underset{\text{Base}}{:\overset{\ominus}{N}H_2} \longrightarrow \underset{\substack{\text{Conjugate base}\\ \text{(Alkoxide)}}}{CH_3{-}CH_2{-}O^{\ominus}} + \underset{\text{Conjugate acid}}{H{-}NH_2}$$

Any factor that increases the stability of the conjugate base will increase the acidity of an acid. Stabilisation can be by either bringing the negative charge closer to the positively charged nucleus, or by spreading the negative charge over a larger volume. For example, the pKa of ethanol is 16 and that of 2,2, 2-trifluoroethanol is 12.



$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H \rightleftharpoons H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O^{\ominus} + H^{\oplus}$ (pKa = 16)

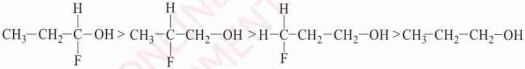
Ethanol　　Conjugate base of ethanol



$F-\underset{F}{\overset{F}{C}}-\underset{H}{\overset{H}{C}}-O-H \rightleftharpoons F-\underset{F}{\overset{F}{C}}-\underset{H}{\overset{H}{C}}-O^{\ominus} + H^{\oplus}$ (pKa = 12)

2,2,2-trifluoroethanol　　Conjugate base of 2,2,2-trifluoroethanol

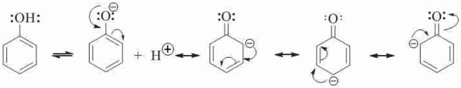
The trifluoroethanol is more acidic than ethanol because its conjugate base is stabilised by inductive effects. That is, the electronegative atom which is fluorine pulls the electron density away from the neighbouring carbon which also pulls the electron away from another carbon, which also does the same from oxygen. The O–H bond is therefore easily deprotonated. The inductive effect of fluorine also depends on its distance from the functional group (OH).



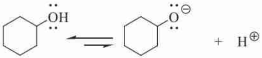
$CH_3-CH_2-\underset{F}{\overset{H}{C}}-OH > CH_3-\underset{F}{\overset{H}{C}}-CH_2-OH > H-\underset{F}{\overset{H}{C}}-CH_2-CH_2-OH > CH_3-CH_2-CH_2-OH$

Most acidic　　Least acidic

The stabilisation of the conjugate base also accounts for the acidity of phenol relative to alcohols. Phenol is more acidic than alcohols because the conjugate base of phenol is stabilised by resonance. That is, the negative charge is delocalised throughout the benzene ring.



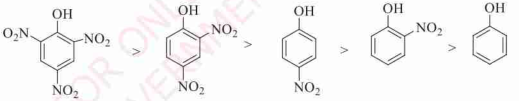
Resonance stabilisation of phenoxide ion (pKa =10) makes phenol to be more acidic than cyclohexanol.



Absence of resonance stabilisation (pka=16) makes cyclohexanol less acidic than phenol

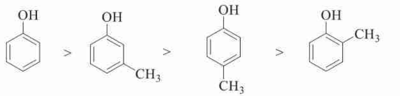
Effect of substituent on acidity of phenol

If the benzene ring of phenol is bonded to an electron withdrawing group, the acidity of phenol increases, while the electron releasing group decreases the acidity of phenol. For example, the presence of nitro group on phenol increases its acidic nature. Therefore, nitrophenol is more acidic than phenol, because of the negative mesomeric effect and a negative inductive effect of the nitro group. The number of nitro groups as well as their positions also affect the acidity of phenol. *Ortho* and *para*-nitro phenols are more acidic than *meta*-nitrophenols. This is because the nitro group at these positions withdraw electrons from the hydroxyl group of phenol by a stronger negative mesomeric effect. On the other hand, the nitro group at *meta* position withdraws the electron by a negative inductive effect (which is weaker), because the *meta* position is not involved in the resonance with the hydroxyl group. The following is a typical order of acidity of nitro phenols.



2,4,6-trinitrophenol 2,4-dinitrophenol 4-nitrophenol 2-nitrophenol Phenol

If a benzene ring of phenol is bonded to an electron releasing group (other than the hydroxyl (–OH) group, the acidity of phenol decreases. For example, methyl phenols are less acidic than phenol because of the positive inductive effects of the methyl groups which increase the electron density on the hydroxyl group, hence low acidity. The larger the number of electrons releasing groups on phenol, the less the acidity. The position of the electron releasing group also affects the acidity of phenols. The acid strength trend of methyl phenols (cresols) is shown in the following order.



Phenol | 3-methylphenol (*m*-cresol) | 4-methylphenol (*p*-cresol) | 2-methylphenol (*o*-cresol)

5.2.5 Chemical reactions of phenols

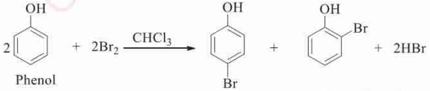
The chemical reactions of phenols can be categorised into three different types: Electrophilic aromatic substitution reactions which involve cleavage of the oxygen-hydrogen bond, reactions which involve the cleavage of the carbon-oxygen bonds and other reactions.

Electrophilic aromatic substitution reactions

Phenols undergo electrophilic aromatic substitution reactions and form *ortho* and *para* substituted products. This is because the hydroxyl group (– OH) is an activating and *ortho-para* directing group. The electrophilic aromatic substitution reactions of phenols are relatively like those of benzene, only that in phenols the reactivity increases and the substituents are directed to specific positions. Some common electrophilic aromatic substitution reactions of phenols are discussed as follows.

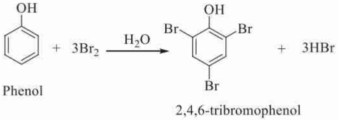
Halogenation

Halogenation of phenols occurs even in the absence of Lewis acid (unlike benzene) because of the highly activating effect of the hydroxyl group. Phenol reacts with bromine in the presence of a solvent of low polarity like chloroform to form monobromophenols.



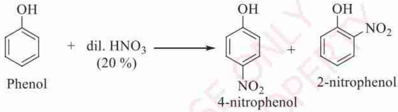
p-Bromophenol (major product) | *o*-Bromophenol (minor product)

With the addition of bromine water, the bromination of phenols forms a white precipitate of 2,4,6-tribromophenol .

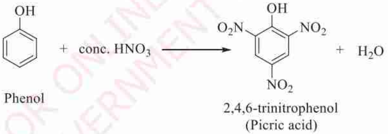


Nitration

Phenol reacts with dilute nitric acid to form a mixture of *ortho* and *para*-nitrophenols. The reaction does not necessarily require the use of a mixture of nitric acid and sulphuric acid because of high reactivity of the hydroxyl group (−OH).

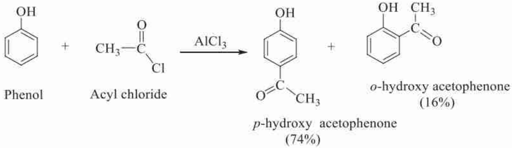


When phenol reacts with concentrated nitric acid, the nitration results in the formation of 2,4,6-trinitrophenol, also called *picric acid*.



Friedel-Crafts acylation

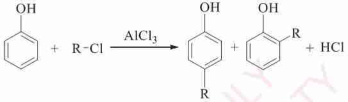
Phenols react with acylchloride in the presence of aluminium trichloride to form a mixture of *para*-hydroxyacetophenone as a major product and *ortho*-hydroxyacetophenone as a minor product.



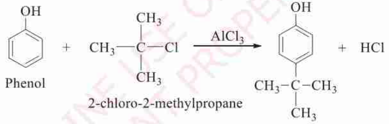
Note that, in the above products, the carbonyl group is the priority group. Therefore, phenol is considered as a substituent group on acetophenone. This type of acylation reaction is known as *C-acylation* in which substitution of the acyl group with hydrogen atom occurs at the benzene ring.

Friedel-Crafts alkylation

Phenol undergoes Friedel-Crafts alkylation using alkyl halide and aluminium trihalide as a catalyst to form a mixture of *ortho* and *para* substituted products.



Example:



Phenol

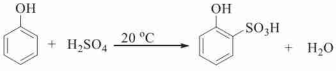
2-chloro-2-methylpropane

4-(tert-butyl)phenol

In the above reaction, the *para* substituted product is favoured due to the steric effect arising at the *ortho* position.

Sulphonation

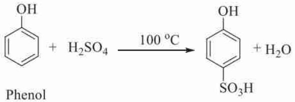
Phenol reacts with sulphuric acid to form an *ortho* or *para* substituted product depending on the temperature at which the reaction takes place. The sulphonation of phenols at 20 °C gives an *ortho* substituted product as the main product.



Phenol

o-Phenolsulphonic acid

When the reaction temperature is raised to 100 °C, the sulphonation of phenol gives a *para*-substituted product as the main product.

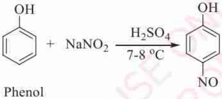


Phenol

p-Phenolsulphonic acid

Nitrosation

Phenol reacts with an acidified solution of sodium nitrite to form nitrosophenol.



Phenol

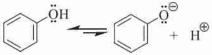
4-nitrosophenol

In this reaction, the first step is the acidification of an aqueous solution of sodium nitrite to form nitrosonium ion ($:N{\equiv}O:^{\oplus}$). The nitrosonium ion which is a weak electrophile then attacks the strongly activated ring of phenol forming nitrosophenol. Since the nitrosonium ion is a very weak electrophile, phenol is among the only few compounds which are attacked by the electrophilic nitrosonium ion ($NO^{\oplus}$) because of its high reactivity.

Reactions which involve cleavage of the oxygen-hydrogen bond (O–H)

Acidic properties

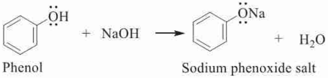
Phenols are stronger acids than alcohols because of the positive mesomerism of the hydroxyl group, which facilitates the release of proton by delocalising the negative charge which is produced on the oxygen atom.



Phenol Phenoxide ion

Reaction with sodium hydroxide

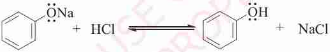
Due to its acidity, phenol reacts with an aqueous solution of a base such as sodium hydroxide to form sodium phenoxide salt and water.



Alcohols cannot react with sodium hydroxide because they are very weak acids.

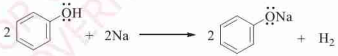
$$R{-}OH + NaOH \leftrightharpoons R{-}\overset{\ominus}{O}\overset{\oplus}{Na} + H_2O$$

The phenol can be recovered from a phenoxide salt by acidifiying using a stronger acid than phenol such as dilute HCl.



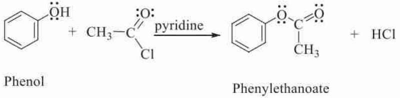
Reactions with reactive metals

Phenols react with reactive metals such as sodium and potassium in the same way that these metals react with aliphatic alcohols, forming phenoxide salts and hydrogen gas.



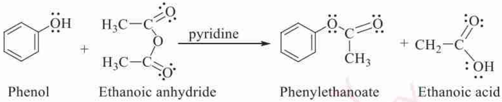
Formation of esters (O-acylation)

The chemical reagents that can introduce acyl groups such as acyl chlorides and carboxylic acid anhydrides, do react with phenols at two different positions which are either at the aromatic ring (C-acylation) or at the hydroxyl oxygen (O-acylation). Friedel-Crafts acylation by C-acylation is a form of electrophilic aromatic substitution which occurs in the presence of aluminium chloride to acylate the benzene ring. The second type of acylation of phenol is *O-acylation* which occurs in the absence of aluminium chloride and involves the cleavage of the oxygen-hydrogen (O–H) bond to form an ester, hence the name esterification.

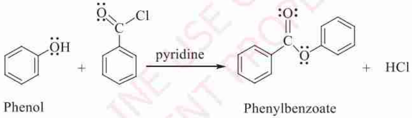


Phenyl ester can also be formed by reacting phenol with acid anhydride

Example:

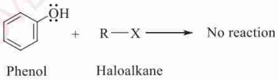


An ester can also be formed by using two phenyl groups without an alkyl group.

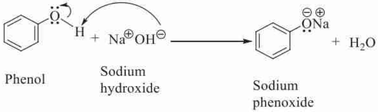


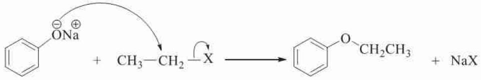
Formation of ethers (Williamson ether synthesis)

Phenol is acidic in nature, it does not react directly with haloalkanes to form ethers.



Initially, phenol reacts with sodium hydroxide to form sodium phenoxide, which then reacts with haloalkane to form ether.



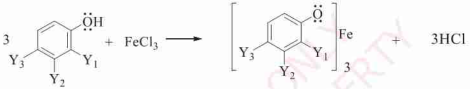


Sodium phenoxide

Ethoxybenzene
(phenoxyethane)

Reaction with ferric chloride ($FeCl_3$)

Phenols react with neutral aqueous solution of ferric chloride ($FeCl_3$) to form bright coloured water-soluble complexes of ferric phenoxide.



Substituted phenol

Neutral
Ferric chloride

Bright coloured ferric phenoxide complex
(blue, green, violet, red-brown)

Note: Y_1, Y_2 and Y_3 represent any substituent group.

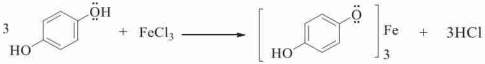
The colour of the complex, and hence the colour of the solution depends on the substituents on phenol. Pure phenol without any other substituent forms a bright purple complex solution with ferric chloride.

Phenol

Ferric chloride
Neutral

Ferric phenoxide
(purple)

4-hydroxyphenol forms a bright green complex solution which then turns brown.



4-hydoxyphenol

Ferric chloride
Neutral

Ferric phenoxide
(bright green)

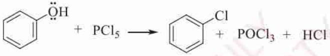
With 2,3-dihydroxyphenol, the reaction gives a brown-red coloured complex. The formation of the complexes with intense colour is used as a chemical test of identifying phenols.

Reactions which involve the cleavage of the carbon-oxygen bond

Phenol reacts with either phosphorus pentachloride, zinc dust or ammonia to form benzene or substituted benzene.

Reaction with phosphorus halide (PX_3 or PX_5)

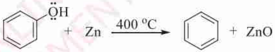
Phenols react with phosphorus halide such as PCl_5 to form chlorobenzene.



However, this reaction is very slow and gives a very low yield.

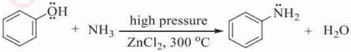
Reaction with zinc dust (reduction)

Phenol reacts with zinc dust at high temperatures to form benzene and zinc oxide. The reaction is used for the preparation of benzene from phenol.



Reaction with ammonia (formation of phenylamine)

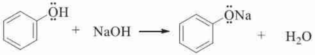
Phenols react with ammonia at 300 °C and high pressure in the presence of $ZnCl_2$ to form phenyl amine (aniline) and water.



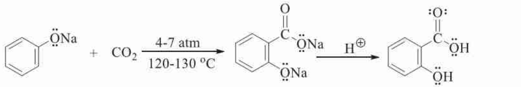
Other reactions

Kolbe's reaction

Kolbe's reaction is the reaction in which 2-hydroxybenzoic acid is formed from phenol. First, phenol reacts with sodium hydroxide to form sodium phenoxide.



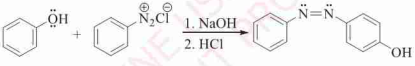
The sodium phenoxide is then heated with carbon dioxide at about 120–130 °C and a pressure of 4-7 atmosphere, followed by acidification to give the 2–hydroxybenzoic acid product.



Sodium phenoxide Sodium salicylate 2-hydroxybenzoic acid (Salicylic acid)

Coupling reaction

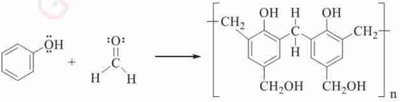
Phenols react with benzene diazonium chloride in a weak alkaline medium to form coloured compounds called *azo dyes*. The reaction occurs at about 0−5 °C.



Phenol Benzene diazonium chloride Azo dyes

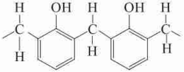
Polymerisation

Phenol reacts with methanal (formaldehyde) in a polymerisation reaction to form a *phenol-formaldehyde resin*, which consists of linear polymer chains and reactive groups that are capable of cross-linking.

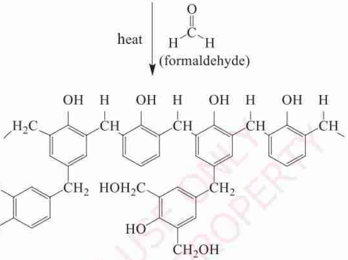


Phenol Formaldehyde Phenol-formaldehyde resin (Bakelite)

Crosslinking of the phenol-formaldehyde resin by heating and adding more methanal forms a hard cross-linked structure.



Phenol-formaldehyde resin (Bakelite)



A hard cross-linked structure

5.2.6 Uses and hazards of phenols

Uses of phenols

Phenol and its derivatives have wide uses in the industries, agriculture as well as in pharmaceutical (medical) and healthy fields.

In the industries, phenol is used as a feedstock chemical (starting material) for making many organic products of great importance. For example, biphenyl, a representative of diphenylmethane group is used in making epoxy resins for paint coatings and mouldings, plastics, and home based electrical appliances. Caprolactam, a cyclic amide of cuproic acid as a derivative of phenol, is used in the manufacture of nylon, polyamide plastics for a wide range of products such as clothes, carpets, fishing nets, and moulded components and packaging. The picric acid (2,4,6-trinitrophenol) is a very reactive chemical which is used in the manufacture of explosives. Also, phenol derivative hydroquinone has been used in photographic field as a component of photographic developer that reduces the exposed silver bromide crystals to black metallic silver. Other industrial uses of phenols and their derivatives include the production of paint remover, surfactants, emulsifiers, detergents, dyes and pigments.

In the pharmaceutical (medical) and healthy fields, phenol has been used as a precursor of many drugs and chemicals including aspirin, paracetamol and propofol (2,6-diisopropylphenol) which is used as an anaesthetic chemical during surgery.

At low concentrations phenol is used as an antiseptic, disinfectant, detergents or soap in house hold cleaners and mouth wash. Phenol has also been used in the treatment of ingrown toe and finger nails, and as an active ingredient in some oral analgesics such as chloraseptic spray used for the temporary treatment of throat inflammation (pharyngitis).

In cosmetology, phenol derivatives are used in the preparation of cosmetics for sunscreens, hair colouring, and skin whitening. In agricultural field, phenol derivatives such as chlorophenols, cresols and others are used in making herbicides, pesticides, and wood preservatives. The less toxic phenol derivatives such as butylated hydroxytoluene (BHT) is used as an antioxidant in foods.

Hazard of phenols

Phenols have sensitasation reaction with repeated exposure to them. They cause severe damage when in contact with eyes and may cause burns on skin. Repeated or prolonged skin exposure to phenol vapour from heated phenol, may cause headache, nausea, dizziness, muscle ache, difficulty swallowing, diarrhea, vomiting, and shock.

Exercise 5.4

1. (a) Explain how the boiling points of phenols vary with the number of carbon atoms and the number of substituents.
   (b) Describe the general trend in the solubility of phenols in water.
2. Explain the following phenomena:
   (a) Phenol has higher boiling point than toluene (methylbenzene).
   (b) Phenol is more soluble in water than toluene.
3. Phenol is a stronger acid than cyclohexanol. Explain.
4. Identify the most acidic phenol from the given pairs of compounds. Give reason(s) for your answer.
   (a) 2,4,6-trimethylphenol or 2,4,6-trinitrophenol

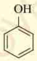
(b) 2,6-dichlorophenol or 3,5-dichlorophenol
(c) 3-nitrophenol or 4-nitrophenol
(d) Phenol or 4-cyanophenol
(e) 2,5-dinitrophenol or 2,6-dinitrophenol

5. (a) Explain why is benzene less reactive than phenol towards chlorine.
(b) Name and draw the structure of the product formed when phenol reacts with bromine.

6. Write a balanced chemical equation for each of the following reactions:
(a) Phenol + sodium hydroxide
(b) Product of part (a) + ethyl bromide
(c) Product of part (a) + acetic anhydride
(d) *o*-Cresol + benzoyl chloride
(e) 2,6-dichlorophenol + bromine

7. Describe the following reactions of phenol:
(a) Williamson synthesis
(b) Ester formation

8. Use the table below to answer the questions that follow: where Y is a substituent group in phenol.

Structure of phenol	**Y**	**pKa**
	–H	9.89
	m –NO_2	8.28
	p –NO_2	7.17
	m –OCH_3	9.65
	p –OCH_3	10.21

(a) Name the weakest acid in the table, and arrange the compounds in the order of increasing acidity.
(b) Which of the acids in the table has the weakest conjugate base? Explain.

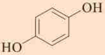
9. Describe the use of phenol and its derivatives in agricultural, industrial, and healthy fields.

Revision exercise 5

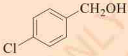
1. Write the structural formula for each of the following compounds:
   (a) 2,4-dichlorohexan-1-ol
   (b) 1-phenylpropan-1-ol
   (c) 3-methyl-3-penten-1-ol
   (d) 2,2,3-trimethylbutan-1-ol
   (e) 2,3-dimethylpentan-1-ol

2. Name each of the following compounds:

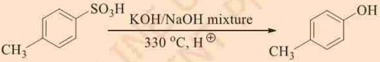
(a)



(b)



3. Write a stepwise mechanism for the conversion of *p*-toluenesulphonic acid to *p*-cresol under the conditions shown in the given equation.



p-Toluenesulphonic acid *p*-Cresol (63-72%

4. Write equations showing all the steps which are needed to convert but-1-ene to each of the following compounds:
   (a) $CH_3CH_2CH(OH)CH_3$
   (b) $CH_3CH_2CH_2CH_2OH$
   (c) $CH_3CH=CHCH_3$

5. Using chemical equations show the necessary catalysts and conditions for the preparation of each of the following:
   (a) Ethyl alcohol from ethylene.
   (b) Benzyl alcohol from toluene.
   (c) *iso*-Propyl alcohol from *iso*-Propyl iodide.

6. Explain the following observations:

   (a) The boiling points of ethanol is higher than that of methoxymethane.

   (b) Phenol is more acidic than ethanol.

   (c) *o*- and *p*-nitrophenols are more acidic than phenol.

7. Give equations to show the steps which are necessary in each of the following conversions:

   (a) *n*-propyl alcohol to isopropyl bromide

   (b) Butan-1-ol to butan-2-ol

8. Explain the observations that would be seen if aqueous phenol was added to potassium. Write an equation for this reaction.

9. Explain the importance of ethanol in daily life.

10. The following alcohols have been prepared by the reaction of Grignard reagent with ethylene oxide. Identify the appropriate Grignard reagent in each case and show the reaction mechanism:

    (a) $CH_3CH_2CH_2CH_2CH_2OH$

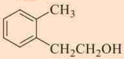
    (b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$

11. Give chemical tests which will distinguish compounds in each of the following pairs:

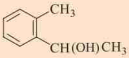
    (a) Phenol from Benzyl alcohol

    (b) Butan-2-ol from 2-methylpropan-2-ol.

    (c)



from



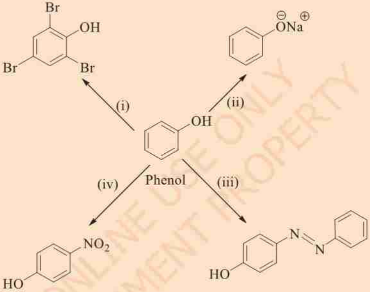
12. Write the mechanism of each of the following reactions:

    (a) Acid catalysed dehydration of an alcohol forming an alkene.

    (b) Acid catalysed hydration of an alkene forming an alcohol.

13. How is the structure of phenol related to its:
    (a) Acidity?
    (b) Higher reactivity as compared to toluene?
    (c) Solubility in water?

14. The diagram below shows some reactions of phenol. In the diagram, identify the reagents that could be used to carry out reactions, (i) to (iv) and name the compounds formed.



Chapter Six

Carbonyl compounds

Introduction

Carbonyl compounds are organic compounds which contain the carbonyl group (C=O) as their functional group. These compounds are categorised into two classes namely aldehydes and ketones. Carbonyl compounds are widely used as preservative agents and solvents in laboratories as well as industries. Also, they are used as starting materials in the manufacturing of alcohols, dyes, pesticides, and perfumes. This chapter covers the structures, nomenclature, preparation, properties, uses and hazards of carbonyl compounds.

6.1 Structures and nomenclature of carbonyl compounds

In this section, you will learn about the structures and nomenclature of carbonyl compounds.

6.1.1 Structure of carbonyl compounds

The carbon atom of the carbonyl group in carbonyl compounds consists of sp^2 hybridised orbitals lying on the same plane. Oxygen of the C=O is also sp^2 hybridised and has three sp^2 orbitals. Therefore, one sp^2 orbital of carbon overlaps with an sp^2 orbital of oxygen atom to form a sigma (σ) bond. The remaining two sp^2 orbitals of the carbon atom overlap with s or sp^2 or sp^3 of hydrogen, carbon or other elements. The p orbital of carbon overlap with unhybridised p orbital of oxygen to form a π-bond between carbon and carbonyl oxygen as shown in Figure 6.1

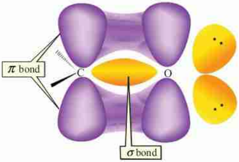
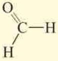
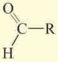
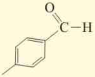
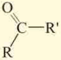
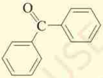


Figure 6.1 Structure of carbonyl group

It can therefore be deduced that, in both aldehydes and ketones the three atoms bonded to the carbonyl carbon atom give rise to a trigonal planar arrangement. The condensed structural formula of aldehydes and ketones are given in Table 6.1.

Table 6.1 Structural formula of aldehyde and ketones

Structure	Class
  	Aldehydes
 	Ketones

6.1.2 Nomenclature of carbonyl compounds

Carbonyl compounds are numerous and therefore, when dealing with specific compounds it is necessary to know its specific name for convenient communication. Thus, systems of naming carbonyl compounds were developed and these are the common system and the IUPAC system.

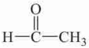
Naming of aldehydes using the common system

According to this system, aldehydes are original compounds from which the corresponding organic acids are derived. Therefore, they are named after the acids which they produce on oxidation. The aldehyde which produces formic acid is called formaldehyde. Similarly, the aldehyde which produces acetic acid is called acetaldehyde. Thus, the suffix *-oic* plus the word acid of the acid name is replaced by suffix - *aldehyde*.

Examples:

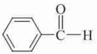
$$H-\overset{\overset{O}{\|}}{C}-H$$

Formaldehyde

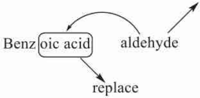


$$H-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetaldehyde

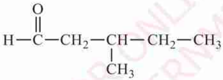


Benzaldehyde



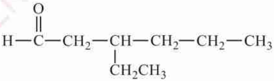
Naming of aldehyde using the IUPAC system

The rules which govern the IUPAC system of nomenclature are also used in the naming of aldehydes. The naming starts by identifying the longest chain of carbon atoms containing the carbonyl group. The number of carbon atoms in this chain is counted to obtain the name of the corresponding hydrocarbon. For example, if there are five carbon atoms, it is a derivative of pentane. The ending *-e* of the hydrocarbon is changed into *-al*. If there are other substituent groups in the chain, they are indicated by suitable numbers. The position of the carbonyl carbon should not be designated because it is always at the terminal of the parent hydrocarbon and therefore assigned position number one.



$$H-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$$

3-methylpentanal

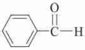


$$H-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

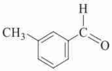
3-ethylhexanal

If the aldehyde group is attached to a ring, the aldehyde is named by adding the word *carbaldehyde* to the name of the cyclic compound.

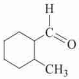
Examples:



Benzene
carbaldehyde



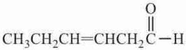
3-methylbenzaldehyde
(3-methylbenzenecarbaldehyde)



2-methylcyclohexanecarbaldehyde

If the compound has the functional group of alkene and aldehyde, the suffix *–e* of the alkene name is replaced with the suffix *–al.*

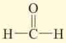
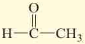
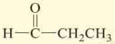
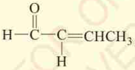
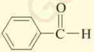
Example:



$$\mathrm{CH_3CH_2CH{=}CHCH_2\overset{\overset{O}{\Vert}}{C}-H}$$

3-hexenal

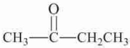
Table 6.2 Common and IUPAC names of some aldehydes

Formula	Common name	IUPAC name
 $\mathrm{H-\overset{\overset{O}{\Vert}}{C}-H}$	Formaldehyde	Methanal
 $\mathrm{H-\overset{\overset{O}{\Vert}}{C}-CH_3}$	Acetaldehyde	Ethanal
 $\mathrm{H-\overset{\overset{O}{\Vert}}{C}-CH_2CH_3}$	Propanaldehyde	Propanal
 $\mathrm{H-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{C}{=}CHCH_3}$	Crotonaldehyde	2-butenal
	Benzaldehyde	Benzene carbaldehyde

Naming of ketones using the common system

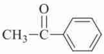
To arrive at the name of the ketone using a common system, the two aryl or alkyl groups constituting the compound are written first in the alphabetical order followed by the word ketone.

Examples:



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

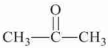
Ethylmethyl ketone



Methylphenyl ketone

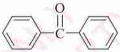
If the aryl or alkyl groups which are attached to the carbonyl group are similar, the names are written beginning with prefix *di-*.

Examples:



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Dimethyl ketone

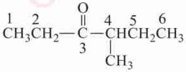


Diphenyl ketone

Naming of ketones using the IUPAC system

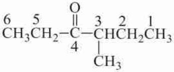
To obtain the name of the ketone, the longest carbon chain containing the carbonyl group is identified first followed by counting the total number of carbon atoms it contains. The ketone is named as a derivative of the corresponding hydrocarbon, by replacing the suffix *-e* of the hydrocarbon by the new suffix *–one.* If any substituent group is attached to the selected chain, it is indicated by a suitable number. The carbonyl carbon of the ketone must be given the lowest possible number. This number appears in the name before the suffix *–one.*

Examples:



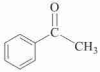
$$\overset{1}{CH_3}\overset{2}{CH_2}-\underset{3}{\overset{O}{\overset{\|}{C}}}-\underset{\underset{CH_3}{|}}{\overset{4}{CH}}\overset{5}{CH_2}\overset{6}{CH_3}$$

4-methylhexan-3-one
(correct naming)



$$\overset{6}{CH_3}\overset{5}{CH_2}-\underset{4}{\overset{O}{\overset{\|}{C}}}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}\overset{2}{CH_2}\overset{1}{CH_3}$$

3-methylhexan-4-one
(Incorrect naming)

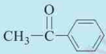


Phenylethanone
(Acetophenone)

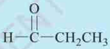
The first two members which do not exhibit isomerism are named simply as derivatives of their corresponding alkanes, namely propanone and butanone.

Exercise 6.1

1. Give the structural formula of the following compounds:
   (a) 4-ethylbenzene carbaldehyde
   (b) 3-ethylpentan-2-one
   (c) 3-methylbutan-2-one
2. From the given condensed structural formula of carbonyl compounds (a) to (e), identify the class to which each compound belongs and give reasons for your classification.

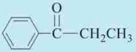


(a)



$H-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

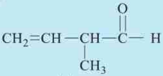
(b)



(c)

$H-\overset{O}{\overset{\|}{C}}-H$

(d)



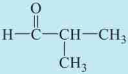
$CH_2=CH-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$

(e)

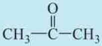
3. (a) Give the IUPAC names of the following compounds:

(i) 

$H-\overset{O}{\overset{\|}{C}}-H$

(ii) 

$H-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

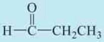
(iii) 

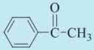
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

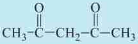
(iv) 

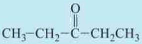
$H-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$

(b) Give the common names of the following compounds:

(i) 
$H-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

(ii) 

(iii) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(iv) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

4. (a) Draw structural formula of each of the following compounds.

(i) Pentan-2,4-dione

(ii) Propan-1,3-dial

(iii) Phenylpropanone

(iv) 3-methylbutanal

(b) Use the following common names to draw structures of the given compounds:

(i) Methylphenylketone

(ii) Diphenylketone

(iii) Ethylmethylketone

(iv) Benzaldehyde

6.2 Preparation of carbonyl compounds

Aldehydes and ketones can be prepared by using a variety of methods. Although the methods of preparation can be the same, the starting materials and sometimes the reaction conditions can be different. In this section you will learn about the laboratory preparation methods of aldehydes and ketones.

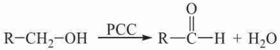
6.2.1 Laboratory preparation of aldehydes and ketones

Oxidation of alcohols

Alcohols can be oxidised to carbonyl compounds by using two possible alternatives which are oxidation by using oxidising agents and catalytic dehydration of alcohols. The detailed discussion is given in the following section.

Oxidation of alcohols by using oxidising agents

When primary alcohols react with weak oxidants such as pyridinium chlorochromate (PCC), aldehydes are formed.

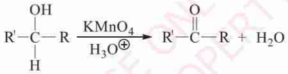


$$R-CH_2-OH \xrightarrow{PCC} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Example:

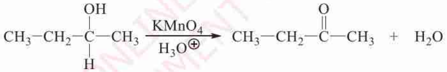
$$CH_3CH_2-CH_2-OH \xrightarrow{PCC} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

When secondary alcohols are treated with acidified potassium permanganate or potassium dichromate solutions, ketones are formed.



$$R'-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R \xrightarrow[H_3O^{\oplus}]{KMnO_4} R'-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$

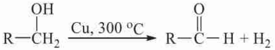
Example:



$$CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow[H_3O^{\oplus}]{KMnO_4} CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

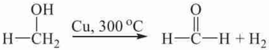
Catalytic dehydrogenation of alcohols

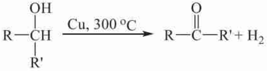
Catalytic dehydrogenation of alcohol is the oxidation reaction in which hydrogen is removed (lost) from an alcohol in the presence of a catalyst. In this reaction, alcohol vapour is passed over a heated copper metal as a catalyst. The primary alcohols are converted to aldehydes, whereas secondary alcohols are converted to ketones as described by using the following chemical reactions.

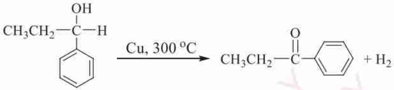


$$R-\overset{\overset{\displaystyle OH}{|}}{CH_2} \xrightarrow{Cu,\ 300\ ^{o}C} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2$$

Examples:

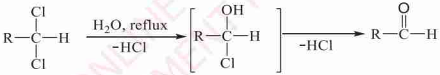




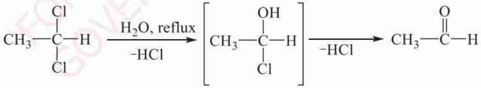


Hydrolysis of *n*, *n*-dihaloalkanes

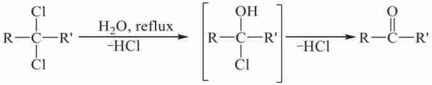
The hydrolysis of dihaloalkanes to form aldehydes and ketones depends on the value of n. If hydrolysis involves dihaloalkane with n = 1 (1,1-dihaloalkane), an aldehyde is formed.



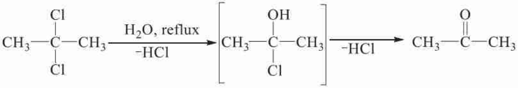
Example:



When hydrolysis involves dihaloalkanes in which n is not equal to 1, the product is always a ketone.



Example:



$$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3 \xrightarrow[-HCl]{H_2O,\ reflux} \left[CH_3-\overset{OH}{\underset{Cl}{C}}-CH_3\right] \xrightarrow{-HCl} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Reactions of Grignard reagents

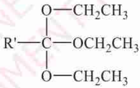
Haloalkanes react with a suspensions of magnesium turnings in dry ether to yield cloudy solutions of alkyl magnesium halides which are commonly known as Grignard reagents (RMgX).

$$R-X + Mg \xrightarrow[reflux]{dry\ ether,\ warm} RMgX$$

The Grignard reagents can be used to form aldehydes and ketones in two different ways.

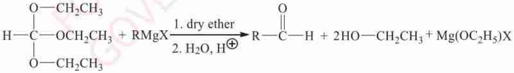
With triethoxyalkanes

Triethoxyalkanes are ethers produced by the reaction between a 1,1,1-triol and iodoethane. They have the following general formula:



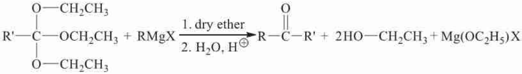
$$R'-\overset{O-CH_2CH_3}{\underset{O-CH_2CH_3}{C}}-OCH_2CH_3$$

If triethoxymethane is used, then the carbonyl compound formed is an aldehyde.



$$H-\overset{O-CH_2CH_3}{\underset{O-CH_2CH_3}{C}}-OCH_2CH_3 + RMgX \xrightarrow[2.\ H_2O,\ H^{\oplus}]{1.\ dry\ ether} R-\overset{O}{\overset{\|}{C}}-H + 2HO-CH_2CH_3 + Mg(OC_2H_5)X$$

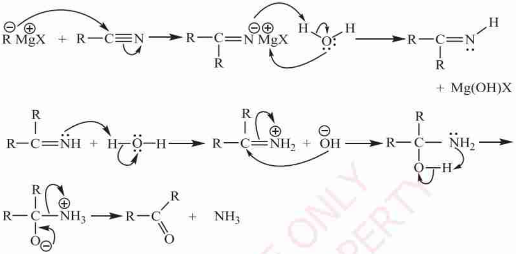
If ethane-1,1,1-triol or any other 1,1,1-triols are used to form a higher triethoxyalkane, then the resulting carbonyl compound is a ketone.



$$R'-\overset{O-CH_2CH_3}{\underset{O-CH_2CH_3}{C}}-OCH_2CH_3 + RMgX \xrightarrow[2.\ H_2O,\ H^{\oplus}]{1.\ dry\ ether} R-\overset{O}{\overset{\|}{C}}-R' + 2HO-CH_2CH_3 + Mg(OC_2H_5)X$$

With nitriles (Stephen's reduction)

Propanenitrile and higher nitriles react with Grignard reagents to yield carbonyl compounds which are ketones as shown in the following reaction mechanism:

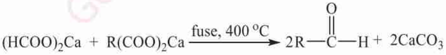


Decarboxylation and decomposition

Decarboxylation reaction is the reaction which removes carbon atoms from the organic compound. Therefore, the intended product of the reaction has less number of carbon atoms than the reactant. This reaction can be achieved by using two different ways which are decarboxylation of calcium salts and that of carboxylic acid.

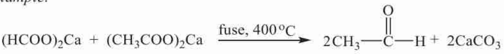
Decarboxylation of calcium salts

When a calcium salt of methanoic acid is fused with another calcium salt of carboxylic acid in a distillation flask, the obtained vapour is condensed to get a liquid aldehyde. The reaction can be expressed by the following equation:



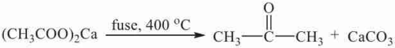
$$(HCOO)_2Ca + R(COO)_2Ca \xrightarrow{\text{fuse, } 400\,^{\circ}C} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2CaCO_3$$

Example:



$$(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{\text{fuse, } 400\,^{\circ}C} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2CaCO_3$$

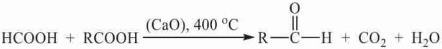
Where only one calcium salt of any other carboxylic acid, which is not methanoic acid is used, a ketone is formed. The following reaction equation illustrates this type of decarboxylation reaction.



$$(CH_3COO)_2Ca \xrightarrow{\text{fuse, 400 °C}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CaCO_3$$

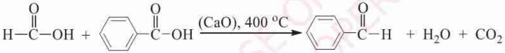
Catalytic decomposition of carboxylic acids

When a mixture of methanoic acid and another carboxylic acid is heated and the vapour is allowed to pass over heated MnO_2, CaO or ThO_2 at higher temperature, an aldehyde is produced.



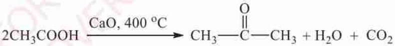
$$HCOOH + RCOOH \xrightarrow{\text{(CaO), 400 °C}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + CO_2 + H_2O$$

When formic acid and benzoic acid are heated and the vapour is passed over heated CaO at about 400 °C, the following reaction equation takes place.

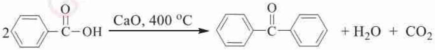


When another carboxylic acid (not formic acid) is used, a ketone is formed. The following reaction equation represents the formation of ketone by heating a carboxylic acid followed by passing the resulting vapour over heated CaO.

$$2RCOOH \xrightarrow{\text{CaO, 400 °C}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + H_2O + CO_2$$

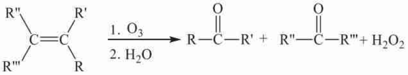


$$2CH_3COOH \xrightarrow{\text{CaO, 400 °C}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + H_2O + CO_2$$



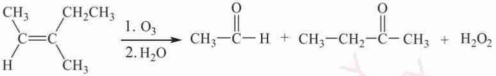
Ozonolysis of alkenes

When alkenes are treated with ozone followed by hydrolysis, they produce aldehyde, ketones or both depending on the substituent groups (R', R", R"') in the alkene used. The reaction forms explosive ozonide thus it is carried out below 20 °C in non aquous solvent.



If R''' = H, the products are an aldehyde, a ketone and H_2O_2. The aldehyde formed is oxidised by H_2O_2 to form a carboxylic acid.

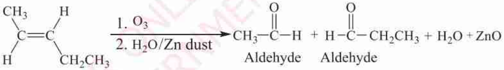
Example:



$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

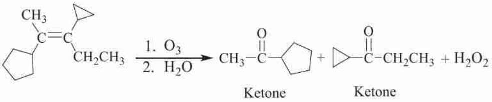
If R' = H and R''' = H, in the presence of zinc dust, the products of ozonolysis are aldehydes.

Example:



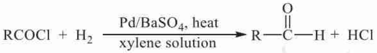
If R, R', R'' and R''' are hydrocarbon groups then the products of ozonolysis are ketones.

Example:

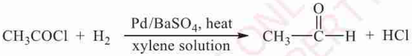


Hydrogenation of acyl chlorides

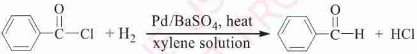
This reaction is also known as *Rosenmund-reaction* and leads to the formation of aldehydes. Under this reaction, hydrogen gas is passed through a hot solution of acyl chloride (RCOCl where R is a hydrocarbon group such as methyl (CH_3–)) which occurs in xylene as a solvent and poisoned palladium as a catalyst. The catalytic activity of palladium is weakened by the addition of barium sulphate to prevent further reduction of aldehyde into alcohol.



$$RCOCl + H_2 \xrightarrow[\text{xylene solution}]{Pd/BaSO_4,\ \text{heat}} R{-}\overset{\overset{\large O}{\|}}{C}{-}H + HCl$$

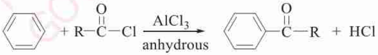


$$CH_3COCl + H_2 \xrightarrow[\text{xylene solution}]{Pd/BaSO_4,\ \text{heat}} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}H + HCl$$

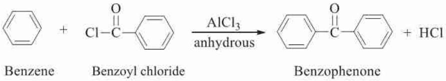


Friedel-Craft acylation

Under this reaction, if an aromatic hydrocarbon is treated with compounds containing acyl (–COCl) group in the presence of anhydrous $AlCl_3$ it yields an aromatic ketone.

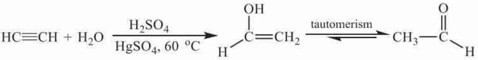


Example:



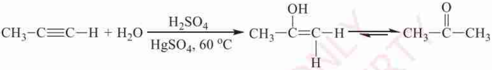
Hydration of alkynes

Alkynes containing three or more carbon atoms produce ketones upon hydration. Ethyne produces an aldehyde. This is done by allowing the alkyne to pass through a solution of dilute H_2SO_4 containing $HgSO_4$. The reactions can be represented by the following chemical equations.



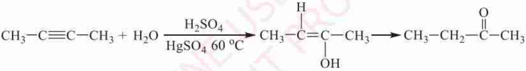
$$HC\equiv CH + H_2O \xrightarrow[HgSO_4,\ 60\ ^{o}C]{H_2SO_4} H\!-\!\overset{OH}{\overset{|}{C}}\!=\!CH_2 \xrightleftharpoons{\text{tautomerism}} CH_3\!-\!\overset{O}{\overset{\|}{C}}\!-\!H$$

Unstable
(Enol)



$$CH_3\!-\!C\equiv C\!-\!H + H_2O \xrightarrow[HgSO_4,\ 60\ ^{o}C]{H_2SO_4} CH_3\!-\!\overset{OH}{\overset{|}{C}}\!=\!\underset{H}{\underset{|}{C}}\!-\!H \rightleftharpoons CH_3\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_3$$

Unstable
(Enol)

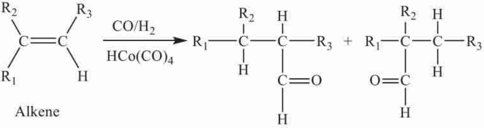


$$CH_3\!-\!C\equiv C\!-\!CH_3 + H_2O \xrightarrow[HgSO_4\ 60\ ^{o}C]{H_2SO_4} CH_3\!-\!\overset{H}{\overset{|}{C}}\!=\!\underset{OH}{\underset{|}{C}}\!-\!CH_3 \longrightarrow CH_3\!-\!CH_2\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_3$$

Unstable
(Enol)

Oxo-process

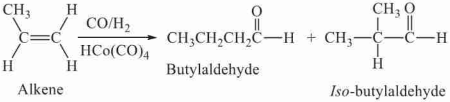
The oxo-process reaction is also known as hydroformylation. The *oxo-process* is the chemical reaction of carbon monoxide and hydrogen (water gas) with alkenes at high temperature and pressure in the presence of cobalt tetracarbonylhydride ($HCo(CO)_4$) as the catalyst to form isomeric aldehydes. The oxo-process products range from C_3 to C_{15} and are used as important intermediates to organic compounds such as alcohols, acids, and esters through reduction, oxidation or condensation reactions.



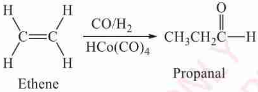
Alkene

Isomeric aldehydes

The hydrofomylation of propene yields two isomeric aldehydes which are butylaldehyde and isobutylaldelyde.



The hydroformylation of ethene yields only propanal.



Exercise 6.2

1. (a) Write the equations (including reagents and conditions) for the following conversions:

   (i) Ethanol $\longrightarrow$ Ethanal

   (ii) 1,1-dichloropropane $\longrightarrow$ Propanal

   (b) Complete the following chemical reactions

   (i) $CH_2{=}CH_2 + O_3 + H_2O \xrightarrow{Zn}$

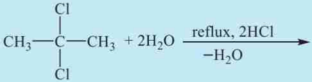
   (ii) $(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{CaO,\ 400\ ^{o}C}$

2. (a) In the following conversions, give the necessary reagents, conditions, and chemical equations.

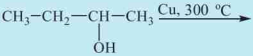
   (i) Suitable Grignard reagent + propanonitrile $\longrightarrow$ Butanone

   (ii) Suitable acid chloride + benzene $\longrightarrow$ Phenylethanone

(b) Complete the following chemical reaction equations:

(i) 

$$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3 + 2H_2O \xrightarrow[-H_2O]{\text{reflux, 2HCl}}$$

(ii) 

$$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{\text{Cu, } 300\ ^{\circ}\text{C}}$$

3. Account for the observation that the decarboxylation reaction involving formic acid and any other carboxylic acid yields a mixture of an aldehyde and a ketone.

4. When hydrogen gas is bubbled through a solution of acetyl chloride in xylene in the presence of deactivated palladium as a catalyst an aldehyde **X** is formed.

   (a) Identify the aldehyde **X** with the help of chemical equation(s)

   (b) Explain why the product of the reaction changes when the catalyst is not deactivated

5. Draw the structural formula of alkenes that yield the following products on ozonolysis:

   (a) Methanal and pentan-2-one

   (b) Ethanal and propanone

6.3 Properties of carbonyl compounds

The carbonyl group largely determines the properties of carbonyl compounds (aldehydes and ketones). Due to its high electronegativity, the oxygen atom in the carbonyl group withdraws bond electrons to itself, thus making the carbonyl bond polar. The polarity of the bond has a significant influence on the physical and chemical properties of carbonyl compounds. Although the two classes of carbonyl compounds consist of carbonyl group as the functional group, they show marked differences in their properties. In this section you will learn about the physical and chemical properties of carbonyl compounds.

6.3.1 Physical properties of aldehydes and ketones

The physical properties that will be discussed are physical state, odour, melting and boiling points as well as solubility.

Physical state

The first and second members of aldehydes which are methanal and ethanal are gases at room temperature. Higher members of aldehydes and ketones (up to C_{11}) are liquids at room temperature while the rest members are solids.

Odour

Lower aldehydes (up to C_7) have pungent smell while aldehydes with C_8 to C_{14} and ketones have pleasant odour and thus are used in perfumery formulations.

Melting and boiling points

Aldehydes and ketones have high melting points and boiling points in comparison to their corresponding alkanes due to the intermolecular forces caused by the polarity of the carbonyl group. However, they have lower boiling point than alcohols and carboxylic acids due to absence of acidic hydrogen atom that is required for hydrogen bonding.

Solubility

Lower aliphatic carbonyl compounds (less than C_4) are miscible with water. The solubility of these compounds is attributed to the formation of strong hydrogen bonds with water. However, as the size of the alkyl group increases, the solubility of higher carbonyls is lowered due to hydrophobic nature of the alkyl group.

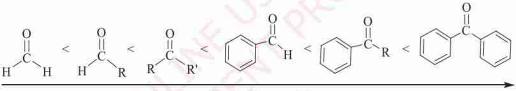
6.3.2 Chemical properties of aldehydes and ketones

The carbonyl group of aldehydes and ketones are polar and possess π-electrons. Due to the strong polarised carbonyl bond and the presence of reactive π-electrons, aldehydes and ketones undergo a large number of reactions. These reactions can be grouped into three types which are nucleophilic addition, reaction of the alkyl group adjacent to the carbonyl carbon atom, and redox reactions.

Nucleophilic addition reactions of carbonyl compounds

Due to the polarity of the carbonyl group, carbonyl compounds are susceptible to nucleophilic addition. The partial positive charge at the end of carbon-oxygen bond is attacked by a nucleophile while the partial negative charge at the end of carbon-oxygen bond attack an electrophile. A nucleophilic addition is the reaction in which the addition of molecules to the carbonyl compound takes place with the initiation of the negative part of the adding molecule. For example, the negative part of the adding molecule $CN^{\ominus}$ which is obtained from the mixture of dil. H_2SO_4 and KCN, adds first to the positive carbon of the carbonyl group, followed by the attachment of the positive part of the adding molecule to the negative oxygen. Note that, cyanides are very poisonous.

The ease of the nucleophilic attack depends on the structure of the groups attached to the carbonyl carbon. The stronger and the more numerous electron releasing groups that are attached to the carbonyl carbon are, the less electropositive it becomes and hence the less susceptible it becomes to nucleophilic attack. The ease of nucleophilic attack of carbonyl compounds, therefore decrease in the order:



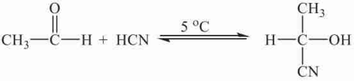
decrease in reactivity

Alkyl groups release electrons by a positive inductive effect (+I) while aryl groups release electrons by a positive mesomeric effect (+M). The following are nucleophilic addition reactions exhibited by carbonyl compounds.

Reaction with hydrogen cyanide

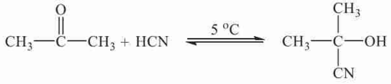
When a mixture of aldehyde or ketone and hydrogen cyanide (formed in situ by the action of dilute H_2SO_4 on KCN) is allowed to react at about 5 °C, 2-hydroxyalkanonitrile is formed.

Examples:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \underset{}{\overset{5\ ^{\circ}C}{\rightleftharpoons}} H-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

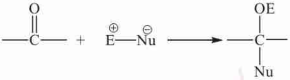
2-hydroxypropanonitrile



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCN \overset{5\ ^{o}C}{\rightleftharpoons} CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

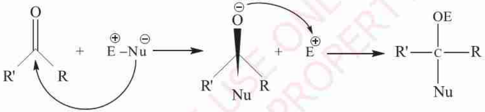
2-hydroxy-2-methylpropanonitrile

In general, the nucleophilic addition reaction of carbonyl compounds can be represented as:



$$-\overset{\overset{\displaystyle O}{\|}}{C}- + \overset{\oplus}{E}-\overset{\ominus}{Nu} \longrightarrow -\underset{\underset{\displaystyle Nu}{|}}{\overset{\overset{\displaystyle OE}{|}}{C}}-$$

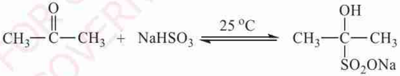
Mechanism



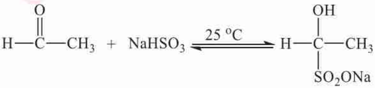
Reaction with sodium hydrogen sulphite

Most aldehydes and methyl ketones, when shaken with excess 40% aqueous sodium hydrogen sulphite solution at 25 °C, carbonyl hydrogen sulphites are formed.

Examples:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + NaHSO_3 \overset{25\ ^{o}C}{\rightleftharpoons} CH_3-\underset{\underset{\displaystyle SO_2ONa}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

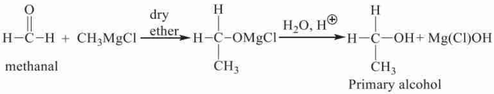


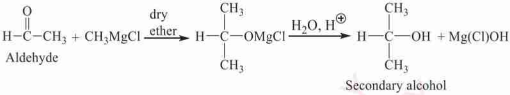
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + NaHSO_3 \overset{25\ ^{o}C}{\rightleftharpoons} H-\underset{\underset{\displaystyle SO_2ONa}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

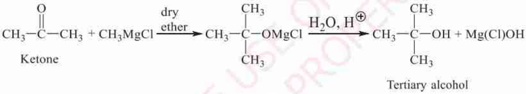
Reaction with Grignard reagent

Carbonyl compound react with Grignard reagents to form alcohols. This can be used to prepare all three classes of alcohols. If the carbonyl compound is methanal, then a primary alcohol will be formed. Other aldehydes react with Grignard reagent to give secondary alcohols while ketones give tertiary alcohols.

Examples:

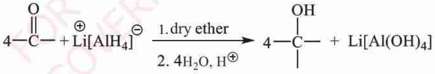




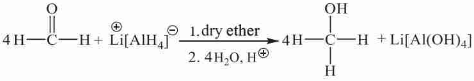


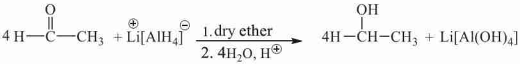
Reaction with $LiAlH_4$ or $NaBH_4$

When aldehyde and ketones are treated with $LiAlH_4$ or $NaBH_4$ in dry ether, followed by acidic hydrolysis, an alcohol is formed.

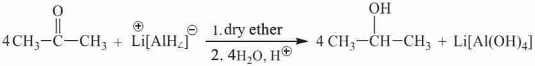


Examples:





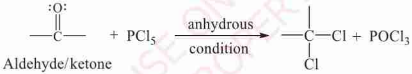
$$4\,H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + \overset{\oplus}{Li}[AlH_4]^{\ominus} \xrightarrow[2.\ 4H_2O,\ H^{\oplus}]{1.\ \text{dry ether}} 4H-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 + Li[Al(OH)_4]$$



$$4\,CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + \overset{\oplus}{Li}[AlH_4]^{\ominus} \xrightarrow[2.\ 4H_2O,\ H^{\oplus}]{1.\ \text{dry ether}} 4\,CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 + Li[Al(OH)_4]$$

Reaction with PCl_5

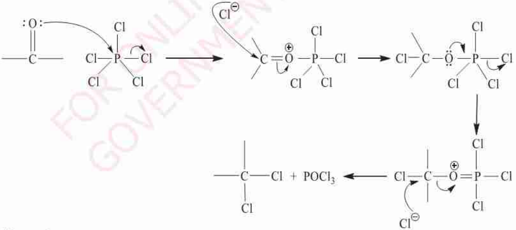
Although this is not a simple nucleophilic addition reaction, PCl_5 acts as a nucleophile by replacing the carbonyl oxygen with two chlorine atoms. This reaction takes place under anhydrous conditions. The reaction can be represented by the following general chemical equations:



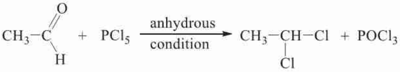
$$\overset{\overset{:O:}{\|}}{-C-} + PCl_5 \xrightarrow[\text{condition}]{\text{anhydrous}} -\underset{\underset{Cl}{|}}{\overset{|}{C}}-Cl + POCl_3$$

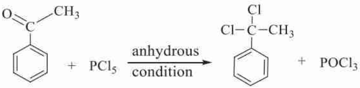
Aldehyde/ketone

Mechanism



Examples:

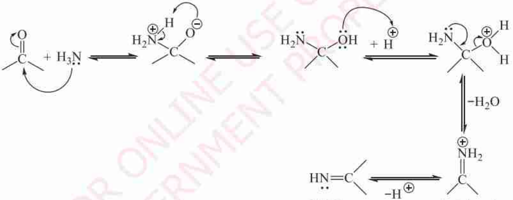




This reaction can be used to distinguish carbonyl compounds from alcohols since HCl gas is not evolved, where similar reactions in alcohols, HCl gas is evolved. Note that, methanal does not react this way.

Condensation reaction

Under this reaction, nucleophilic addition is followed by an elimination reaction. Derivatives of ammonia which contain the nucleophile (–NH$_2$) group can add to the carbonyl group. Ammonia is an example of a primary amine which reacts with an aldehyde or a ketone at pH of 4 or 5 to form an imine, which is also known as a *Schiff''s base*. The reaction mechanism is shown in the following equation:



Imine

Iminium ion

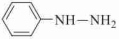
Hydroxylamine, hydrazine, phenylhydrazine, 2,4-dinitrophenylhydrazine and primary amines which are examples of compounds containing nucleophilic –NH$_2$ group and their structures are shown as follows.

H_2N-OH

Hydroxylamine

H_2N-NH_2

Hydrazine

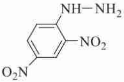


Phenylhydrazine

$R-NH_2$

Alkylamine

Phenylmethanamine



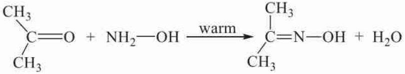
2,4-dinitrophenylhydrazine

Thus, these compounds can be used in the condensation reaction with carbonyl compounds as illustrated by the reaction equations.

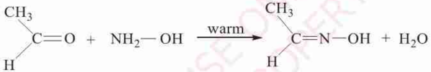
Condensation with hydroxylamine

When warmed with hydroxylamine, carbonyl compounds form oximes.

Examples:



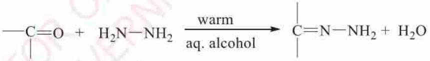
Propan-2-one   Propan-2-one oxime



Acetaldehyde   Acetaldehyde oxime

Condensation with hydrazine

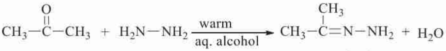
Aldehyde and ketone react with hydrazine to give hydrazones.



$$-\overset{|}{C}=O + H_2N-NH_2 \xrightarrow[\text{aq. alcohol}]{\text{warm}} \overset{|}{\underset{|}{C}}=N-NH_2 + H_2O$$

Carbonyl   Hydrazine   Hydrazone

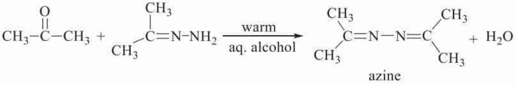
Example:



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2N-NH_2 \xrightarrow[\text{aq. alcohol}]{\text{warm}} CH_3-\overset{CH_3}{\overset{|}{C}}=N-NH_2 + H_2O$$

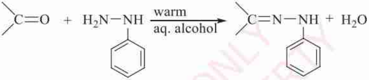
Propanone hydrazone

If the carbonyl compound is in excess, the hydrazone will attack a second carbonyl molecule to form azine as shown in the following equation.

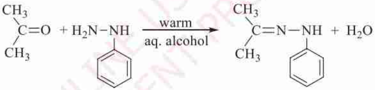


Condensation with phenylhydrazine

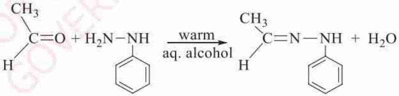
When warmed with phenylhydrazine in aqueous alcohol carbonyl compounds react to yield phenylhydrazone. This reaction can be generally presented as:



Examples:



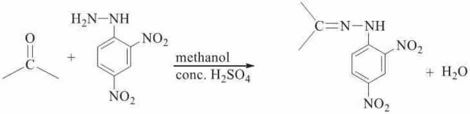
Propanone phenylhydrazone



Ethanal phenylhydrazone

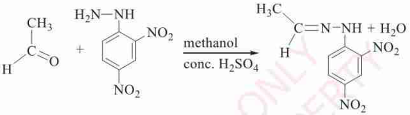
Condensation with 2,4-dinitrophenylhydrazine

When treated with 2,4-dinitrophenylhydrazine in methanol and concentrated H_2SO_4, carbonyl compounds react to yield 2,4-dinitrophenylhydrazones. This reaction, which gives yellow crystalline solids, is used to distinguish between carbonyl compounds and other compounds.



Yellow crystalline solid

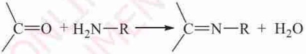
Example:



Yellow crystalline solid

Condensation with primary amines

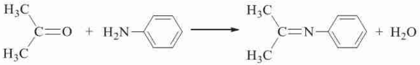
Carbonyl compounds react with primary amines to form Schiff's bases known as imines.



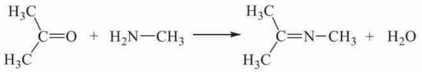
Schiff's base

Imines or Schiff's bases in which the carbon atom or the nitrogen atom attached to an alkyl group are unstable because of the positive inductive effect produced by alkyl group, which destabilises the amine groups. Thus, aliphatic aldehydes and aliphatic primary amines or aliphatic ketones and aliphatic primary amines form unstable Schiff's bases while other combinations form stable Schiff's bases.

Example:



Stable Schiff 's base



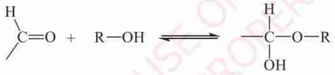
Unstable Schiff 's base

Special nucleophilic addition of aldehydes

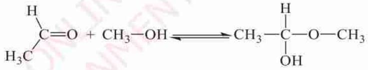
Aldehydes exhibit special nucleophilic addition reactions such as addition of alcohols and addition of ammonia.

Addition of alcohols

When aldehydes are treated with dry alcohols, 1-alkoxy-alcohols are formed. The following general equation represents such reaction.

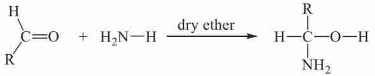


Example:



Addition of ammonia

When aliphatic aldehydes (except methanal) are treated with gaseous ammonia, in dry ether they react to produce white precipitates of hydroxylamine.

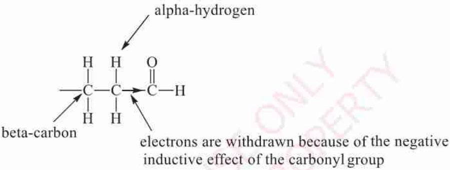


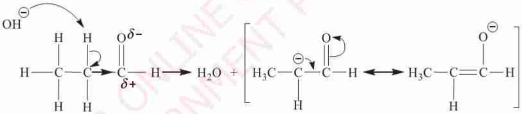
Aldehyde Ammonia Hydroxylamine

Methanal and aromatic aldehydes do not form stable hydroxylamines.

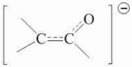
Reaction of alkyl groups adjacent to carbonyl carbon

Because of its electrophilic nature, the carbonyl carbon atom withdraws bond electron from the α-carbon atom by a negative inductive (–I) effect. As a result, because of its electron deficiency, α-carbon begins to withdraw the electrons from the α-hydrogen, making the α-hydrogen electrophilic and therefore susceptible to nucleophilic attack. Thus, under alkaline conditions α-hydrogen atom can be easily removed by a base to give a carbanion. The following structures can serve as illustrative examples:





Carbanions are usually unstable, they undergo electron resonance which is the distribution of electrons to form the most stable structure known as enolate anion as shown in the following structure:

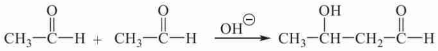


Enolate anion

The formation of enolate anion is made possible because of the negative mesomeric effect (-M) of the carbonyl group. Because of the formation of enolate anion, the reactions such as aldol condensation, haloform, and chlorination are made possible. The detailed description of chemical reactions is discussed in the following sections.

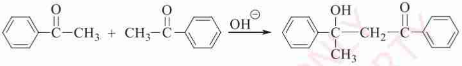
Aldol or ketol reaction

Aldehydes or ketones having α-hydrogens, under alkaline conditions can dimerise without the elimination of small molecules like water to form aldols or ketols. The following are examples of equations of aldol or ketol reactions in alkaline conditions.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{OH^{\ominus}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-H$$

Ethanal Ethanal 3-hydroxybutanal



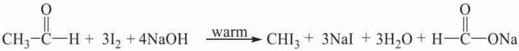
Phenylethanone Phenylethanone 3-hydroxy-1,3-diphenylbutan-1-one

Trihalomethane (haloform) reaction

The carbonyl compounds which have three α-hydrogen atoms react on warming with halogens under alkaline conditions to give trihalomethane and carboxylate salts. The general reaction is given by the following equation.

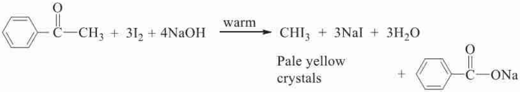
$$CH_3-\overset{\overset{O}{\|}}{C}- + 3I_2 + 4NaOH \longrightarrow CHI_3 + 3NaI + 3H_2O + -\overset{\overset{O}{\|}}{C}-ONa$$

Secondary alcohols containing the group $CH_3C(OH)-$, also react with halogens under the same conditions. This is because, under these conditions, the hydroxyl group will be oxidised to give alkanone. If iodine is used, the triiodomethane (CHI_3), precipitates as pale-yellow crystals which are easily noticeable. Thus, the reaction is known as triiodomethane or iodoform test and is used to distinguish alkan-2-one or alkan-2-ol with other ketones or alcohols, respectively. Ethanal is the only aldehyde which reacts in this way. Examples of triiodomethane reactions are shown by the following reactions:



$$CH_3-\overset{\overset{O}{\|}}{C}-H + 3I_2 + 4NaOH \xrightarrow{warm} CHI_3 + 3NaI + 3H_2O + H-\overset{\overset{O}{\|}}{C}-ONa$$

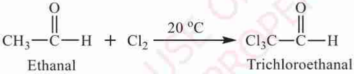
Pale yellow
crystals



Chlorination

When chlorine gas is bubbled through a dry ether solution of carbonyl compound containing CH_3CO- group at a temperature below 20 °C, substitution of the α-hydrogen atoms by chlorine takes place. Each time a chlorine atom is substituted at α-carbon atom, the negative inductive effect (^-I) of that α-carbon atom increases making it even more electrophilic. This makes any remaining α-hydrogen atom even more acidic, so they are more easily substituted by excess chlorine.

Example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + Cl_2 \xrightarrow{20\ ^\circ C} Cl_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

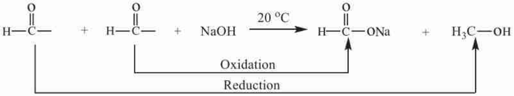
Ethanal Trichloroethanal

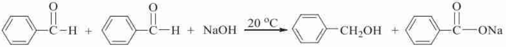
Redox reactions

Carbonyl compounds can undergo reduction and oxidation reactions. Aldehydes can be reduced to primary alcohols or oxidised to carboxylic acids. Ketones can be reduced to secondary alcohols but cannot be oxidised to carboxylic acid or any other products without breaking their carbon skeleton. Some aldehydes can undergo disproportionation reaction, in other words, the reduction and oxidation of the same molecule in the same reaction. Thus, redox reactions of aldehydes and ketones fall under three categories, namely Cannizzaro reaction, reduction and oxidation. The following discussion gives the details on each category.

Cannizzaro reaction or disproportionation reaction

Aldehydes which have no α-hydrogen atoms such as methanal, benzenecarbaldehyde and some aldehydes in which the α-carbon atom is a tertiary carbon, exhibit Cannizzaro reaction. This reaction occurs when such an aldehyde is treated with 40 – 60 % (w/v) aqueous solution of alkali at room temperature. An alcohol and the carboxylate salt are the products of the reaction. The following equations are examples of Cannizzaro reactions.

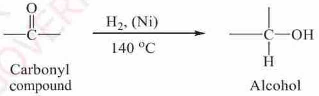




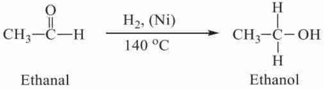
Cannizzaro reaction involves the disproportionation of two molecules of aldehydes. The resulting products are one molecule of alcohol which acquires an increase in the number of hydrogen atoms (reduction) and one molecule of carboxylate salt which acquires an increase in the number of oxygen atoms (oxidation).

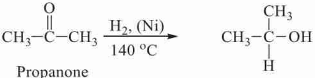
Reduction

Reduction of carbonyl compounds can produce alcohols or hydrocarbons depending on the condition under which the reaction is conducted. Aldehyde can be reduced by using reducing agents such as $LiAlH_4$ or $NaBH_4$ and by hydrogen in the presence of a catalyst. The products of the reaction are primary alcohols. Similarly, ketones can be reduced to secondary alcohols. The general equation for the catalytic reduction of carbonyl compounds using gaseous hydrogen is given in the following equations:



Examples:



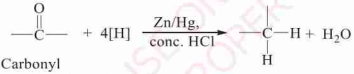


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[140\ ^{o}C]{H_2,\ (Ni)} CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Propanone

Propan-2-ol

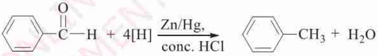
When a reaction is conducted using a reducing agent such as $LiAlH_4$ or $NaBH_4$, such a reaction proceeds to form alcohols as previously discussed. Under suitable conditions, aldehydes and ketones react to give hydrocarbons. This reaction is known as *Clemmensen reaction*. A mixture of aldehyde or ketone with zinc amalgam and concentrated hydrochloric acid reacts to yield a hydrocarbon with an equal number of carbon atoms to the original aldehyde or ketone. The following general equations serve as illustrative examples.



$$-\overset{\overset{O}{\|}}{C}- \ + 4[H] \xrightarrow[\text{conc. HCl}]{\text{Zn/Hg,}} -\underset{\underset{H}{|}}{\overset{|}{C}}-H + H_2O$$

Carbonyl compound

Hydrocarbon

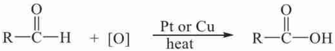


Benzaldehyde

Toluene

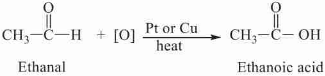
Oxidation

Aldehydes are powerful reducing agents and therefore, they can be easily oxidised to carboxylic acids. They can be oxidised by oxygen in air or by oxidising agents such as acidified potassium permanganate or potassium dichromate. For instance, when aldehyde vapour is mixed with air and passed over heated finely divided particles of Pt or Cu as catalyst, a carboxylic acid is formed as shown in the following general equation.



$$R-\overset{\overset{O}{\|}}{C}-H \ + [O] \xrightarrow[\text{heat}]{\text{Pt or Cu}} R-\overset{\overset{O}{\|}}{C}-OH$$

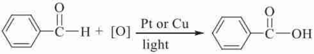
Example:



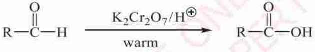
$$CH_3-\overset{\overset{\large O}{\|}}{C}-H + [O] \xrightarrow[\text{heat}]{\text{Pt or Cu}} CH_3-\overset{\overset{\large O}{\|}}{C}-OH$$

Ethanal   Ethanoic acid

Aromatic aldehydes are difficult to oxidise but benzene carbaldehyde is oxidised to benzene carboxylic acid when exposed to air and light.



When aldehydes and ketones are warmed with acidified potassium permanganate or potassium dichromate, they react to give carboxylic acids.



$$R-\overset{\overset{\large O}{\|}}{C}-H \xrightarrow[\text{warm}]{K_2Cr_2O_7/H^{\oplus}} R-\overset{\overset{\large O}{\|}}{C}-OH$$

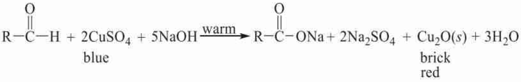
The purple colour of the potassium permanganate or the orange colour of potassium dichromate changes to colourless and light green, respectively. Ketones do not undergo oxidation reaction, therefore, they have no effect on either potassium permanganate or potassium dichromate.

Other important reactions of carbonyl compounds

Redox reactions can further be discussed in terms of chemical tests such as Fehling's test, Benedict's test, and silver mirror test. The discussion on each test is given as follows:

Fehling's test

Fehling's test involves mixing of one volume of Fehling's **A** solution (aqueous solution of copper (II) sulphate which is deep blue) with an equal volume of Fehling's **B** solution (a colourless aqueous solution of sodium potassium tartrate) in alkali (NaOH) and few drops of aldehyde followed by heating the resulting mixture. Aldehyde reduces $CuSO_4$ solution to Cu_2O which precipitates out as brick red precipitate. The reaction can be represented by the following general chemical equation.



$$R-\overset{\overset{\large O}{\|}}{C}-H + \underset{\text{blue}}{2CuSO_4} + 5NaOH \xrightarrow{\text{warm}} R-\overset{\overset{\large O}{\|}}{C}-ONa + 2Na_2SO_4 + \underset{\text{brick red}}{Cu_2O(s)} + 3H_2O$$

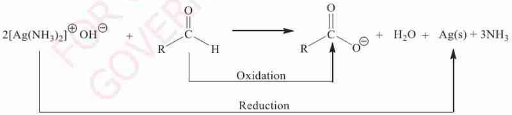
From the equation above it can be observed that the carbonyl carbon loses a hydrogen and gains an oxygen atom, hence it is said to be oxidised. Aromatic aldehydes do not reduce Fehling's solution. In excess of NaOH, sodium tartrate (Rochele salt) prevents the precipitation of copper(II) hydroxide in alkaline solution by formation of copper complex.

Benedict's test

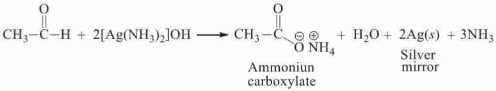
Benedict's test is the same as Fehling's test, the only difference is the composition of the reagent. In Fehling's test, the reagent consists of Rochelle salt (solution of potassium sodium tartrate) to prevent precipitations of $Cu(OH)_2$, whereas in the Benedict's test the reagent consists of sodium citrate and sodium carbonate to prevent precipitation of $Cu(OH)_2$. The colour changes from clear blue to brick red signifying the reduction of Cu(II) to Cu(I). When an aldehyde is added to the Benedict's solution, the reaction described in (a) takes place. The reaction can be used to distinguish aldehydes from ketones except α-hydroxy ketones.

Silver mirror test

When a few drops of an aldehyde are added to a solution of silver(I) nitrate in excess ammonia, aldehyde reduces the $[Ag(NH_3)_2]^{\oplus}$, (Tollen's reagent) to silver atoms which stick on the inner surface of the reaction vessel to form a silver mirror. This method is used to distinguish between aldehydes and ketones except α-hydroxy ketone. The carboxylate ion can be converted to carboxylic acid by acidifying the solution. The following general equation represents the above reactions:



Example:



$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H + 2[Ag(NH_3)_2]OH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\ominus}{O}\,\overset{\oplus}{N}H_4 + H_2O + 2Ag(s) + 3NH_3$$

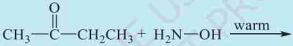
Exercise 6.3

1. By referring to the physical state, odour, melting and boiling points, solubility in water and intermolecular attraction, write brief notes on the physical properties of carbonyl compounds.

2. Account for each of the following:
   - (a) Although propanal and acetone have the same molar mass, the boiling point of acetone is higher than that of propanal
   - (b) There is no intermolecular hydrogen bonding between the molecules of carbonyl compounds

3. (a) What is a nucleophilic addition reaction?
   - (b) Describe the mechanism of nucleophilic addition reaction to a carbonyl compound.
   - (c) Explain why ethanal is more reactive than acetone towards nucleophilic addition.

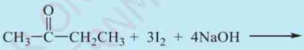
4. Complete the following chemical reactions:

(a) 

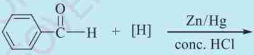
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3 + H_2N-OH \xrightarrow{\text{warm}}$$

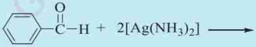
(b) 

$$2H-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{OH^{\ominus}}$$

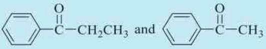
(c) 

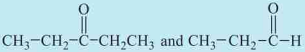
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3 + 3I_2 + 4NaOH \longrightarrow$$

(d) 

(e) 

5. How would you distinguish the following pairs of compounds?

(a) 

(b) 

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \text{ and } CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$$

6.4 Uses and hazards of carbonyl compounds

Carbonyl compounds have wide applications in various fields like medicines, agriculture, and pharmaceutical industries. Inspite of these useful applications, they pose some health hazards to human and the environment. In this section, the uses and hazards of carbonyl compounds will be covered.

Uses of carbonyl compounds

Carbonyl compounds play a very significant role in chemical industries as valuable starting materials in various syntheses such as the synthesis of alcohols, dyes, pharmaceuticals, pesticides, and perfumes. This section, describes the uses of some specific carbonyl compounds.

(a) Methanal is widely used to produce phenol-methanal and carbamide-methanal resins in plastic industries. It is also often used as formalin which is a 40% aqueous solution used for preserving anatomical specimens and as an antiseptic. It is also used extensively in the construction, wood processing, furniture, textiles, and carpeting.

(b) Ethanal is used as intermediate or starting material in the industrial synthesis of ethanoic acid, ethanoyl chloride, and butanal.

(c) Benzene-carbaldehyde is used in the synthesis of many dyes and flavouring of food staff and beverages to provide an almond flavour. It is also used in perfumery industries.

(d) Acetone is widely used as solvent in perfumery industries to substitute ethanol and as a nail polish remover. Acetone is also used in the manufacturing of polymer known as *Perspex* (Poly(methylmethacrylate) that is often used in sheet form as a lightweight or shatter-resistant alternative to glass.

(e) The reaction of formaldehyde solution and Tollen's reagent is used in the manufacture of mirrors.

Hazards of carbonyl compounds

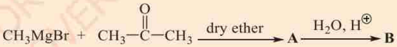
Even though carbonyl compounds are among the most important categories of chemicals, there are few increasing concerns due to their adverse effects on public health. Some carbonyl compounds such as formaldehyde (methanal), acetaldehyde (ethanal), and propionaldehyde (propanal) are listed as air toxins by USA and some European countries. Methanal, which is one of the most abundant carbonyl compounds in air, has been classified as a human carcinogen by the international agency for research on cancer (IARC) due to its carcinogenicity. Ethanal, which is another abundant airborne carbonyl compound has been classified as a suspected human carcinogen by the United State Environmental Protection Agency (US-EPA).

People who are excessively exposed to these chemicals have an increased probability of getting degenerative diseases. Inhalation of high doses of formaldehyde (methanal) can cause nasal tumours, irritation of the eyes and air passages in humans. Aldehyde inhalation can alter the breathing patterns by narrowing air way opening (airway constriction). It can also damage cells lining along the air ways prompting white blood cells to inter the lungs.

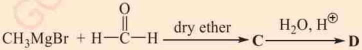
Carbonyl compounds have relatively low boiling points and high vapour pressures. Because of these properties, they are readily released from indoor and outdoor sources. Humans can therefore be exposed to carbonyl compounds through inhalation and dermal contact. Indoor sources of carbonyl compounds can be the furnishing materials such as curtains, wood furniture, and carpets. Carbonyls can also be released from computers, photocopiers, decoration materials, building materials and through infiltration from outdoor. Motor vehicles using gasoline and diesel fuels blended with methanol or ethanol or using methanol or ethanol alone are the major sources of aldehydes and ketones.

Revision exercise 6

1. Complete the following chemical reactions:

(a) 

$$CH_3MgBr + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{dry ether}} \mathbf{A} \xrightarrow{H_2O,\ H^{\oplus}} \mathbf{B}$$

(b) 

$$CH_3MgBr + H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{dry ether}} \mathbf{C} \xrightarrow{H_2O,\ H^{\oplus}} \mathbf{D}$$

2. Give the structural formula of the following compounds:

(a) 4-phenylpentan-2-one

(b) 3,5- dichloroacetophenone

(c) 3-methylpentan-2-one

(d) 2-bromopropanal

(e) Hexanedial

3. Give the formulae of alkenes which on ozonolysis followed by hydrolysis will give the following products:

   (a) Methanal and ethanal

   (b) Propanal as the only product

   (c) Propanone as the only product

4. Give the equation (including reagents and conditions) for the following conversions:
   (a) Hex-3-ene to hexan-2-one
   (b) Butan-1-ol to butanal
   (c) Butan-1-ol to butanone
   (d) Butan-1-ol to heptan-4-one

5. A carbonyl compound **A** was reduced with $LiAlH_4$ to give compound **B**. Compound **B** was dehydrated with conc. sulphuric acid to give one product, **C** (molecular formula C_5H_{10}). Ozonolysis of **C** gave ethanal and another compound **D** with molecular formulae C_3H_6O. Compound **D** gives a positive iodoform test. Identify compounds **A** to **D** by giving their IUPAC names and structural formula. Give the chemical equations for the above reactions.

6. (a) Explain why 2-pentanal and 2-methyl-2-propanone do not exist.

   (b) Draw the structure of:

      (i) A ketone that is an isomer of butanal

      (ii) 3-phenylbutanal

7. Compounds **X** and **Y** have the same molecular formula, C_3H_6O. Compound **X** gives a positive iodoform test, but compound **Y** does not. Use the given information to suggest the structures of **X** and **Y**. What is/are the functional group(s) of **X** and **Y**?

8 (a) Name types of organic compounds from the following descriptions of their functional groups:

   (i) Polar double bond group that must be at the end of the chain.

   (ii) Polar double bond group that cannot be at the end of a chain.

   (b) Although both aldehydes and ketones contain carbonyl group, ketone is less susceptive to nucleophilic attack. Explain.

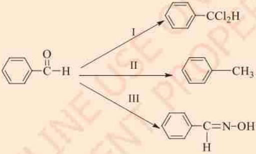
(c) Vanillin is a naturally occurring flavouring agent which is used in many food products.

Vanillin

(i) What would you expect to observe when a sample of vanillin is warmed with iodine in alkaline solution?

(ii) Why does a mixture of vanillin with acidified potassium permanganate decolourise upon warming?

9. Benzaldehyde is used as an artificial almond flavouring. Some chemical transformations of benzaldehyde are given as shown:



(a) Suggest the reagents and conditions for each of the reactions I, II, and III.

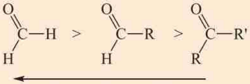
(b) Describe the type of the reaction undergone in each case.

10. Why does the addition of HCN to carbonyl group in butanal proceeds via initial nucleophilic attacks on the carbonyl carbon atom, but there is no electrophilic attack on the carbonyl oxygen atom?

11. Explain the following observations:

(a) Aromatic aldehydes do not reduce Fehling's solution.

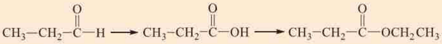
(b) Nucleophilic attack of carbonyl compounds follows the order



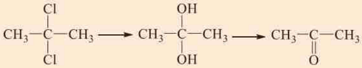
Increase in reactivity

(c) Ethanol, ethanal and propanone give positive triiodomethane test but propanal and propan-1-ol do not.

12. Give the necessary reagents and conditions for the following conversions:

(a) 

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$$

(b) 

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

(c) $C_6H_5OOC-Ca-COOC_6H_5 \longrightarrow$ Diphenylmethanone

(d) 

$$CH_3-\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-COOH$$

13. Unsaturated hydrocarbon, **A** (C_5H_{10}) on ozonolysis gives a mixture of two compounds **B** and **C**. Compound **A** gives positive Fehling's and iodoform tests contrary to compound **C** which gives negative Fehling's test and a positive iodoform test. Identify compounds **A**, **B** and **C** and write all the reactions including their condition(s).

14. An aromatic compound **D**, C_8H_8O gives a positive 2, 4-dinitrophenylhydrazine test. It gives a yellow precipitate of compound **E** on treatment with iodine and sodium hydroxide solution. Compound **D** gives negative Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid **F**, $C_7H_6O_2$ which is also formed along with the yellow compound in the above reaction.

(a) Identify **D**, **E** and **F**

(b) Write all the reactions involved.

15. Compound **G** of molecular formula C_3H_6O is identified as a carbonyl compound:

(a) Write down functional isomers of **G**.

(b) Which isomer of **G** will react faster with HCN and why?

(c) Show the mechanism of the reaction in (b)

(d) (i) Will the reaction in (b) go to completion with the conversion of all reactants into the product at reaction conditions?

(ii) If a strong acid is added to the reaction mixture what will be the effect on the concentration of the product and why?

16. When liquid **M** is treated with a freshly prepared ammoniacal silver nitrate solution, it gives a positive test. The liquid forms a white crystalline solid on treatment with sodium hydrogen sulphate(VI). Liquid **N** also forms a white crystalline solid with sodium hydrogen sulphate but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions.

Chapter Seven

Carboxylic acids and their derivatives

Introduction

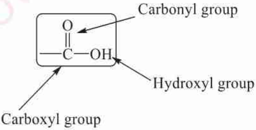
Carboxylic acids are organic compounds containing a carboxyl (–COOH) as a functional group. The term carboxyl is derived from a combination of a carbonyl group (−C=O) and hydroxyl group (–OH). The carboxylic acids and their derivatives are applicable in various industrial processes such as production of soap, vinegar, drugs, perfumes, and coagulants. In this chapter, you will learn about the structure, nomenclature, preparation, properties, uses and hazards of carboxylic acids and their derivatives.

7.1 Carboxylic acids

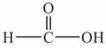
In this section, you will learn about the structure of the carboxyl group, naming using IUPAC system, preparation, uses and hazards of carboxylic acids.

7.1.1 Structure of carboxyl group

Carboxylic acids are organic compounds containing a carboxyl group (–COOH) as the functional group which consists of two parts, the carbonyl group (–C=O) and the hydroxyl group (–OH).

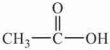


The two simplest aliphatic carboxylic acids are shown by the following structures:



$H-\overset{\overset{\large O}{\|}}{C}-OH$

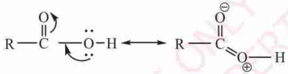
Formic acid (methanoic acid)



$CH_3-\overset{\overset{\large O}{\|}}{C}-OH$

Acetic acid (ethanoic acid)

Because of the dual nature of their functional group, carboxylic acids show properties different from those of carbonyl compounds and alcohols. Bonds in both, the carbonyl and hydroxyl groups in isolation are strongly polar. When combined together, the π-bonds of carbonyl carbon interact with lone pairs of oxygen atom of the hydroxyl group (undergo delocalisation). This results into the split of oxygen-hydrogen bond to release $H^{\oplus}$ and the reduction of positive charge on the carbon atom. This makes it less susceptible to nucleophile attack.



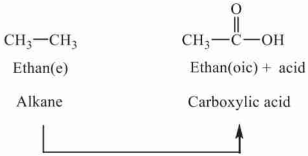
7.1.2 Nomenclature of aliphatic and aromatic carboxylic acids using IUPAC system

According to the IUPAC system, the names of carboxylic acids are derived from the names of their corresponding alkanes. All rules which are used to name alkanes according to the IUPAC system are applied to carboxylic acids, except that the suffix *-e* of the alkane is replaced.

Naming of aliphatic carboxylic acids

The name of the acid is obtained from the name of the corresponding alkane where by the suffix *-e* of the alkane is replaced by the suffix *-oic* followed by the separate word *acid*.

Example:



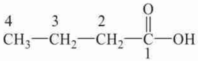
CH_3-CH_3 $\qquad$ $CH_3-\overset{\overset{\large O}{\|}}{C}-OH$

Ethan(e) $\qquad$ Ethan(oic) + acid

Alkane $\qquad$ Carboxylic acid

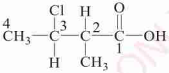
In naming of substituted acids according to the IUPAC system, the groups and positions where they are attached must be indicated. The numbering of the positions is done by starting from the carboxyl group which is considered carbon number one, the next carbon will be number two the trends continue up to n^th^ number of carbon atoms, depending on the length of the parent carbon chain.

Example:



$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-OH$$

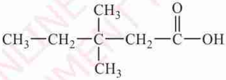
Thus, if a substituent group is attached to any of the numbered carbon atoms, it is easy to name the compound.



$$\overset{4}{CH_3}-\underset{H}{\overset{Cl}{\overset{|}{C}}}{}^{3}-\underset{CH_3}{\overset{H}{\overset{|}{C}}}{}^{2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-OH$$

3-chloro-2-methylbutanoic acid

If more than one similar substituent groups are attached to the parent chain, the suffix *di, tri, tetra,* and *pent* can be used.



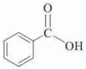
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

3,3-dimethylpentanoic acid

Naming of aromatic carboxylic acids

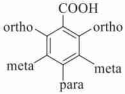
The simplest aromatic carboxylic acid is benzoic acid. Its IUPAC name is obtained from the name of the corresponding hydrocarbon benzene by substituting the suffix *-ene* by the suffix *-oic* followed by the separate word *acid.*

Example:



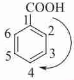
Benzoic acid

Other groups may be attached to the ring and indicated by mentioning the positions where the substituent groups are attached. The carbon on the ring next to the carboxyl (-COOH) group is *ortho* (o), next to ortho is *meta* (m) and next to meta is *para* (p).



However, in the IUPAC system, the carbon atom to which the carboxyl group is attached is taken as carbon number one and then the positions are counted clockwise or anticlockwise in order to ensure the smallest ratios of the substituents groups.

Example:

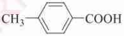


Clockwise

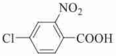
Anticlockwise

The names benzoic acid or benzene carboxylic acids are used in the IUPAC system. Consider the following examples:

2-chlorobenzoic acid
(*ortho*-chlorobenzoic acid)



4-methylbenzoic acid
(*para*-methylbenzoic acid)

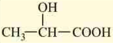
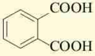


4-chloro-2-nitrobenzoic acid

Naming of carboxylic acids using common system

Many carboxylic acids are better known by their common names than by systematic names (IUPAC names). The names are usually derived from Latin or Greek words but do not follow any rule except that they all end up with suffix *ic acid*. The common and systematic names of some carboxylic acids are given in Table 7.1.

Table 7.1: Systematic and common names of some carboxylic acids

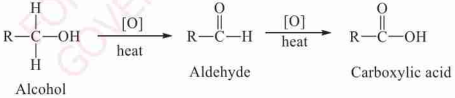
Structural formula	Sytematic names	Common names
HCOOH	Methanoic acid	Formic acid
CH_3COOH	Ethanoic acid	Acetic acid
 $CH_3-\overset{\overset{\large OH}{\vert}}{C}H-COOH$	2-hydroxypropanoic acid	Lactic acid
$HOOC-CH_2-CH_2-COOH$	Butanedioic acid	Succinic acid
	1,2-benzenedicar boxylic acid	Phthalic acid
	1,4-benzenedi carboxylic acid	Terephthalic acid

7.1.3 Preparation of carboxylic acids

Both aliphatic and aromatic carboxylic acids can be prepared using a variety of methods. The most common methods used are described in the following sections.

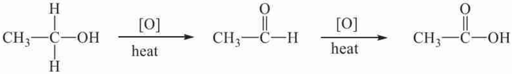
Oxidation of alcohols and aldehydes

Oxidation can be carried out in the presence of either acidified $KMnO_4$, K_2CrO_7 or with dilute nitric acid. When primary alcohols or aldehydes are heated under reflux with $KMnO_4$ or K_2CrO_7, carboxylic acids are formed. The following general equation represents the reaction:

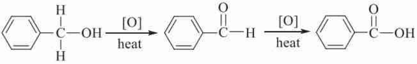


$$R-CH_2-OH \xrightarrow[\text{heat}]{[O]} R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{heat}]{[O]} R-\overset{\overset{O}{\|}}{C}-OH$$

Example:

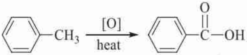


$$CH_3-CH_2-OH \xrightarrow[\text{heat}]{[O]} CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{heat}]{[O]} CH_3-\overset{\overset{O}{\|}}{C}-OH$$



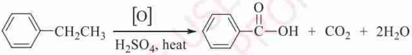
Oxidation of alkylbenzene

Regardless of the side chain length of the alkylbenzene, on oxidation with a strong oxidising agent such as acidified $KMnO_4$, K_2CrO_7 or HNO_3, degrades alkyl groups with longer chain than methyl to form benzoic acids.



Methylbenzene Benzoic acid

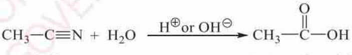
The following equation represent the oxidation of ethylbenzene using acidified potassium permangate:



Hydrolysis of nitriles (cyanides) and amides

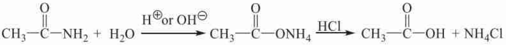
When nitriles and amides are treated with mineral acids or alkalis at room temperature, they give carboxylic acids and other products.

Examples:



$$CH_3-C\equiv N + H_2O \xrightarrow{H^{\oplus}\text{or } OH^{\ominus}} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Nitrile Carboxylic acid

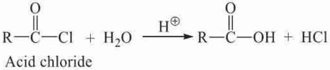


$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{H^{\oplus}\text{or } OH^{\ominus}} CH_3-\overset{\overset{O}{\|}}{C}-ONH_4 \xrightarrow{HCl} CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_4Cl$$

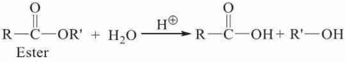
Hydrolysis of acid derivatives

Acid derivatives such as acid chlorides, esters, amides and acid anhydrides can be hydrolysed to give carboxylic acids. Hydrolysis takes place at room temperature when the above named acid derivatives are treated with water in the presence of acid.

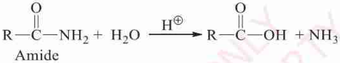
Examples:



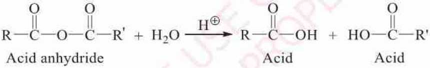
$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2O \xrightarrow{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH + HCl$$



$$\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O \xrightarrow{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

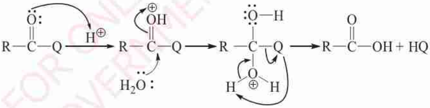


$$\underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O \xrightarrow{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$$



$$\underset{\text{Acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'} + H_2O \xrightarrow{H^{\oplus}} \underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Acid}}{HO-\overset{O}{\overset{\|}{C}}-R'}$$

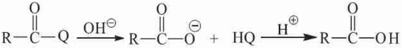
The following scheme represents the mechanism of hydrolysis of acid derivatives in acidic medium:



where Q stands for Cl, NH_2, OR and OCOR

In alkaline conditions acid derivatives are hydrolysed to form salts of acids. If salts of acids are acidified, carbroxylic acids are formed.

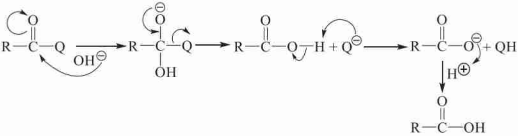
Example:



$$R-\overset{O}{\overset{\|}{C}}-Q \xrightarrow{OH^{\ominus}} R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + HQ \xrightarrow{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH$$

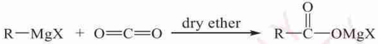
where Q stands for Cl, NH_2, OR, and OCOR

In alkaline medium the scheme for the reaction mechanism is given as:



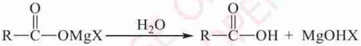
Action of carbon dioxide on alkyl or phenyl magnesium halide

When gaseous carbon dioxide is bubbled through alkyl or phenyl magnesium halide (Grignard reagent) in dry ether, an addition product R—COOMgX is formed, where R is an alkyl or a phenyl group and X is a halogen.



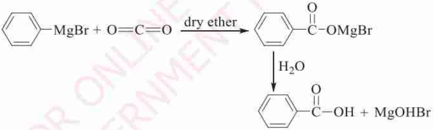
$$R-MgX + O=C=O \xrightarrow{\text{dry ether}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OMgX$$

Hydrolysis of the obtained product yields carboxylic acid and other products.



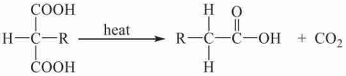
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OMgX \xrightarrow{H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + MgOHX$$

Example:



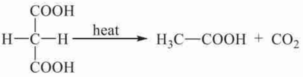
Decarboxylation reactions

Compounds containing two carboxyl groups attached to the same carbon atom such as HOOC$-$ CH$_2$$-$ COOH are unstable to heat. These compounds when heated they decompose to give carboxylic acid and a molecule of carbon dioxide is lost.

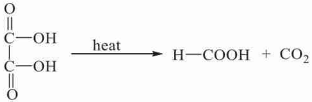


$$H-\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle COOH}{|}}{C}}-R \xrightarrow{\text{heat}} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CO_2$$

Examples:



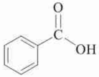
$$H-\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle COOH}{|}}{C}}-H \xrightarrow{\text{heat}} H_3C-COOH + CO_2$$



$$HOOC{-}COOH \xrightarrow{heat} H{-}COOH + CO_2$$

Preparation of benzoic acid

The simplest and most important aromatic carboxylic acid is benzoic acid. It is a solid that is only slightly soluble in water and widely used as a food preservative as well as in the manufacture of cosmetics, dyes, and insects' repellents.

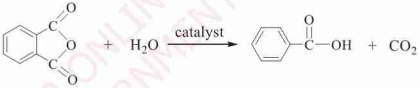


Benzoic acid

Benzoic acid can be prepared in the laboratory by using the following methods:

Decarboxylation of benzene-1,2-dicarboxylic anhydride

When steam is passed into a molten benzene-1,2-dicarboxylic anhydride in the presence of catalyst (chromium(III) benzene-1,2-dicarboxylate), benzoic acid is formed.



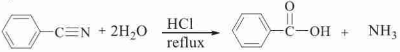
Benzene-1,2-dicarboxylic anhydride

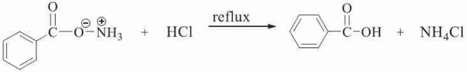
Benzoic acid

Hydrolysis of benzene carbonitrile or ammonium salt of benzoic acid

When boiled under reflux with concentrated hydrochloric acid, benzene carbonitrile hydrolyses to give benzene carboxylic acid.

Examples:





7.1.4 Properties of carboxylic acids

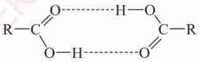
The carboxyl (–COOH) group has a dual nature because it possesses two functional groups within one functional group. This property makes it peculiar in its physical and chemical properties.

Physical properties of carboxylic acids

Benzoic acid is a solid at room temperature, its melting point is 121 °C and the boiling point is 249 °C. It has a density of 1.32 gcm^{-3} which is higher than that of water (1 gcm^{-3}). It is sparingly soluble in water and in most cases it is soluble in organic solvents. On the other hand, simple aliphatic carboxylic acids with the number of carbon atoms ranging from one to ten per molecule are colourless liquids at room temperature. The higher members of this family such as fatty acids and others are solids. Liquid carboxylic acids have a strong smell. The first members such as ethanoic acid possess a sharp pungent smell like that of vinegar. Butanoic acid and pentanoic acid have unpleasant smell of rancid butter (spoiled butter).

Melting and boiling points of carboxylic acids increase with increase in the relative molecular masses of the compounds. Acids whose molecules contain an even number of carbon atoms have considerably higher melting points than those containing uneven numbers of carbon atoms. This is because molecules with even number of carbon atoms can park together more closely in the crystal lattice. Hence, their intermolecular forces are greater and therefore need higher temperatures to break these lattices.

Carboxylic acids exhibit hydrogen bonding between their molecules. Lower carboxylic acids exist as dimers where a pair of molecules is linked by two hydrogen bonds.

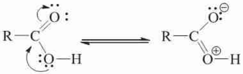


Dimer of carboxylic acid

Hydrogen bonding makes carboxylic acids to have higher boiling points when compared to other compounds of comparable molar masses. Carboxylic acids that possess up to four carbon atoms in a molecule are completely soluble in water. This is because they consist of a relatively polar functional group with only a short nonpolar alkyl group. As the alkyl group increases in length the acids become less soluble in polar solvents but more soluble in nonpolar solvents. Thus, carboxylic acids with carbon atoms from eight and above are practically insoluble in water.

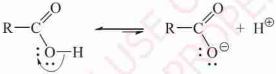
Chemical properties of carboxylic acids

Carboxylic acids are represented by R—COOH structure where the lone pairs of the hydroxyl group allow the delocalisation by orbital overlap of π-system of the carbonyl group. Therefore, carboxyl group of the acid exhibits resonance.



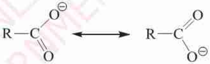
Structure I Structure II

Looking at the two structures, it can be observed that they do not contribute equally to the actual structure. Consequently, the resonance energy, which estimates the stability of a compound is less. On the other hand, the carboxylate ion which is obtained by removing one hydrogen atom of the carboxyl group is much more stable.

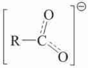


Carboxylate ion

The two resonating structures of the carboxylate ion are:



These structures are similar and contribute equally to the actual structure. Since the double bond is changing its position, the carboxylate ion can be represented as:



The stability of the carboxylate ion implies that it can exist separately with hydrogen ion. This facilitates the release of protons ($H^{\oplus}$). Thus, the ionisable hydrogen of the carboxyl group is responsible for the following chemical reactions:

Acidic nature

Both aliphatic carboxylic acids and benzoic acids turn blue litmus paper red. This indicate the acidic nature of the carboxyl group.

$$\mathrm{RCOOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{RCOO^{\ominus}} + \mathrm{H_3O^{\oplus}}$$

Activity 7.1 To investigate the acidic nature of carboxylic acids

Requirements: Seven test tubes, four beakers, two measuring cylinders of 10 mL, masking tapes, filter papers, stirrer, one knife, mineral acids (HCl, H_2SO_4 and HNO_3), litmus papers, lemon, orange, tomatoes, sour milk, vinegar, and filter papers.

Procedure

1. Cut a lemon, orange, and tomatoes transversely into two halves.
2. Squeeze their juices into different beakers until 2 mL of each is obtained and label them **A**, **B** and **C**, respectively.
3. Add 1 mL of pure water to each juice in the beakers. Filter and collect the filtrate into the test tubes.
4. Test the solutions using litmus papers and record the observations.
5. Measure 2 mL of sour milk and vinegar into different beakers and label them **D** and **E**, respectively.
6. Add 1 mL of pure water to each beaker and stir the mixture thoroughly and filter.
7. Collect the filtrate into two different test tubes and label them **F** and **G**, respectively.
8. Test acidity using litmus papers, methyl orange and phenolphthalein indicators. Record the observations.

Questions

1. Explain the observations of each experiment.
2. Explain the necessity of adding pure water in each mixture.
3. Why was each mixture filtered before the final experiment of testing acidity?

Liberation of hydrogen

Electropositive elements like Na, K, and Ca react with carboxylic acids to produce hydrogen gas with the formation of salts.

Examples:

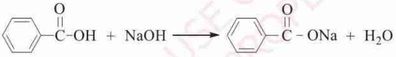
$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$
$$2CH_3COOH + Ca \longrightarrow (CH_3COO)_2Ca + H_2$$

Salt formation

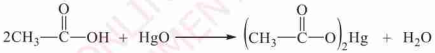
Carboxylic acids react with alkalis, metallic oxides, bicarbonates, carbonates, and ammonia to give salts. These reactions can be represented by the following equations:

$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH + KOH \longrightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-OK + H_2O$$

Potassium acetate

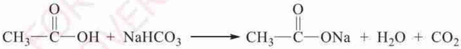


Sodium benzoate



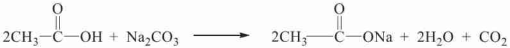
$$2CH_3-\overset{\overset{\large O}{\|}}{C}-OH + HgO \longrightarrow \left(CH_3-\overset{\overset{\large O}{\|}}{C}-O\right)_2Hg + H_2O$$

Mercuric acetate



$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH + NaHCO_3 \longrightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-ONa + H_2O + CO_2$$

Sodium acetate



$$2CH_3-\overset{\overset{\large O}{\|}}{C}-OH + Na_2CO_3 \longrightarrow 2CH_3-\overset{\overset{\large O}{\|}}{C}-ONa + 2H_2O + CO_2$$

Sodium acetate

$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-ONH_4$$

Ammonium acetate

Activity 7.2 Preparation of bar soap

Requirements: Sunflower oil (vegetable oil), 2 M sodium hydroxide solution, distilled water, 4 M sodium chloride solution, jam jar, filter papers, heat source, three measuring cylinders of 100 mL, oily piece of cloth, and one beaker of 250 mL.

Procedure

1. Measure 25 mL of sunflower oil and pour into an empty jam jar.
2. Add 100 mL of 2 M sodium hydroxide solution in the jam jar containing sunflower oil.
3. Light the heat source and heat the mixture gently for 30 minutes so that the contents mix.
4. Continue heating and stirring the mixture while adding distilled water from time to time until no more solids separate out.
5. Allow the mixture to cool and then add 10 mL of 4 M sodium chloride solution. Stir the mixture continuously for 5 minutes.
6. Pour the solution into a fresh beaker and allow it to settle. A solid should separate from the solution.
7. Use a small piece of the solid soap obtained to clean an oily piece of cloth.

Questions

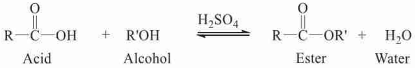
1. Explain the role of sodium hydroxide and sodium chloride in this experiment.
2. Why was the mixture of sunflower oil and sodium hydroxide heated?
3. Explain what happened when a small piece of the solid soap was used to clean an oily piece of cloth.
4. Name and define the process involved in this experiment.

Replacement of the hydroxyl group

The hydroxyl group (–OH) of the carboxylic acid can be replaced by –OR, –Cl, $-NH_2$, and –OCOR groups to form esters, acid chlorides, amides and acid anhydrides respectively.

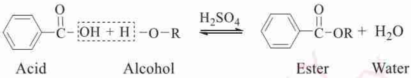
Ester formation or esterification

When carboxylic acids are mixed with alcohols and heated in the presence of a strong mineral acid like H_2SO_4, esters are formed. This reaction is reversible and can be represented by the following chemical equations:

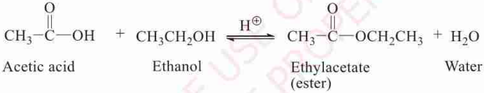


$$R-\overset{\overset{O}{\|}}{C}-OH + R'OH \xrightleftharpoons{H_2SO_4} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

or

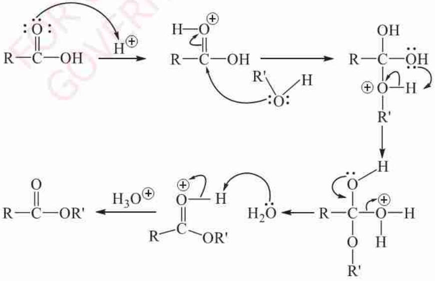


Example:

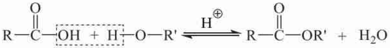


$$CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2OH \xrightleftharpoons{H^{\oplus}} CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + H_2O$$

The hydrogen ion ($H^{\oplus}$) from the acid protonates the carbonyl oxygen of the carboxyl group; as a result, the carbon atom becomes more electrophilic and undergoes nucleophilic attack by the OH of the alcohol. The mechanism of the reaction proceeds as illustrated in the following equations:



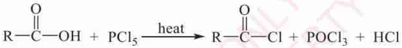
It can be summarised that esterification involves the cleavage (breaking) of the oxygen-hydrogen bond (O—H) of the alcohol and carbon-hydroxyl bond (C—OH) of the carboxylic acid. Thus, the reaction can be written in a simplified way.



$$R-\overset{O}{\overset{\|}{C}}-\boxed{OH\ +\ H}-O-R' \xrightleftharpoons{H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

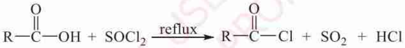
Formation of acyl chlorides

When a carboxylic acid is treated with phosphorous pentachloride (PCl_5) or thionyl chloride ($SOCl_2$), acyl chloride (RCOCl) is produced. The reaction can be represented by the following chemical equations:



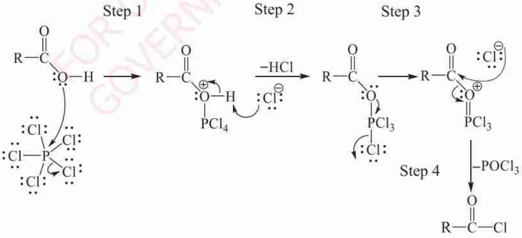
$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \xrightarrow{heat} R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

or



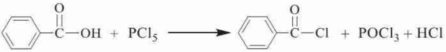
$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{reflux} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

In this reaction, the -Cl replaces the -OH group and the formation of acyl chloride is not a simple nucleophilic substitution reaction as the following mechanism depicts:



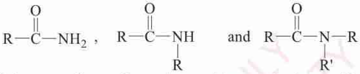
The carbon in the carbonyl group only becomes susceptible to nucleophilic attack after the formation of the phosphonyl bond (stage IV). Then the chloride ion attacks the carbon liberating phosphoryl trichloride ($POCl_3$).

Example:



Formation of acid amides

Acid amides are derivatives of carboxylic acids with the following general structural formulae:

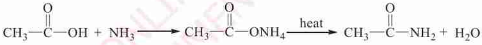


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2\ ,\quad R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R}{|}}{NH}\quad \text{and}\quad R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R'}{|}}{N}-R$$

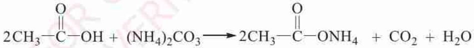
Primary amide Secondary amide Tertiary amide

Primary amides can simply be prepared from carboxylic acids by treating the acids with ammonia or ammonium carbonates. In this reaction, the carboxylic acid is first converted into an ammonium salt of the carboxylic acid, which on heating, yield an amide.

Examples:

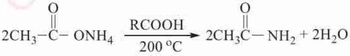


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4 \xrightarrow{\text{heat}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2O$$



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + (NH_4)_2CO_3 \longrightarrow 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4 + CO_2 + H_2O$$

Adding excess carboxylic acid;

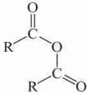


$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4 \xrightarrow[200\ ^{o}C]{RCOOH} 2CH_3\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + 2H_2O$$

Excess carboxylic acid (RCOOH) is added to prevent dissociation of ammonium salt before it dehydrates.

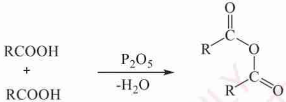
Formation of acid anhydride

Acid anhydrides are organic compounds derived from the dehydration of two molecules of carboxylic acid.



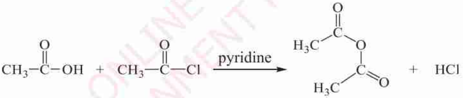
where R can be an alkyl or aryl group.

When two molecules of carboxylic acid are heated and the vapours passed over P_2O_5, one molecule of water is eliminated, resulting in the formation of acid anhydride.



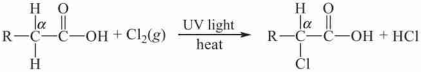
Carboxylic acid　　Acid anhydride

Acid anhydride can also be obtained by reacting carboxylic acid and acid chloride in the presence of pyridine. Pyridine facilitates the reaction by combining with the produced HCl [Acid sponge/trapper].



Free radical substitution of α-hydrogen

Hydrogen atoms which are bonded to the carbon atom which is directly bonded to the carbon of the carbonyl group are known as α-hydrogen. The bubbling of chlorine gas through a hot carboxylic acid in the presence of ultra violet light, results into the replacement of α-hydrogen atom with chlorine atom. The reaction can be represented by the following equation.



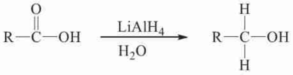
$$R-\underset{H}{\overset{H}{\underset{|}{\overset{|\alpha}{C}}}}-\overset{O}{\overset{\|}{C}}-OH + Cl_2(g) \xrightarrow[\text{heat}]{\text{UV light}} R-\underset{Cl}{\overset{H}{\underset{|}{\overset{|\alpha}{C}}}}-\overset{O}{\overset{\|}{C}}-OH + HCl$$

2-chlorocarboxylic acid

The reaction can proceed until all α-hydrogen atoms are completely substituted by chlorine.

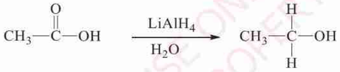
Reduction

Carboxylic acids undergo reduction only by strong nucleophilic reducing agents such as hydride ions of lithium aluminium hydride ($LiAlH_4$). The product is always a primary alcohol. Weak (mild) reducing agents such as $NaBH_4$ will not reduce the acid.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[H_2O]{LiAlH_4} R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

Example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[H_2O]{LiAlH_4} CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

7.1.5 Uses and hazards of carboxylic acids

Carboxylic acids are useful in our daily life and mostly in the industries. However, they can still pose serious health hazards.

Uses of carboxylic acids

They are used as preservatives (sorbic acid and benzoic acid), as main ingredients of common vinegar (acetic acid), acidulant in carbonated beverages and foods (citric acid and lactic acid). Carboxylic acids are also used as antipyretic and analgesic (acetylsalicylic acid), active for the manufacture of medicines based on vitamin C (ascorbic acid), fungicide (caprylic acid), manufacture of some laxatives (hydroxybutanedioic acid). Other uses are in the manufacture of toothpaste (e.g salicylic acid), production of perfumes (e.g benzoic acid) and manufacture of polyester (e.g terephthalic acid)

Hazards of carboxylic acids

Some carboxylic acids are highly corrosive to the skin and eyes. Others can damage internal organs if ingested or inhaled. Low molecular weight carboxylic acids have relatively wide flammability limits thus considered as moderate fire hazards.

Exercise 7.1

1. The following names of organic compounds are incorrect according to the IUPAC system of naming chemical compounds:

   (a) 3,6-diethylheptanoic acid.

   (b) 2,2-dimethylethanoic acid.

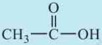
   (c) Butanedioic acid.

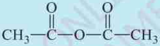
   (d) 2-methyl-2-phenylethanoic acid

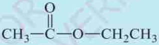
      (i) Write a structural formula and the correct IUPAC name for each compound.

      (ii) In each case, state which rule was initially violated.

2. Suppose you are provided with bromoethane as the only organic compound, usual facilities of a school chemistry laboratory and any inorganic reagents required. Give the names of the reagents, reaction conditions and the structures of the intermediate compounds formed when preparing each of the following compounds:

(a) 
$\mathrm{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$

(b) 
$\mathrm{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}$

(c) 
$\mathrm{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2CH_3}$

(d) 
$\mathrm{Br-\underset{\displaystyle Br}{\overset{\displaystyle Br}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$

3. The following scheme shows the outline of a synthesis of butanoic acid:


$\mathrm{CH_3-CH_2-CH_2-Br \xrightarrow{I} J \xrightarrow{II} CH_3-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$

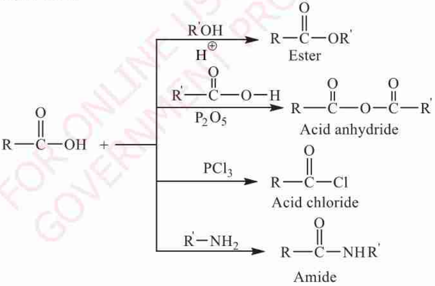
(a) Suggest the reagents and conditions for reactions **I** and **II**.

(b) Draw the structural formula of the intermediate product **J**.

4. Mention two uses for each of the compounds:
   (a) Benzene carboxylic acid
   (b) Ethanedioic acid
   (c) Ethanoic acid
   (d) Methanoic acid
   (e) Benzene-1,2-dicarboxylic acid
   (f) Fatty acid

7.2 Derivatives of carboxylic acids

The derivatives of carboxylic acids are formed if the hydroxyl group of the carboxylic acid is replaced with other functional groups such as –OR, –OCOR, –Cl, and –NH_2; the compounds formed are esters, acid anhydrides, acid chlorides, and acid amides, respectively. The scheme below illustrates the carboxylic acid derivatives which are obtained after the replacement of hydroxyl (–OH) group of the carboxylic acids.



where R can be either an alkyl or aryl group.

In this section, only esters will be discussed. Therefore you will learn about the IUPAC naming, preparations, properties uses, and hazards of esters.

Esters are organic compounds which are obtained by replacing the hydroxyl (–OH) group of carboxylic acids by – OR'. In the laboratory, they can be synthesised by reacting carboxylic acids with alcohols to form esters and water.

The fruity smell which is produced in this reaction is due to ester formation. Esters occur widely in nature as they are found in vegetable oils, fats, waxes, and cork. The flavours of many fruits such as pineapple and others are due to esters. Table 7.2 shows a list of some fruits with their corresponding esters.

Table 7.2 Some fruits and their respective flavours

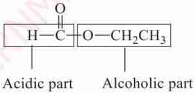
Fruit	Ester
Orange	Octyl ethanoate
Banana	Isopentyl acetate
Apple	Ethyl ethanoate
Pineapple	Ethyl butanoate
Apricot	Pentyl butanoate

Note: A fruit can have more than one ester

7.2.1 IUPAC naming of esters

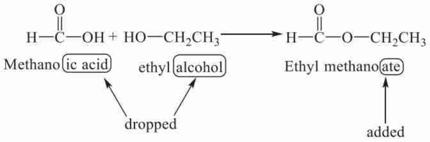
When esters are named using the IUPAC system, the alcohol and acid parts of its molecule should be identified. The alkyl or aryl part of the alcohol or phenol is named first followed by the acid part but the suffix-*ic* and the word *acid* is replaced by the suffix *-ate.*

Example:



$$\boxed{H-\overset{\overset{O}{\|}}{C}}\boxed{O-CH_2CH_3}$$

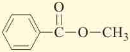
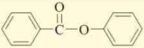
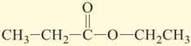
The ester above is obtained from methanoic acid and ethyl alcohol or ethanol. Thus, the name of the ester is obtained by first naming the alkyl part of the alcohol which is ethyl ($-CH_2CH_3$) followed by carboxylic acid part but the ending *ic* and the word *acid* is dropped to get methanoate.



$$H-\overset{\overset{O}{\|}}{C}-OH + HO-CH_2CH_3 \longrightarrow H-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$$

The names of some esters are given in Table 7.3.

Table 7.3 Nomenclature of some esters

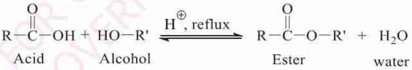
Structural formula	IUPAC system
	Methyl benzoate
	Phenyl benzoate
 $CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3$	Ethyl propanoate

7.2.2 Preparation of esters

Esters can be prepared using a variety of methods. The following methods are commonly used to prepare esters in the laboratory:

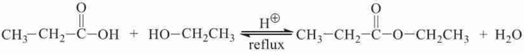
Reactions of carboxylic acids with alcohols

The alkoxy (–OR) from an alcohol molecule replaces the hydroxyl (–OH) of a carboxylic acid molecule and a molecule of water is eliminated. This method is commonly known as esterification. The following general equation represents the esterification reaction between an acid and alcohol:



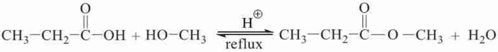
$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Alcohol}}{HO-R'} \xrightleftharpoons{H^{\oplus},\ \text{reflux}} \underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'} + \underset{\text{water}}{H_2O}$$

Examples:



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-CH_2CH_3 \xrightleftharpoons[\text{reflux}]{H^{\oplus}} CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 + H_2O$$

Ethyl propanoate

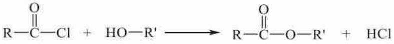


$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-CH_3 \xrightleftharpoons[\text{reflux}]{H^{\oplus}} CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 + H_2O$$

Methyl propanoate

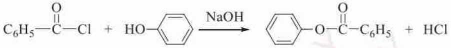
Reactions of acid chlorides or anhydrides with alcohols or phenols

At room temperature, acid chlorides react with alcohols or phenols to form esters. The reaction can be represented by the following general equation:



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-Cl \;+\; HO-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-R' \;+\; HCl}$$

If a compound containing active hydrogen such as phenol, alcohol, or aniline reacts with benzoyl chloride in the presence of aqueous NaOH, an ester is formed and this reaction is called *Schotten-Baumann reaction*.



Benzoyl chloride Phenol Phenyl benzoate

$$\mathrm{CH_3CH_2OH \;+\; C_6H_5COCl \xrightarrow{NaOH} CH_3CH_2OCOC_6H_5 \;+\; HCl}$$

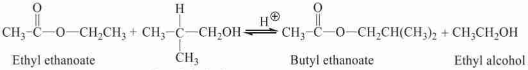
Ethyl alcohol Benzoyl chloride Ethyl benzoate

Transesterification

It is a reversible reaction in which one ester is converted into another by the interchange of alkoxy group of an ester with another alcohol in the presence of an acid or base catalyst. When an ester is treated with an alcohol that is different from the constituent alcohol part of the ester, a displacement reaction takes place, where the two alcohols are interchanged.

$$\mathrm{RCOOR' \;+\; HOR'' \xrightleftharpoons{H^{\oplus}} RCOOR'' \;+\; HOR'}$$

For example, ethyl ethanoate can be converted to butyl ethanoate as represented by the following reaction equation:



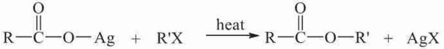
$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2OH \xrightleftharpoons{H^{\oplus}} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH(CH_3)_2 + CH_3CH_2OH}$$

Ethyl ethanoate Butyl alcohol Butyl ethanoate Ethyl alcohol

Since both the reactants and the products are an ester and an alcohol, the reaction is reversible and the equilibrium constant is almost equal to one. The principle factor affecting the equilibrium position is the relative concentrations of the two alcohols.

Heating silver salt of an acid with an alkyl halide

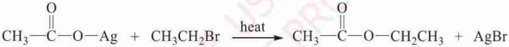
Once a mixture of silver salt of a carboxylic acid and an alkyl halide is heated, it yields an ester. The following general equation represents this reaction:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-Ag + R'X \xrightarrow{\text{heat}} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + AgX$$

Silver salt of an acid　Alkyl halide　Ester　Silver halide

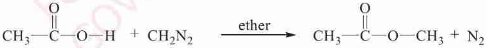
Example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-Ag + CH_3CH_2Br \xrightarrow{\text{heat}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 + AgBr$$

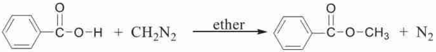
Reaction of a carboxylic acid with diazomethane

A mixture of carboxylic acid and diazomethane in ether reacts to yield an ester and nitrogen gas is liberated. This reaction can be presented by the following equations:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + CH_2N_2 \xrightarrow{\text{ether}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 + N_2$$

Ethanoic acid　Diazomethane　Methyl ethanoate



Diazomethane　Methyl benzoate

Activity 7.3 Preparation of ethyl ethanoate

Requirements: Beakers, round bottomed flask, heat source, measuring cylinders, condensers, thistle funnel, wire gauze, separating funnel, delivery tubes, thermometer, ethanol, ethanoic acid, concentrated sulphuric acid, and distilled water.

Procedure

1. Measure 25 mL each of ethanoic acid and ethanol in a round bottomed flask.
2. Mix them thoroughly and then add 5 mL of concentrated sulphuric acid.
3. Attach the flask to a reflux condenser as shown in Figure 7.1 and heat the mixture for 10 minutes.
4. Distill and collect the product using condenser for simple distillation as illustrated in chapter five (Figure 5.2).
5. Put 2 mL of the product in a test tube and test its smell.

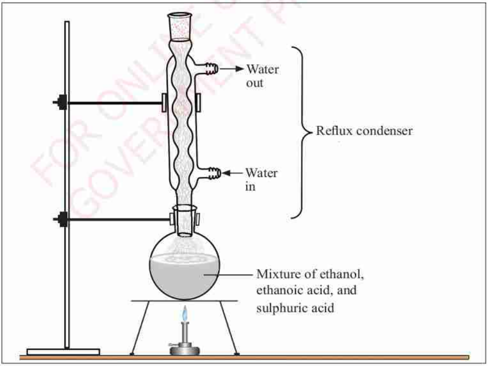


Figure 7.1 Reflux apparutus set up

Questions

1. Why is concentrated sulphuric acid used in this experiment?
2. Write the chemical equations for the reactions.
3. State the smell of the distillate.
4. Name the process investigated in this experiment.

7.2.3 Properties of esters

Esters like other chemical compounds exhibit properties which can be classified as physical and chemical properties.

Physical properties of esters

Esters of lower molecular masses are colourless, volatile liquids with fruity smell. Those with higher relative molecular masses have no odour and are faty or waxy-like substances. Esters are less dense than water. The solubility of esters is comparable to that of ketones, in other words, they are soluble in organic solvents such as alcohols and ethers. Compared to the corresponding carboxylic acids, esters have lower boiling points. This is because esters have no hydrogen bonding.

Chemical properties of esters

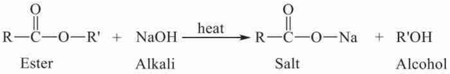
Esters undergo nucleophilic substitution reactions to produce carboxylic acids derivatives. An attack by a nucleophile occurs at the electron-deficient carbonyl carbon and results in the replacement of alkoxy ($-OR'$) group by hydroxyl ($-OH$) or amino ($-NH_2$) group. The electron deficiency at the carbonyl carbon atom which arises as a result of electron withdrawing effect is produced by the two oxygen atoms of the carboxylate group ($-COO-$). The resonance effect of the carboxylate ion, facilitate nucleophilic substitution of the alkoxy group ($-OR'$).

Nucleophilic substitution reactions exhibited by esters

Nucleophilic substitution reaction of esters is a type of reactions involving nucleophiles and acyl compounds. In this type of reaction, a nucleophile such as alcohol, amine or enolate displaces the leaving group of an ester. The resulting product is a carbonyl-containing compound in which the nucleophile has taken the place of the leaving group present in the original compound.

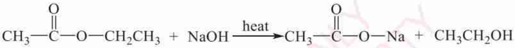
Hydrolysis in the presence of alkali or acid

In the presence of alkali, esters react to give alcohol or phenol and sodium or potassium salt of carboxylic acid. The base catalysed hydrolysis of esters is known as *saponification* (soap formation). The general reaction is represented by the following equation:



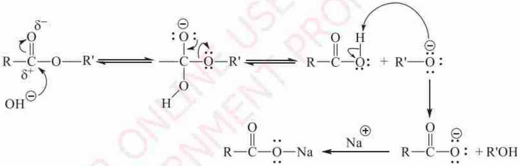
$$\underset{\text{Ester}}{\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R'}} + \underset{\text{Alkali}}{\mathrm{NaOH}} \xrightarrow{\text{heat}} \underset{\text{Salt}}{\mathrm{R-\overset{O}{\overset{\|}{C}}-O-Na}} + \underset{\text{Alcohol}}{\mathrm{R'OH}}$$

Example:

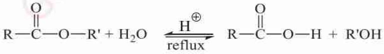


$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + NaOH \xrightarrow{heat} CH_3-\overset{O}{\overset{\|}{C}}-O-Na + CH_3CH_2OH}$$

Mechanism for this reaction is shown by the following scheme:



In the presence of an acid, esters react with water under reflux to give an alcohol and a carboxylic acid as shown in the following reaction equation:

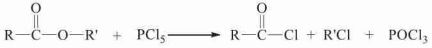


$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O \underset{reflux}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-H + R'OH}$$

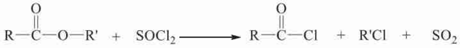
The mechanism of acid catalysed hydrolysis of esters is the reverse of that of esterification or ester formation.

Reaction of esters with PCl_5 or $SOCl_2$

When treated with PCl_5 or $SOCl_2$, esters are converted into acid chlorides. The reaction can be represented by the following equations:

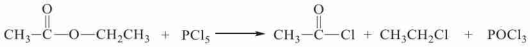


$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R' + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + R'Cl + POCl_3}$$

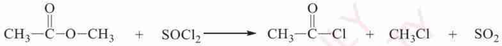


$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R' + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + R'Cl + SO_2}$$

Examples:



$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + PCl_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3CH_2Cl + POCl_3}$$



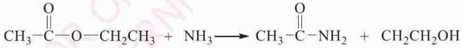
$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3Cl + SO_2}$$

Reaction of esters with ammonia

Esters react with concentrated or alcoholic ammonia to form amides as shown in the following chemical reaction equation:

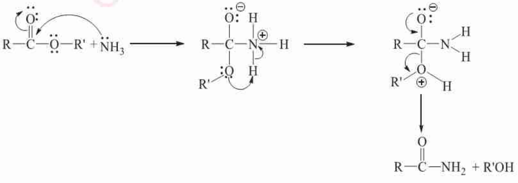
$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R' + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R'OH}$$

Example:



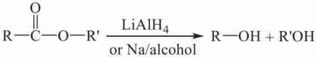
$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + CH_2CH_2OH}$$

Mechanism for this reaction is shown by the following scheme:



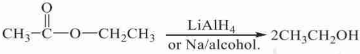
Reduction to alcohols

When treated with sodium metal and alcohols or with a strong reducing agent such as $LiAlH_4$, esters get reduced to primary alcohols. The reaction can be represented by the following equation:



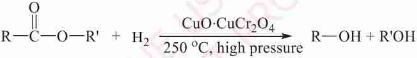
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' \xrightarrow[\text{or Na/alcohol}]{LiAlH_4} R-OH + R'OH$$

Example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 \xrightarrow[\text{or Na/alcohol.}]{LiAlH_4} 2CH_3CH_2OH$$

Esters can also be reduced by catalytic hydrogenation method. The reaction takes place under the conditions of high pressure, temperature of about 250 °C and $CuO{\cdot}CuCr_2O_4$ catalyst. The general reaction equation for this reaction is given by the following equation:

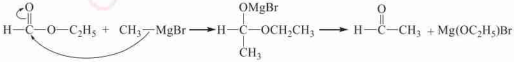


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2 \xrightarrow[250\ ^{o}C,\ \text{high pressure}]{CuO{\cdot}CuCr_2O_4} R-OH + R'OH$$

Reaction with Grignard reagents

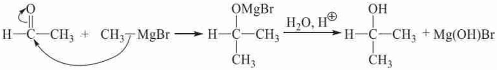
On reacting with Grignard reagents, esters of formic acid give secondary alcohols while those of other acids give tertiary alcohols. The mechanism of the reaction is depicted by the following scheme.

The first case is the reaction between ethyl methanoate and methylmagnesium bromide.



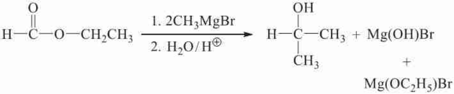
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 + CH_3-MgBr \longrightarrow H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}-OCH_2CH_3 \longrightarrow H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + Mg(OC_2H_5)Br$$

The produced aldehyde reacts with methylmagnesium bromide;



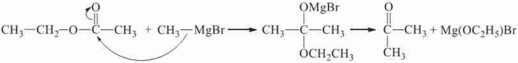
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-MgBr \longrightarrow H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}-CH_3 \xrightarrow{H_2O,\ H^{\oplus}} H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + Mg(OH)Br$$

This reaction can be summarised in the following equation:



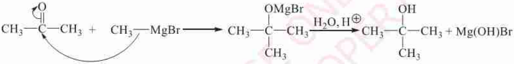
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 \xrightarrow[\text{2. } H_2O/H^{\oplus}]{\text{1. } 2CH_3MgBr} H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + Mg(OH)Br + Mg(OC_2H_5)Br$$

The second case is the reaction between ethyl ethanoate and methyl magnesium bromide.



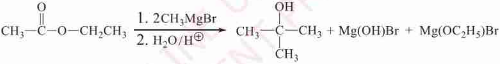
$$CH_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-MgBr \longrightarrow CH_3-\underset{\underset{\displaystyle OCH_2CH_3}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}-CH_3 \longrightarrow \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}}-CH_3 + Mg(OC_2H_5)Br$$

The produced ketone reacts with CH_3MgBr:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-MgBr \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}-CH_3 \xrightarrow{H_2O,\, H^{\oplus}} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + Mg(OH)Br$$

The reaction can be summarised in one equation:

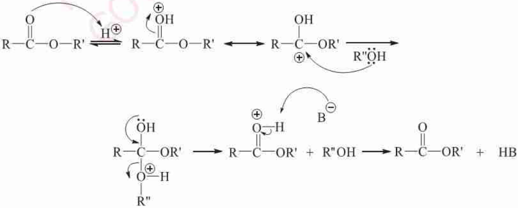


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3 \xrightarrow[\text{2. } H_2O/H^{\oplus}]{\text{1. } 2CH_3MgBr} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + Mg(OH)Br + Mg(OC_2H_5)Br$$

Transesterification

These reactions are often catalysed by the addition of an acid or base. The following scheme describes the mechanism of the reaction.

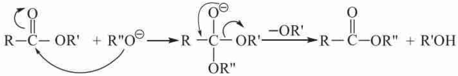
Acid catalysed reaction



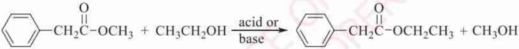
whereby B is a conjugate base and HB is an acid catalyst

Base catalysed reaction

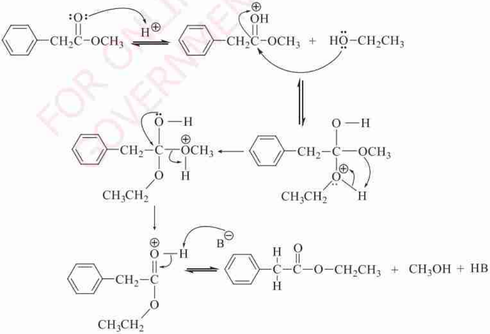
$$\begin{tikzcd}
R''OH + NaOH \arrow[r] & R''ONa + H_2O \arrow[d] \\
& R''O^{\ominus} + Na^{\oplus}
\end{tikzcd}$$



Transesterification is used to prepare complex esters which cannot be prepared by normal esterification. In biodiesel production, vegetable or animal oils are transesterified with methanol and sodium hydroxide to form biodiesel.

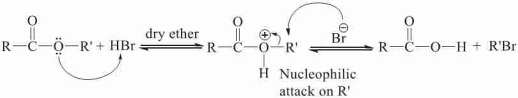


The mechanism for this reaction under acidic condition is given in the following equation:



Cleavage of carboxylate group

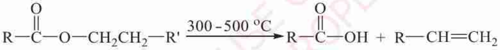
Cleavage of carboxylate group is another reaction which is exhibited by esters. When esters are treated with dry hydrogen bromide, concentrated aqueous hydrogen iodide or concentrated sulphuric acid, they break down to produce carboxylic acid.



$$R-\overset{O}{\overset{\|}{C}}-\ddot{O}-R' + HBr \xrightleftharpoons{\text{dry ether}} R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{\oplus}{O}}}-R' \xrightleftharpoons{\overset{\ominus}{Br}} R-\overset{O}{\overset{\|}{C}}-O-H + R'Br$$

Pyrolysis

This is another reaction which is exhibited by esters. When heated to temperature of 300 –500 °C, esters undergo cracking to produce carboxylic acids and alkenes. The reaction equation represents the pyrolytic cracking or breaking to yield an acid and alkene. This reaction takes place at high temperature.



$$R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-R' \xrightarrow{300-500\ ^{\circ}C} R-\overset{O}{\overset{\|}{C}}-OH + R-CH=CH_2$$

7.2.4 Uses and hazards of esters

Uses of esters

Naturally occurring and synthetic esters are used in the fragrance industries to add fruity, floral and herbal odours to foods, cosmetics, household, deodorisers, and medicines. Some lower esters are used as solvents for nitrocellulose and resins varnishes. Diesters of benzene-1,2-dicarboxylic acid are the most important plasticisers (softeners) for PVC plastics.

Higher esters such as fats and oils are important nutrients in human diet. Fats serve as the body's energy reserve giving out heat when oxidised to maintain body temperatures. Fats and oils are also used as raw materials for making soap, candles, and lubricants.

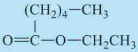
Waxes and cork are also esters of high relative molecular masses. Waxes are used to make candles, soaps, ointments, polishes, waxes models, and wax boutiques. Cork of the oak tree is used mainly for making bottle corks.

Hazards of esters

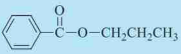
Esters have low to moderate toxicity via dermal and oral exposure. They are highly flamable and can yield highly toxic gases such as carbon monoxide. Also esters form explosive mixture with air and cause *narcotic* effect and their vapours are irritant to the eyes and mucous membrane.

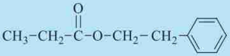
Exercise 7.2

1. (a) You are given the following three esters:

(i) 

$$O{=}\overset{\overset{\displaystyle (CH_2)_4{-}CH_3}{|}}{C}{-}O{-}CH_2CH_3$$

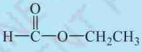
(ii) 

(iii) 

Draw the structures of the carboxylic acids and alcohols portions from which the esters were made.

(b) Give the IUPAC names of all compounds in (a) above.

2. Compound **M** which is commonly added to foods to give them the rum flavour has the following structural formula:



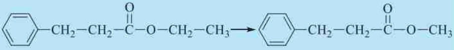
$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2CH_3$$

(a) To which class of organic compounds does compound **M** belong?

(b) How would you synthesise compound **M** from ethanol, methanol, and any other inorganic reagents?

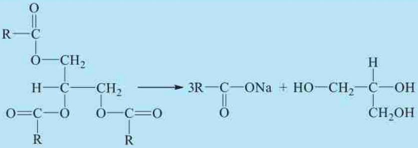
(c) Give the IUPAC name of compound **M**.

3. What are the necessary conditions required to effect the following conversions?

(a) 

(b) Methyl ethanoate ⟶ 3-methylpentan-3-ol

(c)



(d) Give the common names for the reactions (a) and (b) above.

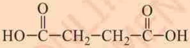
4. (a) Explain how the resonance structure of the carboxylate ion facilitates nucleophilic substitution reactions in esters.

   (b) Why esters have lower melting and boiling points compared to the corresponding carboxylic acids?

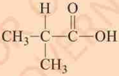
5. With specific examples, mention at least eight uses of esters in the daily life.

Revision exercises 7

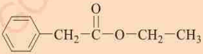
1. (a) Give a systematic IUPAC name for each of the following compounds:

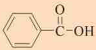
(i) 

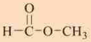
$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

(ii) 

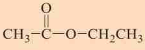
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$

(iii) 

(iv) 

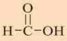
(v) 

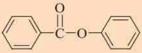
$H-\overset{\overset{O}{\|}}{C}-O-CH_3$

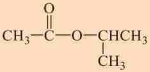
(vi) 

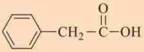
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$

(b) Identify the functional group and classify each of the following into their respective family of organic compounds:

(i) 
$H-\overset{\overset{O}{\parallel}}{C}-OH$

(ii) 

(iii) 
$CH_3-\overset{\overset{O}{\parallel}}{C}-O-\underset{\underset{CH_3}{|}}{C}HCH_3$

(iv) 

2. (a) Draw the expanded structural formula of the compounds with the following IUPAC names:
   (i) Ethanedioic acid
   (ii) Phenyl benzoate
   (iii) 2-chloro-2-methylpropanoic acid
   (iv) Methyl methanoate

   (b) Write the structural formula for the ester and carboxylic acid with the molecular formula, $C_2H_4O_2$ and give the IUPAC name of each compound.

   (c) Explain, with reason(s), which of the two compounds in (b) above has a higher boiling point.

3. (a) Why are the lower members of carboxylic acids soluble in water while higher members are insoluble in water?

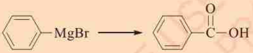
   (b) Carboxylic acids show higher boiling points compared to alcohols of comparable molecular masses. Explain.

   (c) The table below shows melting points of some monocarboxylic acids:

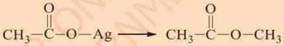
Name	Condensed structural formula	Melting point, °C
Methanoic acid	HCOOH	8
Ethanoic acid	CH_3COOH	17
Propanoic acid	CH_3CH_2COOH	–21
Butanoic acid	$CH_3CH_2CH_2COOH$	–6
2-methylpropanoic acid	$CH_3CH(CH_3)COOH$	–43
Pentanoic acid	$CH_3CH_2CH_2CH_2COOH$	–35
Hexanoic acid	$CH_3CH_2CH_2CH_2CH_2COOH$	–3

Account for the observed irregularity in the melting points of the carboxylic acids.

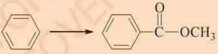
4. By means of equations, show how the following conversions may be achieved in not more than four steps:

(a) 

(b) 

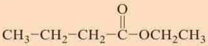
(c) 

$$CH_3-\overset{\overset{\Large O}{\|}}{C}-O-Ag \longrightarrow CH_3-\overset{\overset{\Large O}{\|}}{C}-O-CH_3$$

(d) 

5. (a) Esters of carboxylic acids are often used as components of synthetic fruit flavours.

Ethyl butanoate **Q** is a major component of the strawberry and pineapple flavouring.

Q = 

$$CH_3-CH_2-CH_2-\overset{\overset{\Large O}{\|}}{C}-OCH_2CH_3$$

What reagents and conditions are needed to convert **Q** to form butanoic acid?

(b) Predict the products of the reaction when **Q** in (a) above is heated strongly in the absence of air.

6. Write a balanced chemical equation for each of the following reactions:
   (a) Propanoic acid with sodium hydroxide
   (b) Butanoic acid with sodium carbonate
   (c) Sodium methanoate with hydrochloric acid
   (d) Sodium ethanoate with sulphuric acid
   (e) 2-methylpropanoic acid with sodium carbonate

7. An unknown ester, **E** was found to have molecular formula $C_5H_{12}O_2$. When **E** was hydrolysed with water in the presence of mineral acid, it produced carboxylic acid, **A** and alcohol, **B**. The treatment of **B** with $SOCl_2$ gave an alkyl chloride, **C**. When **C** was treated with KCN, a product **D** was formed which on hydrolysis with water and acid produced carboxylic acid, **A**.
   (a) Use this information to deduce the structure and name of the original ester.
   (b) Identify **A** through **D** and write the chemical equations for the reactions involved.

8. Compounds **F**, C_3H_7Br react with magnesium metal in dry ether and subsequently the mixture of the reaction was treated with carbon dioxide and dilute acid to give compound **G** whose molecular formula is $C_4H_8O_2$. Compound **G**, turns a blue litmus paper red and liberates carbon dioxide gas from an aqueous solution of sodium hydrogen carbonate. When compound **F** is treated with aqueous sodium hydroxide it produces **H**, which when treated with iodine in alkaline solution it gives yellow crystals.
   (a) Identify compounds **F**, **G**, and **H** and write their structural formula.
   (b) Write the chemical equations for all the reactions involved.

9. Account for the following observations:
   (a) Methanoic acid is stronger than ethanoic acid.
   (b) Chloroethanoic acid is stronger than ethanoic acid.

(c) 4-hydroxybenzoic acid is less acidic than benzoic acid but 2-hydroxybenzoic acid is 15 times more acidic than benzoic acid.

(d) Esterification of benzoic acid is easier than that of 2,6-dimethylbenzoic acid.

10. Complete the following reaction equations in symbolic form:

(a) Propanoic acid + sulphur dichloride oxide $\longrightarrow$

(b) Butanoyl chloride + butan-1-ol $\longrightarrow$

(c) Propanamide + sodium nitrite + hydrochloric acid $\longrightarrow$

(d) 2-methylpropanoic acid + diazomethane $\longrightarrow$

11. A sample of 3-phenylpropanoic acid was mixed with a small quantity of phosphorous pentachloride and the mixture was warmed and stirred in the evaporating dish until the reaction was completed.

(a) Write the equation for the reaction and the name of the organic products of the reaction.

(b) Explain why most carboxylic acids will not form esters without acid catalysts.

(c) Show the general mechanism for the hydrolysis of ethanoyl chloride.

12. State at least one commercial use for each of the following compounds:

(a) Ethanoic acid

(b) Fats and oils

(c) Benzene-1,2-dicarboxylic acid

(d) Ethanedioic acid

(e) Methanoic acid

(f) Cork

Chapter Eight Amines

Introduction

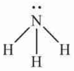
Amines are basic organic compounds that contain nitrogen as the main constituent of their functional group ($-NH_2$). They are defined as a derivatives of ammonia in which one or more atoms of hydrogen are replaced by alkyl or aryl groups. Amines occur widely in plants and animals as important component of proteins. They are found in the form of amino acids, proteins, and nucleic acids such as DNA and RNA. In this chapter, you will learn about the structures, classification, nomanclature, preparation, properties, uses and hazards of amines.

8.1 Structure, classification, and nomenclature of amines

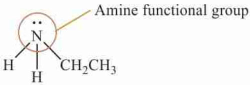
Amines can be regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by the alkyl or aryl groups and have different structures which possess various properties. They can be named either by using common or IUPAC systems. In this section, you will learn about the structure, classification, and nomenclature of amines.

8.1.1 Structure of amines

In alphatic amines, both nitrogen and carbon atoms are sp^3 hybridised and according to the VSEPR theory, the amine has trigonal pyramidal shape where the nitrogen atom is at the apex and the lone pair of electrons above it. For example, in ethylamine, one hydrogen of ammonia has been replaced by ethyl group.

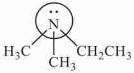


Ammonia



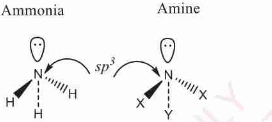
Alkylamine

In ethyldimethylamine, the three hydrogen atoms of ammonia have been replaced by two methyl groups and an ethyl group.



Ethyldimethylamine

Like in ammonia, the nitrogen atom of the amine has sp^3 hybridised orbitals arranged in a trigonal pyramidal geometry as shown in Figure 8.1.



X and Y can be H, R or Ar

Figure 8.1 sp^3-hybridised nitrogen in ammonia and amine

Each of the three sp^3 hybridised orbitals in nitrogen can overlap with orbitals of hydrogen or carbon of alkyl or aryl group depending on the composition of the amine. The fourth orbital of amines contain lone pair of electrons and because of this lone pair, amines act as Brønsted-Lowry bases by donating electrons during covalent bond formation.

8.1.2 Classification of amines

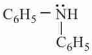
Amines are classified on the basis of the number and nature of the groups attached to nitrogen atom in place of hydrogen.

Classification based on the number of groups attached to the nitrogen atom

On this basis, amines are classified as primary (1º), secondary (2º), and tertiary (3º) amines when one, two, and three hydrogens of ammonia respectively, are substituted by aryl (C_6H_5-) and or alkyl ($C_nH_{(2n+1)}$) group(s); where n = 1, 2, 3, and so on. Examples of the three classes of amines are:

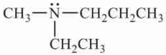
$CH_3-CH_2-\ddot{N}H_2$

Primary (1º) amine



$$C_6H_5-\underset{\displaystyle C_6H_5}{\underset{|}{\ddot{N}}}H$$

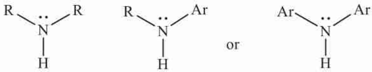
Secondary (2º) amine

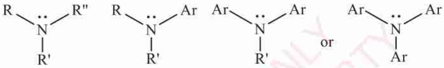


$$CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{\ddot{N}}}-CH_2CH_2CH_3$$

Tertiary (3º) amine

The alkyl groups are represented by symbol R and the aryl group by the symbol Ar. That is to say amines can have either one of the two groups or both groups attached to nitrogen in which case the former are called *simple amines* and the latter are called *mixed amines*. The structures below show the replacement of hydrogen atoms of ammonia by R-alkyl and Ar-aryl groups.





Classification based on the nature of the groups attached to the nitrogen atom

In this type of classification, amines are classified as *aliphatic amines* when there is one or more alkyl groups attached to the nitrogen atom. An attachment of one or more aryl groups to the nitrogen atom leads to *aromatic amines* or arylamines. Below are examples of amines classified under these groups.

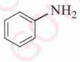
Aliphatic

$CH_3CH_2NH_2$ Ethanamine

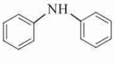
$CH_3CH_2NHCH_3$ *N*-Methylethanamine

$CH_3CH_2N(CH_3)_2$ *N*, *N*-Dimethylethanamine

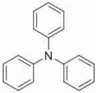
Aromatic



Phenylamine

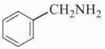


Diphenylamine



Triphenylamine

Mixed



Phenylmethanamine

Dibenzylamine

8.1.3 Nomenclature of amines

Amines are named by using two systems; the common system and the IUPAC system.

Common system

The rules applied in assigning names for common system are:

1. Under the common system, the name of the alkyl group is given first (prefixed) followed by the word amine as a single continuous name that is alkylamine.

   Examples:

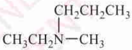
CH_3NH_2	$CH_3CH_2NH_2$	$CH_3CH_2CH_2NH_2$
Methylamine	Ethylamine	Propylamine

2. When two or three different substituent groups (alkyl groups) are present on nitrogen atom, amines are named following the alphabetical order.

   Examples:

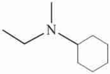
$CH_3CH_2NHCH_3$

Ethylmethylamine



$$CH_3CH_2\overset{\displaystyle CH_2CH_2CH_3}{\overset{|}{N}}-CH_3$$

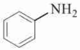
Ethylmethylpropylamine



Cyclohexylethylmethyl amine

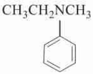
3. For the case of arylamines, the simplest member is aniline, $ArNH_2$ from which all other aromatic amines derive their names. The position of the substituent group is indicated by *N*.

   Examples:



Aniline

N-methylaniline



N-ethyl-*N*-methylaniline

4. When two or more alkyl or aryl groups present on nitrogen are the same, the prefixes *di*- or *tri*- are used before the name of the alkyl or aryl groups.

Examples:

$CH_3\ddot{N}HCH_3$
Dimethylamine

$CH_3\ddot{N}(CH_3)_2$
Trimethylamine

$CH_3\ddot{N}(CH_3CH_2)_2$
Diethylmethylamine

N,*N*-Dimethylaniline

IUPAC system

The IUPAC rules for naming amines are:

1. In IUPAC system, aliphatic amines are named by replacing the *-e* of the parent alkane by the suffix amine. That is from alkan*e* to alkan*amine*. When the amino group ($-NH_2$) is attached at different positions of the parent alkane chain, then its position is indicated by a numeral number.

   Examples:

   CH_3NH_2
   Methanamine

   $CH_3CH_2NH_2$
   Ethanamine

   $CH_3CH_2CH_2NH_2$
   Propan-1-amine

   $CH_3CH(NH_2)CH_3$
   Propan-2-amine

   $CH_3CH{=}CHCH_2NH_2$
   But-2-en-1-amine

   $CH_3CH(NH_2)CH_2CH_3$
   Butan-2-amine

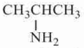
2. When there are more than one amino groups, the prefixes *di-* or *tri-* or *tetra-*are used before the word amine.

   Examples:

   $NH_2CH_2CH_2CH_2NH_2$
   Propan-1,3-diamine

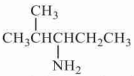
3. In alkyl amines with substituent groups, the parent chain is the one having the amino group and its position is indicated by the numeral prefix. The numbering is done in such a way that the amino group contains the lowest number of carbon bearing it.

   Examples:



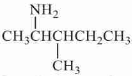
$$CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$$

Propan-2-amine



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2CH_3$$

2-methylpentan-3-amine



$$CH_3\overset{\displaystyle NH_2}{\overset{|}{C}}H\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

3-methylpentan-2-amine

4. The secondary and tertiary amines are considered as the derivatives of primary amines which contain the largest alkyl group. In this case, the position of the groups attached to nitrogen is numbered *N*.

Examples:

$CH_3CH_2NHCH_3$

N-methylethanamine

$CH_3CH_2\underset{\displaystyle NHCH_3}{\underset{|}{C}H}CH_2CH_3$

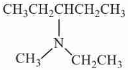
N-methylpentan-3-amine

$CH_3CH_2N(CH_3)_2$

N,N-dimethylethanamine

$CH_3CH_2\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}H}CH_3$

N,N-dimethylbutan-2-amine



$CH_3CH_2\underset{\displaystyle CH_3\diagup\overset{}{N}\diagdown CH_2CH_3}{\underset{|}{C}H}CH_2CH_3$

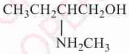
N-ethyl-*N*-methylpentan-3-amine

5. In cases where the molecule contains groups with higher priority than the amine such as carboxylic, alcohol, amide, nitrile, aldehyde, ketone, and thiol the amino group is named as the substituent group.

   Examples:

   $NH_2CH_2CH_2COOH$

   3-aminopropanoic acid

   $CH_3CH_2\underset{\displaystyle NH_2CH_3}{\underset{|}{C}H}CH_2OH$

   2-amino-*N*-methylbutan-1-ol

6. Aromatic amines are named by considering the name of the aryl group followed by the name amine, in which case the later -*e* of benzene is replaced by the word amine to read benzenamine which is the simplest member. Other aromatic amines are considered to be its derivatives and the position of substituent group is indicated by *N*.

   Examples:

Aniline

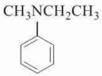
(Benzenamine)

N-methylaniline

(*N*-methylbenzenamine)

N,N-dimethylaniline

(*N,N*-dimethylbenzenamine)

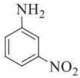


N-ethyl-*N*-methylaniline

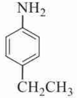
(*N*-ethyl-*N*-methylbenzenamine)

7. When substituent groups are present on benzene ring, the carbon containing the highest priority group is assigned number one.

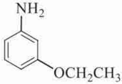
Examples:



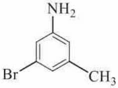
3-nitroaniline



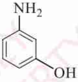
4-ethylaniline



3-ethoxyaniline



3-bromo-5-methylaniline

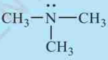


3-aminophenol

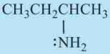
Exercise 8.1

1. Classify the following as primary (1°), secondary (2°) or tertiary (3°) amine:

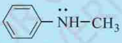
(a) $CH_3CH_2CH_2\ddot{N}H_2$

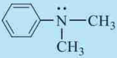
(b) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\ddot{N}}}-CH_3$

(c) 

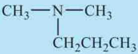
$CH_3CH_2\underset{\displaystyle :NH_2}{\underset{|}{C}}HCH_3$

(d) 

(e) 

2. Provide the common and IUPAC names of the following compounds:

(a) CH_3NH_2

(b) 

$CH_3-\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{N}}-CH_3$

(c) 

$CH_3CH_2CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$

3. Draw the structures of the following molecules:

(a) *N*–methyl–2–propanamine.

(b) 1,6–diaminohexane.

(c) *N,N*–dimethylaniline.

4. (a) Draw the structures of *N,N*-dimethylaminomethane and *N*-ethyl-*N*-methylaminoethane.
   (b) Classify the structures in (a) as either simple or mixed amines.
5. Discuss various classification criteria for amines.

8.2 Preparation and properties of amines

Amines can be prepared using different methods and the properties shown by these compounds are very different. In this section, you will learn about the preparation and properties of amines.

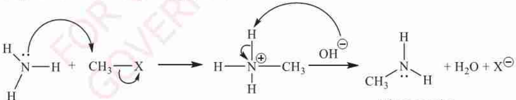
8.2.1 Preparation of amines

The common methods for preparing amines include; alkylation of ammonia, reduction of either amides or nitro compounds, and reductive amination of aldehydes and ketones.

Alkylation of ammonia

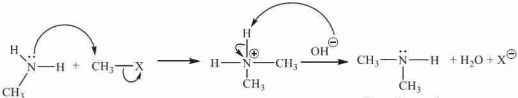
The reaction between ammonia and alkyl halide is a nucleophilic substitution reaction (S_N) where an alkyl ammonium salt is formed which when treated with strong base forms amine. The reaction is carried out either by allowing the reactants to stand together at room temperature or by heating them under pressure. The product formed is a primary amine. The formed primary amine can further react with the available alkyl halide to form secondary or even tertiary amine as shown below.

Step 1: Formation of primary amine



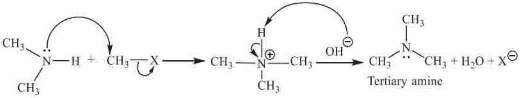
Primary amine

Step 2: Formation of secondary amine



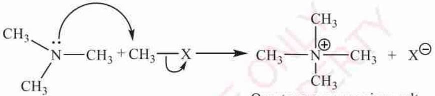
Secondary amine

Step 3: Formation of tertiary amine



In the above reaction mechanisms, X represents any group seven element in the periodic table.

When a tertiary amine reacts with an alkyl halide, a quarternary ammonium salt is formed, which can not undergo further nucleophilic substitution reaction due to absence of replaceable hydrogen.

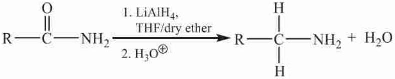


Quartenary ammonium salt

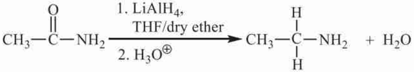
It is worth to note that aryl halides do not undergo simple nucleophilic substitution reactions because of the extra strength of the carbon-halogen bond. For example, in chlorobenzene there is an interaction between one of the lone pairs on the chlorine atom and the delocalised ring electrons, and this strengthens the bond. The mechanisms shown above involve breaking the carbon-halogen bond at some stage. The more difficult it is to break, the slower the reaction will be. Therefore, arylamines can not be prepared by this method.

Reduction of amide with $LiAlH_4$

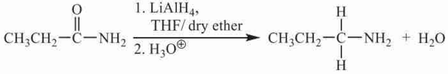
Amides yield primary amines on reduction with lithium aluminium hydride. This reaction is carried out under diethylether or tetrahydrofuran (THF) followed by hydrolysis in acidic medium. Under this reaction; primary, secondary, and tertiary amides are converted into their corresponding amines as shown below.



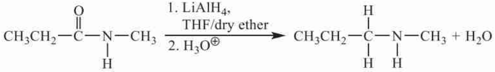
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ LiAlH_4,\ THF/dry\ ether} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-NH_2 + H_2O$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ LiAlH_4,\ THF/dry\ ether} CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-NH_2 + H_2O$$



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{2. } H_3O^{\oplus}]{\text{1. LiAlH}_4\text{, THF/ dry ether}} CH_3CH_2-\underset{H}{\overset{H}{C}}-NH_2 + H_2O$$



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_3 \xrightarrow[\text{2. } H_3O^{\oplus}]{\text{1. LiAlH}_4\text{, THF/dry ether}} CH_3CH_2-\underset{H}{\overset{H}{C}}-\underset{H}{N}-CH_3 + H_2O$$

Hofmann degradation reaction

In this method, amides are converted to amines by treating them with a mixture of aqueous base and bromine (NaOH or KOH + Br_2) to form amines and other inorganic salts. The reaction is called Hofmann bromamide and is represented by the following chemical equation

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

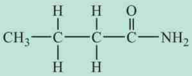
Since the amine formed by this reaction is one carbon atom less than the starting amide, the reaction is known as Hofmann degradation of amide.

Example

Predict the structure and name of the amide which is used to prepare propanamine by Hofmann degradation reaction.

Solution

Propanamine contains three carbon atoms and as Hofmann degradation reactions involve the loss of one carbon atom from amide to amine, the starting amide molecule must contain four carbon atoms. The structure and IUPAC name of the starting material (amide) with four carbon atoms is given as

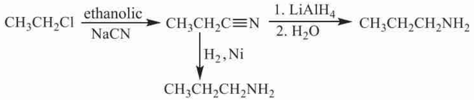


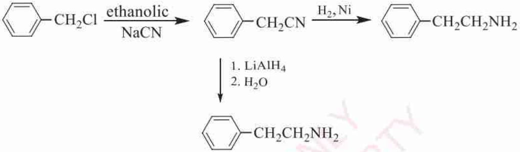
$$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-NH_2$$

Butanamide

Reduction of nitriles

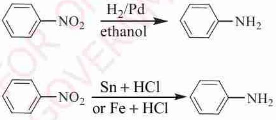
Nitriles can be reduced by lithium aluminium hydride ($LiAlH_4$) followed by water or catalytic hydrogenation to form primary amines. This reaction is used to prepare amines containing additional CH_2 group which was not initially present in haloalkanes or haloaryl compounds.





Reduction of nitroalkanes or nitroaryl

Nitro compounds, R-NO_2 or ArNO_2 can be reduced to their amines by the reaction with hydrogen gas in the presence of finely divided nickel, palladium or platinum catalysts or by using metals such as tin or iron in acidic medium. In acidic medium, metals such as Fe, Sn, and Zn are used for reducing nitro group in nitroaryls to give anilines, and nitroalkanes can also be reduced to their corresponding alkanamines.



$$CH_3CH_2NO_2 + 6[H] \xrightarrow{Fe/HCl} CH_3CH_2NH_2 + 2H_2O$$

The reduction in iron scrap and hydrochloric acid is preferred because the $FeCl_2$ which is formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction under moderate reaction conditions. In addition, iron has a high functional group tolerance.

Nitroalkanes can also be reduced by using lithium aluminium hydride in ether/ THF or by using hydrogen in the presence of catalyst to form amines. The general reaction for the catalytic reduction is,

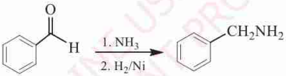
$$R-NO_2 \xrightarrow[\text{or } H_2,\text{ Pt}]{LiAlH_4,\text{THF}} R-NH_2 + H_2O$$

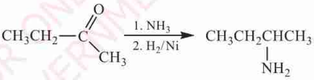
An example of catalytic reduction is given by the reduction of nitroethane into ethanamine in the presence of a catalyst.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow[\text{or } H_2/Pt]{LiAlH_4/\text{ether}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + H_2O$$

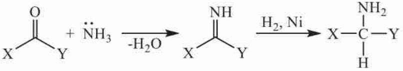
Reductive amination of carbonyl compounds

Aldehydes and ketones on treatment with ammonia and hydrogen in the presence of nickel are converted to amines. This reaction is known as reductive amination of carbonyl compounds.





The above reactions can be represented by the following general chemical equation



where X and Y are R/Ar/H or a combination of either of the two.

8.2.2 Physical properties of amines

The 1°, 2°, and 3° methylamines as well as 1° ethylamines are gases with the smell of ammonia. Amines with C_3 to C_{11} are volatile liquids having fishy smell and those from C_{12} and higher are solids and odourless. They are polar compounds and form hydrogen bonds with each other. Tertiary amines do not form hydrogen bonds since they do not have acidic α-hydrogen in their structures. Hydrogen bonds in amines are weaker than those in alcohols. Therefore, the boiling points of amines are lower than those of alcohols of similar molecular mass. The boiling points of isomeric amines decrease in the order: 1° amines > 2° amines > 3° amines. For example, the boiling points of propanamine, *N*-methylethanamine and *N*,*N*-dimethylmethanamine are 50, 34 and 3 °C, respectively. The comparison between the boiling points of amines and other compounds having similar molecular masses is indicated in Table 8.1.

Table 8.1 Comparison of boiling points of amines and other compounds

Chemical Formula	Name	Molecular Mass	Boiling Point °C
C_2H_6	Ethane	30	−89.0
CH_3NH_2	Methanamine	31	−8.1
CH_3OH	Methanol	32	59.5
$CH_3CH_2CH_3$	Propane	44	−42.5
$CH_3CH_2NH_2$	Ethanamine	45	16.5
CH_3CHO	Ethanal	44	19.5
CH_3CH_2OH	Ethanol	46	77.5
HCOOH	Methanoic acid	46	100.5

The solubility of lower amines is comparable to that of alcohols. Amines with one up to three carbons are completely soluble in water. The solubility in water decreases with the size of alkyl group. However, amines are soluble in alcohol and other non-polar organic solvents such as benzene and ether. It is also important to note that aromatic amines are generally toxic.

8.2.3 Chemical properties of amines

The difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared lone pair of electrons over the nitrogen atom, make amines reactive. The number of hydrogen atoms attached to nitrogen atom also dictates the reactions of amines; that is, primary, secondary, and tertiary amines differ in many reactions. The following are the common reactions of amines.

Basic character of amines

Due to the presence of unshared pair of electrons on nitrogen atom, amines act as bases, and react with acids to form salts.

(a) They react with mineral acids to form salts

$$\text{Primary amine}\begin{cases} RNH_2 + HCl \longrightarrow RNH_3Cl \\ CH_3NH_2 + HCl \longrightarrow CH_3NH_3Cl \end{cases}$$

$$\text{Secondary amine}\begin{cases} R_2NH + HCl \longrightarrow R_2NH_2Cl \\ (CH_3)_2NH + HCl \longrightarrow (CH_3)_2NH_2Cl \end{cases}$$

$$\text{Tertiary amine}\begin{cases} R_3N + HCl \longrightarrow R_3NHCl \\ (CH_3)_3N + HCl \longrightarrow (CH_3)_3NHCl \end{cases}$$

(b) Water soluble amines form substituted ammonium hydroxides which ionise to give hydroxyl ions.

$$R_2NH + H_2O \rightleftharpoons R_2NH_2OH \rightleftharpoons R_2\overset{\oplus}{N}H_2 + OH^{\ominus}$$

$$RNH_2 + H_2O \rightleftharpoons RNH_3OH \rightleftharpoons R\overset{\oplus}{N}H_3 + OH^{\ominus}$$

$$R_3N + H_2O \rightleftharpoons R_3NHOH \rightleftharpoons R_3\overset{\oplus}{N}H + OH^{\ominus}$$

Generally, the base strength of amines follows the order, 2° > 1° > 3° > ammonia >> aniline. This trend is explained by the stabilisation of the positive charge on nitrogen atom as a result of positive inductive effect from alkyl and/or aryl groups. However, the trend is not smooth as primary amines seem to be more basic than the tertiary amines regardless of the three alkyl groups attached to nitrogen atom. This anomaly is explained by the hydration effect on primary amines through hydrogen bonding as compared to tertiary amines which have no hydrogen on nitrogen atom to form hydrogen bond in aqueous solutions. On the other hand, the base strength in tertiary amines is lower than it is expected due to the steric crowding effect that makes it difficult for a proton to approach the lone pair on the nitrogen atom. The base strength of amines compared to that of ammonia is shown in Table 8.2.

Table 8.2 The base strength of amines compared to ammonia

Formula	**Name**	**Type**	K_b	pK_b
NH_3	Ammonia		1.78×10^{-5}	4.78
CH_3NH_2	Methanamine	1°	4.37×10^{-4}	3.36
$(CH_3)_2NH$	*N*-methylmethanamine	2°	5.13×10^{-4}	3.29
$(CH_3)_3N$	*N*,*N*-dimethylmethanamine	3°	5.50×10^{-5}	4.49
$C_2H_5NH_2$	Ethanamine	1°	3.39×10^{-4}	3.47
$(C_2H_5)_2NH$	*N*-ethylethanamine	2°	1.26×10^{-3}	2.90
$(C_2H_5)_3N$	*N*,*N*-diethylethanamine	3°	5.6×10^{-4}	3.25
$C_6H_5NH_2$	Benzenamine (Aniline)	1°	3.8×10^{-10}	9.42
$C_6H_5CH_2NH_2$	Benzylamine	1°	2.25×10^{-5}	4.60
$C_6H_5NHCH_3$	*N*-methylbenzenamine	2°	5.0×10^{-10}	9.30
$C_6H_5N(CH_3)_2$	*N*,*N*-dimethylbenzenamine	3°	11.5×10^{-10}	8.94

Acidic nature of some amines

Predominantly, amines are basic in nature but primary and secondary amines exhibit some acidic properties when treated with alkali metals or Grignard reagents. The acidic nature is demonstrated by the donation of proton and formation of salts. These reactions are generally represented as:

$$2RNH_2 + 2Na \longrightarrow 2RNHNa + H_2$$

$$R_2NH + R'MgX \longrightarrow R_2NMgX + R'H$$

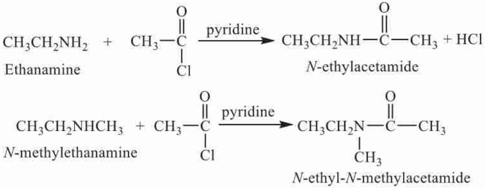
Examples:

$$2CH_3CH_2NH_2 + 2Na \longrightarrow 2CH_3CH_2NHNa + H_2$$

$$CH_3NHCH_3 + CH_3MgCl \longrightarrow (CH_3)_2NMgCl + CH_3H$$

Acylation

When primary and secondary amines are treated with acetyl chloride or acetic anhydrides, they undergo acylation to give *N*-substituted amides. The reaction is carried out in the presence of a base stronger than amine. The strong base is used to remove HCl which is also formed, and shifts the equilibrium to the product side.



$$CH_3CH_2NH_2 + CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} \xrightarrow{\text{pyridine}} CH_3CH_2NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCl$$

Ethanamine N-ethylacetamide

$$CH_3CH_2NHCH_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} \xrightarrow{\text{pyridine}} CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

N-methylethanamine *N*-ethyl-*N*-methylacetamide

Tertiary amines have no unsubstituted hydrogen, therefore do not undergo acylation reactions.

Alkylation

Primary, secondary, and tertiary amines undergo alkylation with akyl halides, R–X, (X stands for a halogen) to form secondary, tertiary, and *n*-alkyl ammonium salts, respectively. The following general equations represent the reaction between amines and akyl halides;

$$RNH_2 \xrightarrow{RX} R_2NH + HX \xrightarrow{RX} R_3N + HX \xrightarrow{RX} [R_4N]^{\oplus} X^{\ominus}$$

Examples:

$$CH_3CH_2NH_2 + CH_3Cl \longrightarrow CH_3CH_2NHCH_3$$

Primary amine

$$CH_3CH_2NHCH_3 + CH_3Cl \longrightarrow CH_3CH_2N(CH_3)_2$$

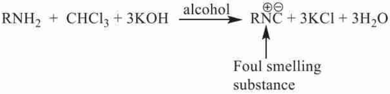
Secondary amine

$$CH_3CH_2N(CH_3)_2 + CH_3Cl \longrightarrow [CH_3CH_2N(CH_3)_3]^{\oplus}Cl^{\ominus}$$

Tertiary amine Ethyltrimethylammonium salt

Carbylamines reactions

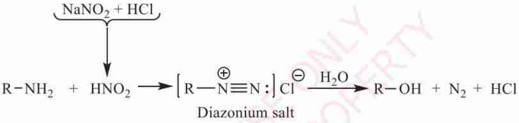
Aliphatic and aromatic primary amines on heating with chloroform and potassium hydroxide in ethanolic (alcoholic) solution form isocyanides or carbylamines. These substances are foul smelling. Secondary and tertiary amines do not show this reaction. Therefore, this is a useful test to distinguish primary amines from secondary and tertiary amines.



$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alcohol}} \underset{\substack{\uparrow \\ \text{Foul smelling} \\ \text{substance}}}{R\overset{\oplus\ominus}{NC}} + 3KCl + 3H_2O$$

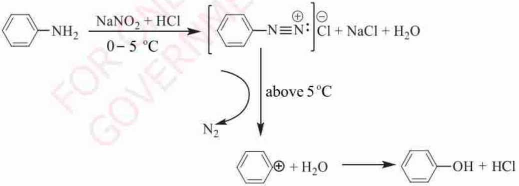
Reaction with nitrous acid

Primary, secondary, and tertiary amines react differently with nitrous acid which is prepared in situ from a mineral acid and sodium nitrite ($NaNO_2 + HCl$). Aliphatic primary amines react with nitrous acid to form aliphatic diazonium salts which are unstable and undergo hydrolysis to form nitrogen gas and alcohol.



$$R-NH_2 + \overset{\overbrace{NaNO_2 + HCl}}{\underset{}{\downarrow} \atop HNO_2} \longrightarrow \underset{\text{Diazonium salt}}{\left[R-\overset{\oplus}{N}\equiv N:\right]Cl^{\ominus}} \xrightarrow{H_2O} R-OH + N_2 + HCl$$

Aromatic primary amines react with nitrous acid at low temperature (0 –5 °C) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds.



Aromatic diazonium chloride salts are more stable due to mesomeric effects. However, at temperatures above 5 °C and in the presence of water they decompose to yield phenol, N_2 and HCl.

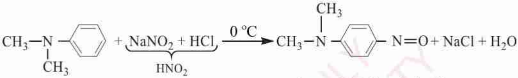
Secondary and arylamines react with HNO_2 to give yellow oily *N*-nitrosoamines.

$$R_2NH + \underbrace{NaNO_2 + HCl}_{HNO_2} \longrightarrow R_2N{-}N{=}O + NaCl + H_2O$$

N-nitrosodialkylamine
Yellow oil

Tertiary aliphatic amines cannot react with HNO_2 because there is no replaceable hydrogen in the amino nitrogen.

Tertiary aromatic amines react with HNO_2 to yield electrophilic substitution products which are green-coloured *p*-nitrosoamines. The reaction is shown in the following equation as an example.



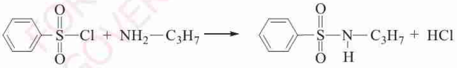
p-nitroso-*N,N*-dimethylaniline

Note: The reactions of amines with nitrous acid are important distinguishing tests for different classes of amines.

Reaction with arylsulphonyl chlorides

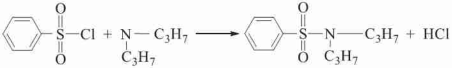
Amines react with benzenesulphonyl chlorides ($C_6H_5SO_2Cl$) which is known as the *Hinsberg's reagent* to produce alkylbenzenesulphonamides.

(a) Reactions of arylsulphonyl chlorides with primary amines yield alkylbenzenesulphonamides which are soluble in alkali solution due to the presence of acidic proton on the nitrogen atom of the sulphonamides.



N-propyl benzenesulphonamide

(b) Secondary amines react with arylsulphonyl chlorides to produce *N,N*-alkylbenzenesulphonamides which are insoluble in alkali solution.



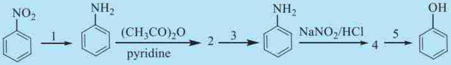
N,N-dipropyl benzenesulphonamide

(c) Tertiary amines do not react with the arylsulphonyl chlorides.

The Hinsberg test is used to distinguish primary, secondary, and tertiary amines based on the identity of the sulphonamide formed. Since tertiary amines do not form stable sulphonamides, the products formed are either from primary or secondary amines. If the sulphonamide that forms dissolves in aqueous sodium hydroxide solution, it is from a primary amine. If the sulphonamide is insoluble in aqueous sodium hydroxide, it is from a secondary amine.

Exercise 8.2

1. Classify the following as primary, secondary or tertiary amines:
   (a) 1-methylcyclohexylamine
   (b) Triethylamine
   (c) *tert*-butylamine
   (d) *N*-methylprop-2-en-1-amine
   (e) Arylmethylamine
2. Arrange the following amines in the order of decreasing basic strength and justify your trend: CH_3NH_2, $(CH_3)_2NH$, aniline, and cyclohexylamine.
3. A colourless substance **R** (C_6H_7N) is slightly soluble in water and gives a water soluble compound **S** when treated with mineral acid. When treated with chloroform and alcoholic potassium hydroxide, **R** produces a horrible smell caused by the formation of **T**. The reaction of **R** with benzenesulphonyl chloride gives compound **U** which is soluble in basic medium. The reaction of $NaNO_2$ and HCl with **R** forms compounds **V** which hydrolyses to give **W**. Identify compounds **S** to **W**.
4. A hydrocarbon **A** (C_3H_6) on reacting with HCl gives compound **B** (C_3H_7Cl) which on reaction with 1 mol of ammonia, gives compound **C** (C_3H_9N). On treating **C** with $NaNO_2$ and HCl followed by hydrolysis, alcohol **D** is formed. Identify and write stuctural formula of compounds **A** to **D** and explain all the chemical reactions involved.
5. Predict the reagent or the product in the following reaction sequence:



8.3 Uses and hazards of amines

Uses of amines

Amines play an important role in everyday life because they are involved in the formation of amino acids which are the building blocks of proteins in living creatures. Moreover, many vitamins are also built from amino acids. Amines like serotonin (5-hydroxytryptamine) functions as one of the primary neurotransmitters for the brain. It affects the state of happiness and helps in regulating the sleeping and waking-up cycle of the brain.

Amines are largely used in pharmaceutical industry. In medicines amines such as morphine and demerol are commonly used as painkillers. Furthermore, novocaine is used as an anesthetic while ephedrine is used as very common stimulant. In addition, amines such as methamphetamines and amphetamines are popular recreational drugs.

Many amines are used in industries for pest control and tanning of leather. For example, aniline finds application in the manufacture of man-made dyes. Being the derivatives of ammonia, amines are basic in nature and are neutralised by acids. The neutralisation process of amines results in the formation of alkylammonium salts which have many applications. For example, choline plays a role in the production of some neurotransmitters in the human body that make the brain work properly.

Hazards of amines

Amines, especially aliphatic amines are moderately toxic. The main health hazard stem from their being caustic, they cause severe burns on contact with skin. They are also severe irritants to the skin, eyes, and mucous membranes. Alkaloids which are natural and/or synthetic amines such as cocaine, heroin, cannabis, and related compounds have adverse health effects on users such that they are considered a serious public health problem. Lower molecular weight amines are highly flammable liquids.

Revision exercise 8

1. Name and classify each of the following compounds as 1°, 2° or 3° amines:

   (a) $CH_3CH_2CH_2NH_2$

   (b) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

   (c) $CH_3CH_2CH_2NHCH_3$

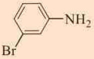
   (d) $N(CH_3)_3$

   (e) $(C_6H_5)_2NH$

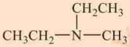
2. Draw the chemical structure for each of the following compounds:
   (a) Tripropylamine
   (b) Ethylenediamine
   (c) Ethanamide
   (d) *p*-ethylaniline
   (e) 2-amino-3-methylpentane

3. Give the IUPAC name of each of the following compounds:

(a)

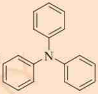


(b)



$CH_3CH_2—\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}—CH_3$

(c)



4. Explain how the following can be prepared from a compound with molecular formula, C_4H_7N.
   (a) $C_4H_{11}N$
   (b) $C_6H_{15}N$

5. Outline the necessary reagents required in the conversion of the following organic compounds:
   (a) *N,N*-diethylpropanamide to *N,N*-diethylpropanamine
   (b) Chloromethane to methylamine
   (c) Nitrobenzene to aniline

6. Give one chemical test to distinguish between the following pairs of amines:
   (a) Methylamine and dimethylamine
   (b) Aniline and benzylamine

7. Arrange the following:
   (a) In the order of increasing base strength.
   $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$, and CH_3NH_2

(b) In the order of increasing solubility in water.

$C_6H_5NH_2$, $(C_2H_5)_2NH$, and $C_2H_5NH_2$

8. Show how the following conversions can be achieved.

   (a) Ethanamine into methanamine

   (b) Methanamine into ethanamine

9. Give the structures represented by the letters **A**, **B**, **C**, **D**, **E**, and **F** in the following reactions:

   (a) $C_2H_5NO_2 \xrightarrow{Fe/HCl} \mathbf{A} \xrightarrow{HNO_2} \mathbf{B} \xrightarrow[heat]{H^{\oplus}} \mathbf{C}$

   (b) $C_3H_5Br \xrightarrow{KCN} \mathbf{D} \xrightarrow{LiAlH_4} \mathbf{E} \xrightarrow[0\ ^{o}C]{HNO_2} \mathbf{F}$

10. Give plausible explanations for each of the following statements:

    (a) Amines are less acidic than alcohols of comparable molecular masses

    (b) Primary amines have higher boiling points than tertiary amines

    (c) Aliphatic amines are stronger bases than aromatic amines

11. Explain the reason for cooks to add lemon juice as they prepare fish for meal.

12. You are provided with the following substances:

    —CH_2Cl, $NaCN(aq)$, $H_2(g)$, and Pt-catalyst

    Suggest how you can use them to synthesise phenylethanamine.

Chapter Nine Polymers

Introduction

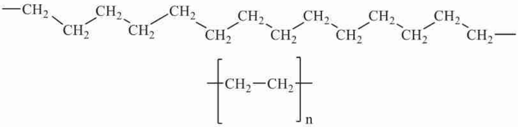
Polymers are a class of macromolecules forming the structure of many natural and synthetic materials. Polymers are important biological molecules of life such as in DNA and RNA. Furthermore, polymers are important in various industrial application such as in the manufacture of plastics, rubbers, composites, nylon, and electrical modulators for drugs delivery. In this chapter, you will learn about the concept of polymers, types, preparation, and properties of polymers as well as their uses and hazards.

9.1 Concept of polymers

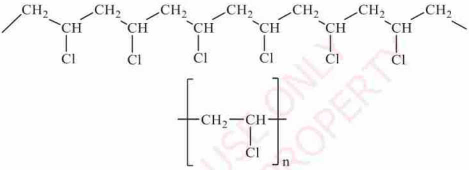
The word polymer is a combination of two Greek words, *poly* (many) and *mer* (units) meaning many units. In its simplest form, a *polymer* is a large molecule consisting of a covalently linked chain of smaller molecules called monomers (from two Greek words *mono*-meaning one and *mer*- meaning unit). *Monomers* are the smallest molecules which join together repeatedly to form a polymer. The number of times a monomer is contained in the polymer molecule is called the *degree of polymerisation*. Polymers whose repeating unit is derived from only one type of monomer are called *homopolymers*, and those whose repeating units are derived from two or more types of monomers are called *copolymers.*

9.1.1 Structure of polymers

Polymers are made of small repeating blocks called *monomers* which are linked together by covalent bonds. The monomers carry a characteristic feature of a polymer. The process through which monomers are linked together to form a long chain is called *polymerisation*. It involves the combination of many units of monomers to form a product with high molecular weight. The following structures are examples of polymers with their corresponding monomers, where *n* represents the degree of polymerisation.



Polyethylene (PE)



Poly(vinyl chloride) (PVC)

9.1.2 General characteristics of polymers

Polymers have the following general characteristics which make them useful in different fields:

(a) Most polymers exhibit resistance to chemical attack, hence they are used to make protective clothing, gloves, goggles, and other materials.

(b) Polymers are poor conductors of heat and electricity; therefore, they are good thermal and electrical insulators. For example, handles of cooking utensils are made of polymeric materials and electric cables are covered with polymeric materials.

(c) Generally, polymers are very light in weight but with the significant degree of strength. They are therefore, used to make different fittings used in aviation and construction industries.

9.2 Types of polymers

Polymers can be classified based on different criteria such as source, structure, physical and chemical properties, and mode of synthesis. Each of these common types of polymers is discussed in the following sections.

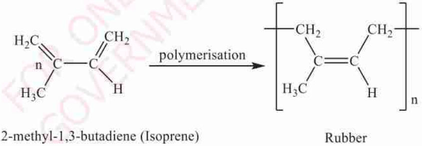
9.2.1 Classification of polymers based on their sources

Under this type of classification, polymers are classified as natural, semi-synthetic, and synthetic polymers. The classes are based on the sources from which a particular polymer originates.

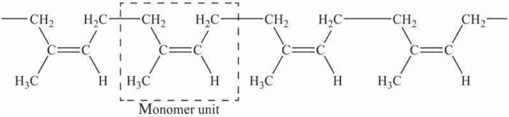
Natural polymers

Polymers which are obtained from natural sources such as plants and animals are called *natural polymers* or *biopolymers*. Examples of natural polymers are cellulose, starch, cotton fibre, silk, wool, protein, glycogen, and natural rubber. Among the mentioned examples of natural polymers, natural rubber is selected for a detailed discussion because of its economic importance.

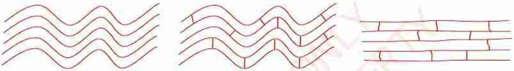
The natural rubber is obtained from rubber trees (*Hevea brasiliensis*). It is made up of 2-methyl-1,3-butadiene (isoprene) monomers. This polymer can also be synthesised from 2-methy-1,3-butadiene molecules obtained from petroleum. The following chemical equation represents the polymerisation reaction of isoprene:



The monomers in a rubber molecule are linked as follows:



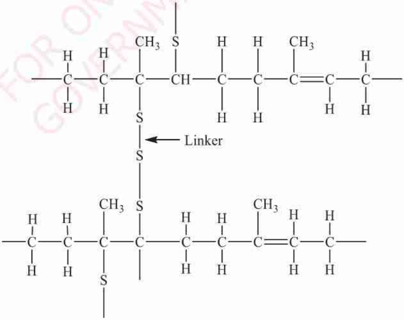
The elastic property of rubber is due to the flexibility of its long chain molecules. However, in the bulk state, rubber is a tangle of polymeric chains and if stretched with enough external force, individual chains slip past one another thereby causing the rubber to lose most of its elasticity. The solution to this problem was found by an American chemist, Charles Goodyear in 1839. He discovered that natural rubber could be cross-linked with sulphur (using zinc oxide as catalyst) to prevent slippage. The process is known as *vulcanisation* and it refers to the process of cross-linking rubber molecules with sulphur atoms to form a more flexible polymer. The vulcanisation process improves the quality of rubber for many practical and commercial uses, such as in manufacturing of automobile tyres and dentures. An example of rubber molecules before and after vulcanisation is given in Figure 9.1 (a-c).



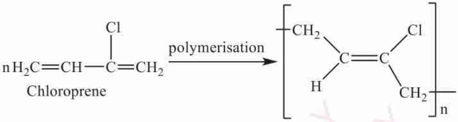
(a) (b) (c)

Figure 9.1 Rubber molecules (a) before vulcanisation, (b) after vulcanisation, (c) stretched vulcanised molecules

As it can be seen in Figure 9.1(c), the molecules are held together by linkers thus minimising the possibility for slippage which would happen if the rubber was not vulcanised as it is seen in 9.1(a). The chemical structure of a vulcanised rubber is shown below.



The shortage of natural rubber has prompted the production of synthetic rubber. Most synthetic rubbers (called elastomers) are made from petroleum products such as ethylene, propylene, and butadiene. For example, chloroprene molecules polymerise readily to form polychloroprene, commonly known as neoprene which has properties that are comparable or even superior to those of natural rubber. The reaction below represents the synthetic polymerisation of chloroprene to polychloroprene.



Polychloroprene

Semi-synthetic polymers

Combining natural and synthetic polymerisation processes gives another type of polymer known as semi-synthetic polymers. Semi-synthetic polymers are obtained when naturally occurring polymers are chemically treated to tailor their properties to meet benchmark's standards. The chemical treatment can be the addition of functional group to the main chain to facilitate cross-linking or copolymerisation. Examples of semi-synthetic polymers are cellulose nitrate and cellulose acetate (rayon) from cellulose.

Synthetic polymers

Polymers which are created in the laboratory from simple molecules are called synthetic polymers. Examples of synthetic polymers are polyethylenes, polyesters, teflon, poly(vinyl chlorides), and nylons.

9.2.2 Classification of polymers based on their structures

Under this category of classification, polymers are classified into three main groups, namely linear, network or cross-linked, and branched chain polymers.

Linear polymers

Linear polymers consist of long and straight chains. Examples of linear polymers are high density polythenes (HDPE) and poly(vinyl chloride) (PVC).

Figure 9.2 Linear polymers

Network or cross-linked polymers

Network or cross-linked polymers contain strong covalent bonds between various linear polymer chains and they are usually formed from *bi*-functional or *tri*-functional monomers (monomers having two or three functional groups, respectively). Examples of network or cross-linked polymers are melamine and bakelite.

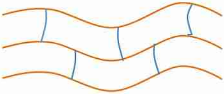


Figure 9.3 Network polymers

Branched chain polymers

Branched chain polymers are made up of linear chains with some branches between them. An example of this type of polymers is a low density polypropene (LDPP).

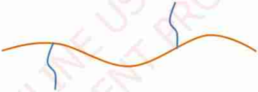


Figure 9.4 Branched chain polymers

9.2.3 Classification of polymers based on physical properties

Based on the type and strength of intermolecular forces of attraction, polymers can further be classified as elastomers, fibres, thermoplastics, and thermosetting polymers.

Elastomers

Elastomers consist of very long polymer molecules with a smaller amount of cross-linking. At room temperature, they are rubber-like elastic material because their molecules are free to move between the cross-linking. Because of their cross-linking, elastomers cannot be melted without decomposition. Vulcanised rubber is an example of elastomers.

Fibres

Fibres are thread-like materials forming a solid which possess high tensile strength due to the presence of strong hydrogen bond. Polyester and nylon-6,6 are examples of fibre polymers.

Thermoplastic polymers

These are linear or slightly branched long chain molecules such as poly(ethylene terephthalate) (PET). The molecules of thermoplastic polymers are not bonded between each other (that is not cross-linked), therefore, they are free to move and are in a constant motion. The movement of molecules depends on the thermal energy available. The more the thermal energy available, the more the polymer molecules will move freely. At higher temperatures, these polymers melt and reform at low temperatures in a repetitive process. This property allows easy processing and facilitates recycling. Furthermore, lack of cross-linking between molecules of this type of polymers accounts for their solubility in organic solvents to give colloidal solutions.

Thermosetting polymers

Unlike thermoplastic polymers, thermosetting polymers do not consist of independent molecules. The molecules of this type of polymers are bonded together by links between them (cross-linked). The extent of cross-linking is higher compared to the one in elastomers. This makes thermosetting polymers strong, hard, and brittle. Since the molecules are not free to move, the polymers do not melt when heated at moderate temperatures. However, strong heating results into the decomposition of the original molecule. The resulting components of the decomposition reactions can melt but the original thermosetting molecules (polymers) cannot be reformed by cooling. Polymers formed from trifunctional monomers are thermosetting polymers. They are hard, brittle, and insoluble in water. Phenol-formaldehyde (Bakelite) and urea-formaldehyde are examples of this type of polymers. Trifunctional monomers are suitable for making cross-linked polymers.

9.2.4 Classification based on the mode of polymerisation or synthesis

Polymerisation mainly occurs in two ways which are addition and condensation polymerisations. The two ways result into two types of polymers known as addition and condensation polymers.

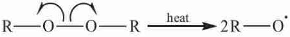
Addition polymers

Addition polymers are formed by the repeated addition of monomers possessing double or triple bonds. The monomers used to synthesise this type of polymers can be from the same type or from two different monomers. Addition polymerisation requires an initiator for the process to take place and it is a three stage process as discussed below.

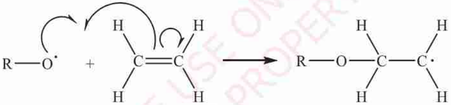
Initiation

The initiation stage involves two steps: the formation of reactive species from an initiator and the reaction between the reactive species with the first monomer. The reactive species can be in form of ions or free radicals depending on the type of addition polymerisation. For instance, in the free radical addition polymerisation of ethene, the process occurs in two steps.

Step 1: Decomposition of the initiator

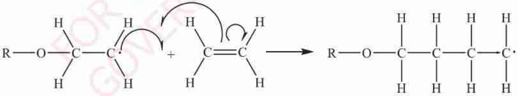


Step 2: Reaction between the reactive species with the first monomer



Propagation

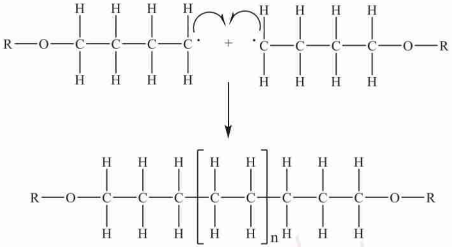
In the propagation stage, the free radical produced in the initiation stage combines with a monomer to form a larger free radical.



The chain is elongated by a combination of several radicals to form a longer chain of monomer units.

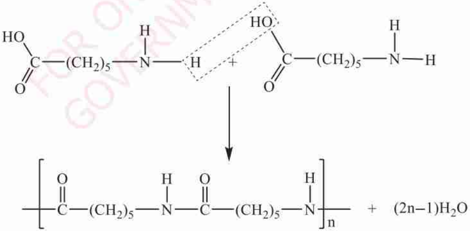
Termination

Chain elongation is terminated when two long chain radicals join together to form a stable molecule through electron pairing.

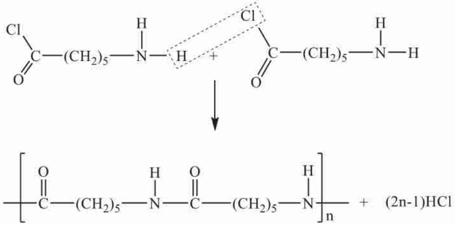


Condensation polymers

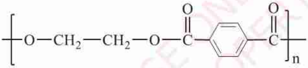
Condensation polymers are formed by combining monomers together which is accompanied with a loss of simple molecules like water, alcohol, carbondioxide, and hydrogen chloride. This type of polymers occurs between bi-functional monomers. The polymer formed contains a functional group as part of the polymer main chain. Terylene, bakelite and nylon-6,6 are examples of condensation polymers. The formation of nylon from 6-aminohexanoic acid monomers is a good example of condensation polymerisation.



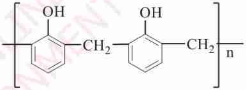
The same polymer can also be formed by condensation polymerisation of 6-aminohexanoyl chloride in which HCl is eliminated.



Examples of other condensation polymers are terylene and bakelite as shown below in the form of their chain section.



Terylene



Bakelite

Condensation polymerisation is characterised by:

(a) The presence of two different or identical functional groups in each monomer.

(b) The functional groups forming the point of linkage between the two monomers.

(c) Elimination of simple molecules such as alcohols, H_2O, HCl, and CO_2 during their formation.

9.3 Preparation of synthetic polymers

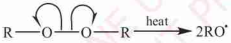
Polymers find vast applications in daily human life due to their perculier properties. Their applications prompt their synthesis to meet the ever growing demand. This section looks at different methods used to synthesise polymers in large scale. In this section, you will learn about the addition and condensation polymerisation methods for synthetic polymers.

9.3.1 Addition polymerisation

Under this type of polymerisation, monomers undergo addition reactions to give polymer molecules only as the final product. The reaction takes place between unsaturated monomers such as alkenes, alkadienes, and their derivatives. Nevertheless, depending on the type of the initiator of the reaction, addition polymerisation can further be classified as free radical and ionic addition polymerisations.

Free radical addition polymerisation

In free radical addition polymerisation, the first step in a chain reaction is the formation of free radicals by an initiator. The initiator can be organic peroxides, R-O-O-R, azo-compounds as in 4-hydroxyphenylazobenzene or oxygen. The initiator is decomposed by heat or UV light to give free radicals.



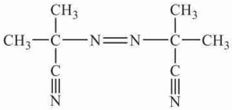
$$R-O-O-R \xrightarrow{\text{heat}} 2RO^{\bullet}$$

When a free radical is formed, it reacts with an unsaturated monomer to give a new free radical and the process repeats with many thousands of monomers before termination takes place.

The process can be detailed in the following three steps:

Step 1: Initiation of the chain reaction

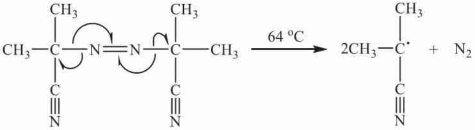
The typical initiator is 2,2-azobisisobutyronitrile (AIBN).



$$CH_3-\underset{\underset{N}{\overset{|||}{C}}}{\overset{CH_3}{\overset{|}{C}}}-N=N-\underset{\underset{N}{\overset{|||}{C}}}{\overset{CH_3}{\overset{|}{C}}}-CH_3$$

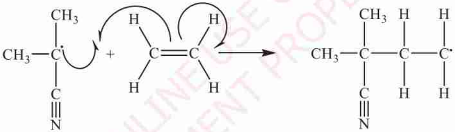
2,2-azobisisobutyronitrile (AIBN)

Decomposition of initiator



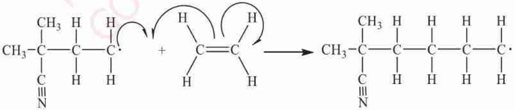
Note: The C—N bond dissociation energy is high but homolysis is driven by the formation of the highly stable N_2 molecule.

The new formed free radical attacks a monomer to start the reaction



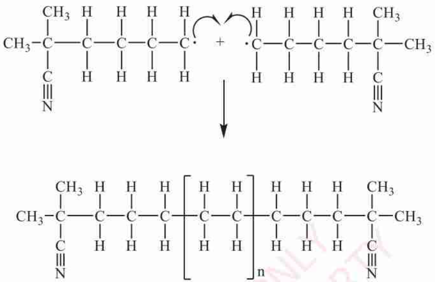
Step 2**:** The propagation of the chain reaction

The new formed free radical attacks a monomer to propagate the reaction



Step 3: The termination of the chain reaction

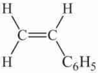
The polymerisation process is terminated by a free radical as illustrated below, and the polymer formed under this method is linear.



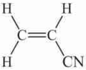
When one of the hydrogen atoms in ethene (monomer) is replaced by an electron withdrawing group such as chlorine, phenyl or cyanide, the addition polymerisation is made easier. The resulting monomers formed by replacing one hydrogen atom of ethene by chlorine, phenyl, and cyanide group are vinyl chloride, styrene, and acrylonitrile respectively. The presence of an electron withdrawing group polarises the bond and increases intermolecular forces between polymer molecules. Chemical structures for ethylene, vinyl chloride, styrene, and acrylonitrile monomers which are used in addition polymerisation are shown below:

Ethylene

Vinyl chloride



Styrene



Acrylonitrile

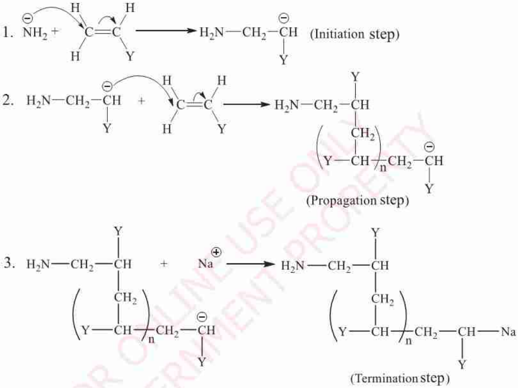
Ionic addition polymerisation

In ionic addition polymerisation, the reaction is initiated by anion or cation. The new formed ion can combine with thousands of monomers before the termination of the reaction. If an anion initiates the reaction, the cation will terminate the polymerisation and vice versa. Initiators of anionic addition polymerisation are bases like $R^{\ominus}$ from a Grignard reagent, or $OH^{\ominus}$, $NH_2^{\ominus}$, or $RO^{\ominus}$. At the same time, the cation initiator can be $H^{\oplus}$ obtained by mixing a Lewis acid such as BF_3 or $AlCl_3$ with a Brønsted-Lowry acid HX or H_2SO_4.

$$HX + BF_3 \longrightarrow H^{\oplus} + BF_3X^{\ominus}$$

Anionic addition polymerisation

With anion as the initiator of the reaction, anionic addition polymerisation reaction can be presented as follows:

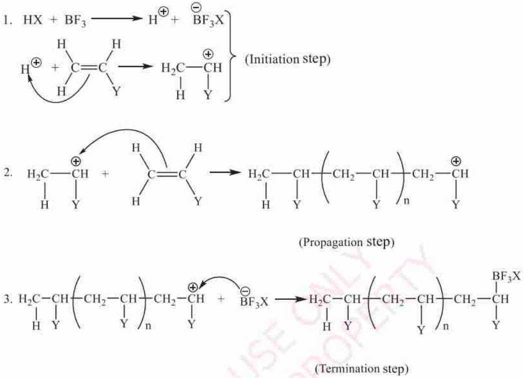


Y- stands for an electron withdrawing group like C_6H_5-, $-CN$, $-COR$, or X (X=Cl, Br, F or I)

The polymerisation process is terminated by cations such as $Na^{\oplus}$ ion. The polymer that is formed is branched because of the Y group.

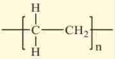
Cationic addition polymerisation

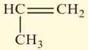
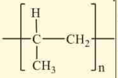
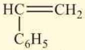
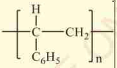
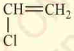
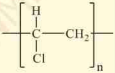
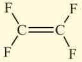
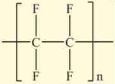
In case of cationic addition polymerisation, the cation is the reaction initiator and the reaction is terminated by anions such as $-BF_3X$ as illustrated below:



Y is an electron releasing group like CH_3- and CH_3CH_2-. The commonly used cationic initiators are H_2SO_4, HF, and Lewis acids such as $AlCl_3$, $SnCl_2$ or BF_3. Some important examples of additional polymers are presented in Table 9.1.

Table 9.1 Some important examples of additional polymers (thermoplastic polymers)

Polymers	Monomer name and formula	Polymer chain	Properties	Uses
Polyethene	$H_2C{=}CH_2$ Ethene	 $-\!\!\left[\overset{H}{\underset{H}{C}}-CH_2\right]_n\!\!-$	-Transparent wax-like, soluble in petrol and benzene. -Resistant to other chemical agents.	Used for making plastic bottle containers, plastic bags, pipes, and electrical insulators.

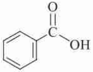
Poly propene	 $\underset{CH_3}{\underset{\vert}{HC}}{=}CH_2$ Propene	 $\left[-\overset{H}{\underset{CH_3}{C}}-CH_2-\right]_n$	Similar to polyethenes but somehow harder	Used for making plastic bottle containers, plastic bags pipes, and electrical insulators.
Poly styrene	 $\underset{C_6H_5}{\underset{\vert}{HC}}{=}CH_2$ Phenylethene	 $\left[-\overset{H}{\underset{C_6H_5}{C}}-CH_2-\right]_n$	Transparent like glass, hard, soluble in benzene and methylbenzene.	Used for making house hold goods, electrical insulators, lacquers, optical lenses and ion exchange resins
Poly(vinyl chloride)	 $\underset{Cl}{\underset{\vert}{CH}}{=}CH_2$ Chloroethene	 $\left[-\overset{H}{\underset{Cl}{C}}-CH_2-\right]_n$	White moulded under pressure, hard, soluble in cyclohexanone.	Used for making cable insulation pipes, hoses and packaging materials.
Polytetrafluoroethene	 Tetrafluoroethene	 $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right]_n$	White, hard, solid and non moulding.	Used for making surface coating of pans, apparatus for chemical plants pipes and gasket.

9.3.2 Condensation polymerisation

The *condensation reaction* (*step polymerisation*) is the reaction of two or more molecules which combine together to form large molecules with a loss of simple molecules such as water, alcohol, ammonia, carbon dioxide or hydrogen chloride, to form a polymer in which the molecular formula of the repeating unit is different from that of the original monomers. Condensation reaction occurs between two bifunctional or trifunctional reagents. Examples of the reactions under this types of polymerisation include the reaction between amines and carboxylic acids or between alcohols and carboxylic acids. In condensation reaction, monomers may react with any of the different sized species as shown hereunder.

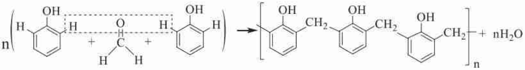
$$\text{Monomer} + \text{Monomer} \longrightarrow \text{Dimer}$$
$$\text{Monomer} + \text{Dimer} \longrightarrow \text{Trimer}$$
$$\text{Dimer} + \text{Dimer} \longrightarrow \text{Tetramer}$$
$$\text{Trimer} + \text{Dimer} \longrightarrow \text{Pentamer}$$
$$\text{Trimer} + \text{Trimer} \longrightarrow \text{Hexamer}$$

As the size of the polymer increases, the degree of polymerisation slowly decreases. This is because, the kinetics favour the interaction between small sized molecules. Once almost all the short chain polymer molecules are consumed, polymerisation continues with the reaction between the end groups of the long chain polymers. Chain termination may be carried out by using a monofunctional monomer (chain stopper) such as benzoic acid.



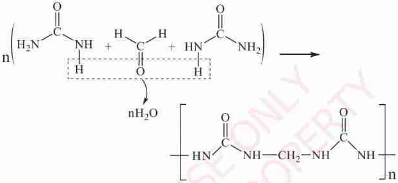
Benzoic acid

Once a monofunctional monomer attaches to the end of a polymer chain, polymerisation will not continue at the end of that chain. Consequently, the chain is said to be terminated. The reaction between phenol and methanal to form bakelite serves as an illustrative example of condensation polymerisation. In this reaction, phenol acts as a nucleophile and attacks methanal to give a condensation product.



Bakelite

Another example of condensation polymerisation is the reaction between urea (monomer) and methanal (monomer). Under alkaline conditions, carbamide (urea) can act as a nucleophile, attacking methanal to give a condensation polymer.

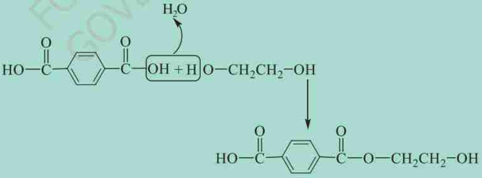


Example

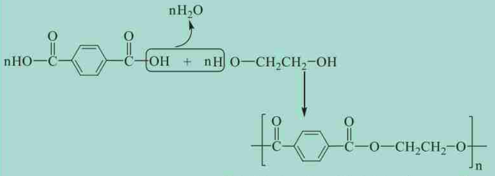
Starting with ethan-1,2-diol and benzene-1,4-dicarboxylic acid as monomers, show how you can effect condensation polymerisation to get poly(ethylene terephthalate) polymer (Dacron).

Solution

The two monomers react together as presented in the following equation:



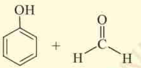
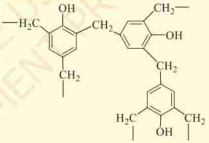
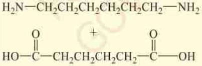
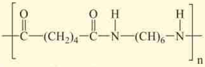
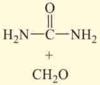
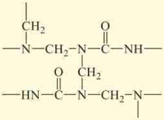
When ethan-1,2-diol and benzene-1,4-dicarboxylic acid monomers are in excess, the reaction continues in the propagation stage to form Dacron as shown below.



Poly(ethylene terephthalate) polymer or Dacron

During the process, water molecules are removed out as the monomers combine together. The process is terminated when there are no more monomers to react. Some examples of condensation polymers are given in Table 9.2.

Table 9.2 Some examples of condensation polymers

Components	Name and structure of polymers
	 Phenol-formaldehyde (bakelite)
 $H_2N-CH_2CH_2CH_2CH_2CH_2CH_2-NH_2$ + $HO-\overset{O}{\overset{\parallel}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\parallel}{C}}-OH$	 $\left[\overset{O}{\overset{\parallel}{C}}-(CH_2)_4-\overset{O}{\overset{\parallel}{C}}-\overset{H}{\overset{\mid}{N}}-(CH)_6-\overset{H}{\overset{\mid}{N}}\right]_n$ Polyamide(nylon- 6,6)
 $H_2N-\overset{O}{\overset{\parallel}{C}}-NH_2$ + CH_2O	 Carbamide-methanal

Identification of monomers

Recall that, polymers are made by the addition or condensation polymerisation. Addition polymers are obtained from unsaturated hydrocarbons or their derivatives. That is, the unsaturated hydrocarbon molecules with one hydrogen atom substituted by a halide (X), cyanide (–CN), or phenyl (C_6H_5–) group, can be used as monomers for polymerisation. On the other hand, condensation polymers are obtained from bi-functional or tri-functional monomers such as diamines, dicarbonyls, dicarboxyl groups, diols, aldehyde and polyhydroxy phenol.

In order to identify the monomers used to make a polymer, careful examination of a polymer molecule is necessary. This gives a clue which helps to judge if the polymer is a product of condensation or addition polymerisation, and hence the monomers used can be predicted. A worked example below gives a brief elaboration of how this can be done.

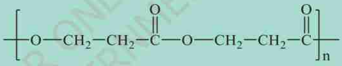
Example

What monomer(s) must be used to produce the following polymers?

(a)

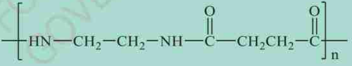
$$\left[\underset{|\atop F}{CH}-CH_2-\underset{|\atop F}{CH}-CH_2-\underset{|\atop F}{CH}-CH_2 \right]_n$$

(b)



$$\left[O-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\overset{O}{\overset{\|}{C}} \right]_n$$

(c)

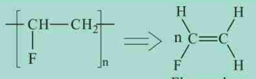


$$\left[HN-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}} \right]_n$$

Solution

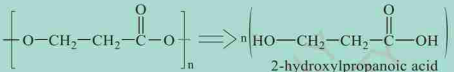
(a) By examining the structure of the polymer molecule (a), it can be deduced that the polymer is the product of addition polymerisation because the absence of phenoxyl, –NH– and CO groups rules out the possibility for the molecule to be the product of condensation polymerisation.

Therefore, the monomer used to make the molecule is obtained by inspecting the repeting unit as shown in the following structure.



Fluoroethene

(b) Examination of the polymer molecule (b) gives a clue that the polymer is the product of condensation polymerisation because there are traces of –COOH and OH groups which remain after the reaction. Therefore, the monomer which is used to make the polymer is obatained by inspecting the repeating unit as shown below.



$$\left[O-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O \right]_n \Longrightarrow n\left(HO-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH \right)$$

2-hydroxylpropanoic acid

(c) The polymer molecule (c) shows that it is a product of condensation polymerisation because of the presence of –NH– and –CO groups which are likely to be the remaining parts of amine and carboxylic groups after the polymerisation reaction. Therefore, the monomers used to make the polymer are obatained by inspecting the repeating unit as in (b) above.

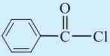
$H_2N-CH_2-CH_2-NH_2$ and

$$HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Ethylenediamine Ethanedioic acid

Exercise 9.1

1. From the following pairs of compounds, choose the pair(s) which is (are) likely to give a polymeric product(s) when they are allowed to react at appropriate conditions. Give reasons for your choice.

(a)  and $HO-CH_2CH_2-OH$

(b) $NaO-CH_2CH_2-ONa$ and $Br-CH_2CH_2-Br$

(c) $CH_3-(CH_2)_{10}-COOH$ and $HO-(CH_2)_{12}-CH_3$

2. (a) Describe the reactions which take place during the vulcanisation of raw rubber. What changes in physical properties accompany this process?

   (b) How does the introduction of side chains on polyethene affect its physical properties?

3. (a) With examples, explain what it means by each of the following terms:
   - (i) Addition polymerisation
   - (ii) Condensation polymerisation

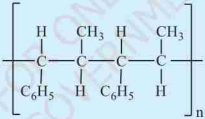
   (b) Briefly describe how the length of the polymer chains can be controlled in addition polymerisation reaction.

4. Identify the monomer(s) used to make the polymer structures given below.

(a)

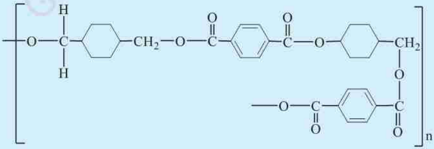
$$\left[-\overset{CH_3}{\underset{C_6H_5}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{C_6H_5}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{C_6H_5}{C}}-\overset{H}{\underset{H}{C}}- \right]_n$$

(b)



$$\left[-\overset{H}{\underset{C_6H_5}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}-\overset{CH_3}{\underset{H}{C}}- \right]_n$$

(c)



9.4 Properties of polymers

Many synthetic polymers are of great use because of their peculiar properties. Different polymers have different arrangement of chains which influence their physical and chemical properties. Inspite of their useful applications in daily life, polymers pose a very huge risk to the human and the environment at large. In this section, you will learn about the properties of polymers.

9.4.1 Physical properties of synthetic polymers

Synthetic polymers range from liquids through plastics to brittle solids. Most solid polymers are not crystalline, instead they are glasses or super cooled liquids. Most pure, low molecular weight polymers have sharp melting points, changing from the solid to the liquid phase within a temperature range of a degree or two. Due to the fact that most polymers are mixtures, they melt over a wide range of temperatures. Polymers are highly viscous such that a 10 percent aqueous solution of a polymer in an organic solvent has a much higher viscosity than the pure solvent. Polymers differ considerably in terms of solubility in organic solvents. A cross-linked, net like structure prevents polymer molecules from entering into solvents. Consequently, it becomes difficult for them to dissolve. For the case when a 'net' structure allows solvents to enter the polymer molecule, the solvent is absorbed making the polymer to swell and increase in volume.

9.4.2 Chemical properties of synthetic polymers

Generally, synthetic polymers are chemically inert. However, some chemical reactions such as depolymerisation, cross-linking, thermal-separation of some molecules like HCl and combustion are known to take place.

Depolymerisation reactions

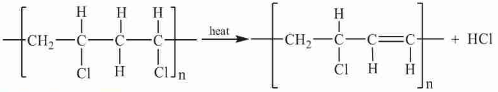
Action of heat, sunlight, oxygen or ozone on polymers can cause break-up of polymer molecules. This reaction is very slow but over a prolonged period of exposure can cause destruction in the polymeric material. This can render the polymer material useless. To prevent depolymerisation, substances which are called stabilisers (e.g. cadmium compounds and soot) are always added. Stabilisers work by absorbing free radicals which are responsible for promoting depolymerisation.

Cross-linking reactions

Monomers containing three functional groups can undergo polymerisation using two functional groups. The polymer obtained, still has a group available for further reactions. The reaction of the third functional group helps to form a cross-link between chains, and hence leads to the formation of thermosetting polymers. Vulcanisation of rubber is an example of this type of reactions.

Reactions which do not affect the length of the polymer chain

There are some synthetic polymers which when heated, the structures of their molecules change by losing groups of compounds like HCl. An example of such reactions is the thermal separation of HCl from poly(vinyl chloride).



$$\left[-CH_2-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}- \right]_n \xrightarrow{heat} \left[-CH_2-\overset{H}{\underset{Cl}{C}}-\underset{H}{C}=\underset{H}{C}- \right]_n + HCl$$

Combustion reactions

Some of the polymers are inflammable, as they burn to give mainly carbon dioxide and water. If the polymer contains atoms of other elements such as nitrogen or sulphur, the smoke may contain oxides of these elements in gaseous form.

9.5 Uses and hazards of synthetic polymers

Uses of synthetic polymers

Polymers find use in daily life activities of human. Synthetic fibres such as polyesters for example dacron are used in clothing, polyethylene polymers are used as packaging material, poly(vinyl chloride) (PVC) polymers are used for various construction works and piping and other civil works, in TV, video, computer casing and parts. Plastics from different monomers are used in window frames, vanishes, containers such as buckets, baskets, motor vehicle parts, airplane parts. Polymers also find applications in medicine such as surgical gloves and tissue implants which uses polylactic ester polymer. Teflon polymers are used in making stainless frying pans. Still polyurethane are polymers used in making foam mattresses.

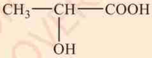
Hazards of synthetic polymers

Polymers are very important materials which today pervade almost every aspect of our daily lives. It is estimated that about 90 percent of today's chemists, including biochemists, work with polymers, a fact which illustrates how important polymers are to the world economy and standard of living of the people. However, on the other side, polymers and specifically plastics, are said to have a significant contribution to the pollution of the environment. They can also be harmful if not properly handled. Unsafe disposal of plastic wastes and other polymeric material wastes contributes to environmental pollution. Synthetic polymers are not biodegradable materials meaning that they do not decay when damped on land or buried underground. Massive production of polymers increases their accumulation around human settlements which is hazardous because they can easily catch fire and burn. The burning process releases poisonous gases such as NO_2, SO_2, and CO. Some polymers can depolymerise when exposed to sunlight for a long time and release carcinogenic monomer vapours and gases such as HCl. Therefore, if not properly handled, polymer wastes can cause depletion of the ozone layer, formation of chemical smog and may cause lung diseases.

To avoid these hazards, good knowledge on waste management must be introduced in the society beginning at the family level to enable the entire population to acquire necessary skills for proper handling of polymeric material wastes before they are destroyed. Incineration is the recommended method for destruction of waste polymeric materials. For example, incineration converts organic matter into CO_2 and H_2O, sulphur and nitrogen into SO_2 and NO_2, respectively. Incineration involves burning the waste at temperatures above 1000 °C in the presence of excess air. The exhaust gases are passed through filters to remove particulates and absorb poisonous gases. The resultant aqueous solution containing dissolved gases can be treated to get useful products out of it.

Revision exercise 9

1. Define and give an example on each of the following:
   - (a) Addition polymerisation
   - (b) Condensation polymers
   - (c) Homopolymers
   - (d) Monomer
2. What structural features must be present in a monomer that can form both an addition polymer and a condensation polymer?
3. Lactic acid is used to synthesise polyester used for tissue implants and surgical sutures that have ability to dissolve in the body.



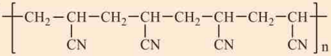
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$$

Lactic acid

Draw the structure of a portion of this polyester.

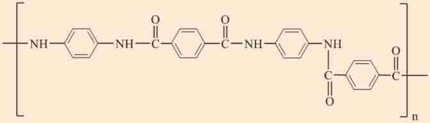
4. Write the name(s) of monomers of the following polymers:

(a)

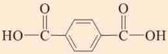


$$\left[-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-\right]_n$$

(b)



5. Draw the polymer that would be produced from condensation of the two monomer units below.



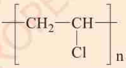
and

6. Assuming that the average chain lengths of the following polymers are equal, in which of the polymers would you expect to find the stronger intermolecular forces?

$$\left[\text{CH}_2-\text{CH}_2\right]_n$$

Polyethylene

and



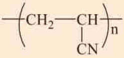
$$\left[\text{CH}_2-\underset{\text{Cl}}{\underset{|}{\text{CH}}}\right]_n$$

Poly(vinyl chloride)

7. Use an example to show how the branching and cross-linking can affect the physical behaviour of a polymer.

8. Explain the environmental impact and mitigation measures of polymers.

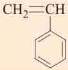
9. When acrylic polymers are burnt, toxic fumes are produced. Using polyacrylonitrile (PAN), as an example, what would you expect to be one of the most toxic gaseous combustion products created in the reaction?



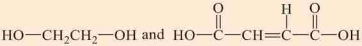
$$\left(\text{CH}_2-\underset{\text{CN}}{\underset{|}{\text{CH}}}\right)_n$$

(PAN)

10. Cross-linking adds strength to polymers. Polyesters containing double bonds are often cross-linked by reacting the polymer with styrene,



(a) Draw the structure of the copolymer of the monomers,



$$HO-CH_2CH_2-OH \text{ and } HO-\overset{O}{\overset{\|}{C}}-CH=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

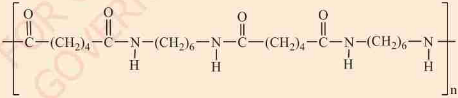
(b) Draw the structure of the cross-linked polymer produced if the copolymer obtained in (a) above is reacted with styrene.

11. (a) Define the following terms:
    - (i) Thermosetting polymer
    - (ii) Elastomer
    - (iii) Vulcanisation

    (b) Bakelite is a condensation thermosetting polymer. Justify this statement.

    (c) Classify the following polymers on the basis of action of heat on each:
    - (i) Nylon
    - (ii) Polyethylene
    - (iii) Teflon
    - (vi) Bakelite

12. Nylon 6,6 is a polymer with the following structure:



$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\right]_n$$

(a) Draw two monomers that could have formed this polymer.

(b) Draw the repeating unit on nylon 6,6 polymer.

13. (a) Mention features that can be considered in classifying a polymer as an addition or condensation polymer.

    (b) List some common uses of polymers.

(c) Why are addition polymers chemically more stable than their monomers?

14. (a) Most synthetic polymers are not biodegradable. Which method is suitable for the destruction of synthetic polymer wastes that cannot be recycled? Give reason(s) for your choice.

(b) Suggest the properties that make polymers suitable for use in making insulators, handles for cooking pans, ropes and a variety of domestic utensils.

(c) Polymers whose monomers contain a methyl group and those that contain a carbonyl group are soluble in organic solvents such as acetone. Which of the two is more soluble? Explain.

15. (a) Synthetic polymers can be made through two different methods. Mention the two methods and the functional groups common to the monomers that make up the polymers in each method.

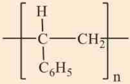
(b) Saran is a polymer used to make food wrapping materials. This polymer is made by alternating chloroethene and 1,1-dichloroethene monomers.

(i) Which type of polymerisation reaction is used to make saran polymers?

(ii) Draw the structure of the repeating unit in saran.

(iii) What type of force holds together molecules in saran?

(c) (i) Is the following a homopolymer or a copolymer? Explain.



$$\left[- \overset{\displaystyle H}{\underset{\displaystyle C_6H_5}{C}} - CH_2 - \right]_n$$

(ii) Write the name(s) of the monomer(s) of this polymer.

Glossary

Acid anhydrides	Organic compounds derived from the dehydration of two molecules of carboxylic acid
Activator	Electron donating group which makes benzene more reactive towards an electrophile
Addition reaction	Any chemical reaction which results in an increase in the number of atoms in a molecule
Alcohols	Organic compounds which contain one or more hydroxyl groups bonded to aliphatic hydrocarbons carbon(s)
Aldehydes	Organic compounds which have at least one hydrogen atom attached to a carbonyl carbon atom
Alkanes	Saturated aliphatic hydrocarbons which contain only carbon-carbon single bonds
Alkenes	Unsaturated hydrocarbons which contain carbon-carbon double bonds (C=C) or both carbon-carbon single and double bonds
Alkylation reaction	A chemical reaction that involves the transfer of an alkyl group as a carbocation, free radical or carbonium ion from one molecule to another
Alkynes	Unsaturated hydrocarbons which contain carbon-carbon triple bond or both carbon-carbon single and triple bonds
Amination	Formation of an amine either by addition of an amino group to an organic acceptor compound or by reduction of a nitro compound
An alkyl group	A hydrocarbon group, which is formed when one hydrogen is removed from an alkane

Aromaticity	Extra stability of a highly conjugated unsaturated molecule that exists as a planar ring with circular cloud of delocalised π-electrons
Branched polymer	A polymer having secondary polymer chains linked to a primary backbone, resulting in a variety of polymer architectures such as star, H-shaped, pom-pom and comb-shaped polymers
Benzene diazonium salts	Salts formed when an aromatic primary amine such as aniline is treated with a mixture of sodium nitrite and hydrochloric acid at a very low temperature of 0 – 5 °C
Carbanion	An organic ion containing a negatively charged carbon atom
Carbocation	An organic ion containing a positively charged carbon atom
Carboxylic acid	Organic compound containing carboxyl group as a functional group
Copolymer	A polymer formed when two or more different types of monomers are linked in the same chain
Cracking	A process by which heavy hydrocarbon molecules are broken down into lighter alkanes and alkenes
Cross-linked polymer	A polymer in which monomer units are cross-linked together to form a characteristic hard, rigid, and brittle network structure
Cumene process	An industrial process that forms phenol and acetone from benzene and propylene
Deactivator	Electron withdrawing group which reduces electron density from the benzene ring and makes it less reactive towards an electrophile

Decarboxylation reaction	Reaction which removes a carboxyl group as CO_2 from an organic compound
Degree of polymerisation	The number of times a monomer is contained in a polymer
Dehalogenation	Chemical reaction that involves the removal of a halogen atom from an alkyl halide molecule
Dehydrohalogenation	A chemical reaction that involves the removal of hydrogen halide from alkyl halides to form an alkene or alkyne depending on the number of moles of hydrogen halide being removed per mole of alkyl halide
Depolymerisation	Breaking up of polymer molecules by the action of heat, sunlight, oxygen, or ozone
Dihydric alcohol	An alcohol which contains two hydroxyl groups (–OH)
Disproportionation	A reaction in which a substance is simultaneously oxidised and reduced giving two different products
Dow's process	Process of extracting bromine from brine or is one method of preparing phenol from chloro benzene
Electrophiles	Positively charged or neutral species (Lewis acids) which are deficient in electrons such that they can accept a pair of electrons to form a bond
Elimination reaction	A type of organic reaction which involves the removal of an atom or a group of atoms from a saturated compound to form an unsaturated compound
Fermentation	A metabolic process that consumes sugars in the absence of oxygen to form organic acids, gases or alcohols

Free radical	An atom or group of atoms which contain at least one unpaired electron
Geometrical isomers	*Cis–trans* stereoisomers which have different orientations of groups around a double bond or similar structural feature
Halohydrocarbon	An organic compound that contains carbon, hydrogen and at least one carbon-halogen bond (C—X)
Homologous series	A series of organic compounds with the same functional group, similar properties and each member differs from the other by a methylene ($-CH_2$) group
Hückel's rule	Any planar cyclic conjugated system will be aromatic only if there are $4n + 2$ delocalised π-electrons systems
Hybridisation	The process of mixing orbitals to form hybrid orbitals involved in formation of stable bonds of molecular orbitals
Hydrocarbons	Organic compounds that consist of carbon and hydrogen only
Hydrogen bond	Special type of dipole-dipole interactions between hydrogen atoms which is covalently bonded to more electronegative atom with another highly electronegative atom that possesses lone pairs of electrons
Hydrogenation	The reaction which involves the addition of hydrogen atoms to unsaturated hydrocarbon compound or carbonyl compound
Inductive effect	A slight shift of bonded electrons towards the more electronegative atom resulting in a polarised bond

Isomerism	The existence of compounds having the same molecular formula but different structural formula
Isomers	Compounds which have the same molecular formula but differ in the type of structural arrangement, sequence of bonding of their atoms or in the arrangement of their atoms in space
Ketones	Organic compounds that have two hydrocarbons (alkyl or aryl) groups attached to a carbonyl carbon atom
Kolbe's reaction	Reaction in which 2-hydroxybenzoic acid is formed from phenol and CO_2
Linear polymer	A polymer in which monomers are joined together to form a single long straight chain
Lucas' reagent	A solution of anhydrous zinc chloride and concentrated hydrochloric acid in an equimolar amount
Malting	A process that converts raw grains into malt which is used for brewing
Markovnikov's rule	When the electrophilic addition reaction involves the use of unsymmetrical alkene, the electrophile $(H^{\oplus})$ attacks the carbon which already contains a large number of hydrogen atoms (less substituted carbon)
Mesomeric effect	The effect of withdrawing or releasing electrons attributed to a particular substituent through the delocalisation of *pi*-bond electrons
Monohydric alcohol	An alcohol which contains only one hydroxyl (–OH) group

Monomer	A single organic molecule that can link repeatedly to form a chain of a lager organic compound called polymer
Nucleophile	A reagent containing an atom with unshared or lone pair of electrons which can be shared with another atom to form a new covalent bond
Optical isomers	A pair of stereoisomers in which a molecule and its corresponding mirror image cannot be superimposed on each other
Organic colloids	Colloids formed from the microbial decomposition of organic matter
Osmosis	The process whereby the solvent molecules move from a region of dilute solution to a region of concentrated solution through a semipermeable membrane
Oxidation state	The number of electrons gained, shared or lost by an atom during combination with other atoms
Ozonolysis	Oxidative cleavage of the carbon-carbon double bond with ozone, followed by hydrolysis to form carbonyl compounds
Phenols	Organic compounds consisting of a hydroxyl (–OH) group bonded to an aromatic ring
Polymer	A large molecule or macromolecule composed of many repeated subunits called monomers
Polymerisation	Is the process of forming a large molecule (polymer) by joining together small subunits called monomers
Primary alcohol	An alcohol which consists of a hydroxyl group that is bonded to a carbon containing only one alkyl group

Saponification	Soap formation by the reaction of an ester and an alkali
Secondary alcohol	An alcohol which consists of a hydroxyl group that is bonded to a carbon containing two alkyl groups
Sulphonation	A substitution reaction in which one hydrogen atom of an aromatic ring is replaced with a sulphonic acid group
Tertiary alcohol	An alcohol which consists of a hydroxyl group that is bonded to a carbon containing three alkyl groups
Transesterification	A reversible reaction in which one ester is converted into another by the interchange of alkoxy group of an ester with another alcohol in the presence of an acid or base catalyst
Trihydric alcohol	An alcohol which contains three hydroxyl (–OH) groups

Bibliography

Abdallah, A., McGuire P., Nkunya, M. H., & Schiess, M. (1986). *Chemistry for A- level and 1st year undergraduate students* (Vol. III). Dar es Salaam: Tanzania Publishing House.

Bruice, P. Y. (2015). *Essential organic chemistry* (3rd ed.). Cheltenham: Pearson Education.

Chang, R. & Goldsby, K.A. (2015). *Chemistry* (12th ed.). New York, NY: McGraw-Hill Science Engineering.

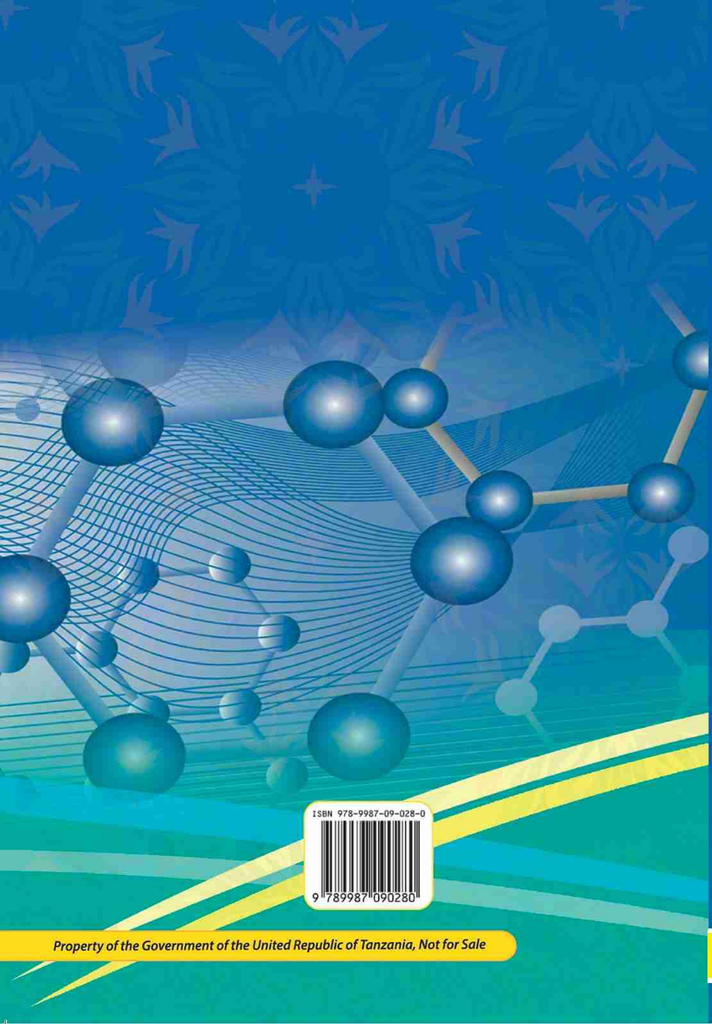
Carey, F.A. (2000). *Organic Chemistry* (4th ed.). New York: McGraw-Hill Companies Inc.

Ramsden, E.N. (2000). *Advanced Level Chemistry* (3rd ed.). Cheltenham: Nelson Thrones Publishers Ltd.

Silberberg, S.M. (2002). *Chemistry, The molecular nature of matter and change* (3rd ed.). New York, NY: McGraw-Hill Science Engineering.

Solomons, T.W.G. & Fryhle, C.B. (2004. *Organic chemistry* (8th ed.). USA: John Wiley & Sons, Inc

Index



ISBN 978-9987-09-028-0

Property of the Government of the United Republic of Tanzania, Not for Sale