15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

OBJECTIVES

This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.

- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. ..... etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate (NH_4 CNO).

$$2KCNO + (NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_4CNO + K_2SO_4$$

or $$Pb(CNO)_2 + 2NH_4OH \xrightarrow{\Delta} 2NH_4CNO + Pb(OH)_2$$

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$$NH_4CNO \xrightarrow[\text{Rearrangement}]{\Delta} NH_2CONH_2$$

Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.

ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

15.1 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation.**
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol^{-1}) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is C > Si ≈ S>P>N>O.

15.2 Classification into open chain and cyclic compounds

The organic compounds are classified into two main types, namely.

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(1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

Examples

$CH_3 - CH_2 - CH_3$ propane

$CH_2 - CH_2 - CH(CH_3) - CH_3$

2– methylbutane or isopentane

$CH_3 - C(CH_3)_2 - CH_3$ neopentane

(2) Closed chain or cyclic compounds

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

(a) Homocyclic or carbocyclic compounds

(b) Heterocyclic compounds

(a) Homocyclic compounds : In these compounds the ring structure is made up of only carbon atoms.

These compounds are further classified into

(i) Aromatic compounds and

(ii) Alicyclic compounds

(i) Aromatic compounds (Benzenoid) : Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

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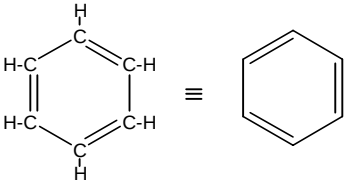
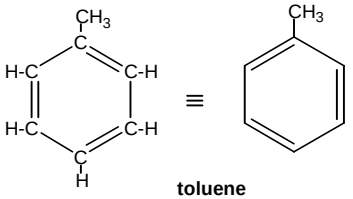
Examples

Monocyclic

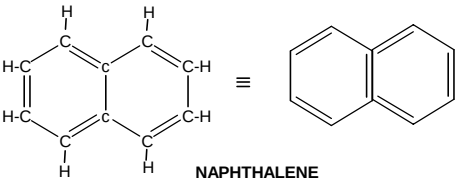


benzene

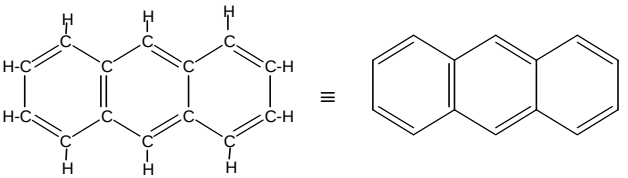


toluene

Polycyclic



NAPHTHALENE



ANTHRACENE

Heterocyclic compounds (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.

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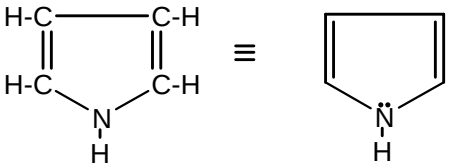
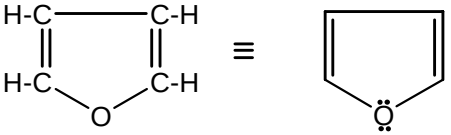
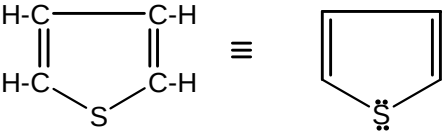
Examples



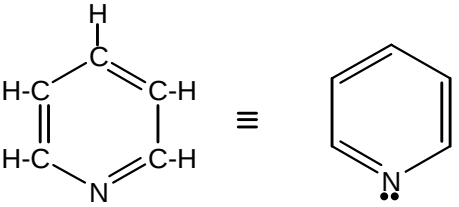
pyrrole



furan



thiophene

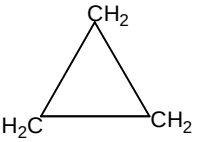


pyridine

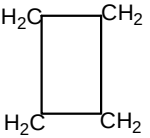
The above compounds are aromatic non-benzenoid compounds.

(ii) Alicyclic compounds : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

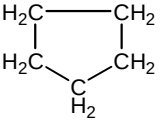
Examples



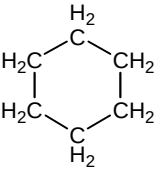
cyclopropane



cyclobutane



cyclopentane



cyclohexane

The above classification can be schematically represented as follows :

Organic Compounds

- Open chain or acyclic compounds eg : ethane, propylene, isobutane
- Closed chain or cyclic compounds
  - Homocyclic or carbocyclic compounds
    - Aromatic compounds eg : benzene, toluene, naphthalene,anthracene (benzenoids)
    - Alicyclic compounds eg : cyclopropane, cyclobutane, cyclopentane, cyclohexane
  - Heterocyclic compounds eg : pyridine, pyrrole, thiophene, furan (Aromatic non-benzenoids)

Characteristics of organic compounds

All organic compounds have the following characteristic properties

(1) Many organic compounds are inflammable

(2) They are mostly covalent compounds

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(3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
(4) They have generally low boiling point and melting point.
(5) They exhibit isomerism

Homologous series

A group or class of organic compounds related to each other by a general molecular formula contributes homologous series.

Characteristics of homologous series

Homologous series have the following characteristics :

(1) All members of a series contain same elements and the same functional groups.
(2) All the members of a homologous series can be represented by a general formula

Examples

Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}

(3) All the members of a homologous series can be prepared by similar methods.
(4) All members of a homologous series usually undergo similar chemical reactions.
(5) Successive members in a series differ by a $-CH_2$ group
(6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

15.3 Functional groups

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	– X
Alcohol	– OH
Ether	– O –

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Aldehyde – CHO

Ketone –C(=O)–

Carboxylic acid – COOH

Ester – COOR

Amide –C(=O)–NH_2

Acid halide –C(=O)–X (X = –Cl, –Br, –I)

Acid anhydride –C(=O)–O–C(=O)–

Amine – NH_2

Nitro compounds – NO_2

15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

(1) Common or Trivial system (2) IUPAC system

IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

(a) Root word (b) Suffix (c) Prefix

Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g. Meth - for Methane
Eth - for Ethane
Prop - for Propane
But - for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.

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e.g. Pent - is derived from penta for five
Hex - is derived from hexa for six
Hept - is derived from hepta for seven
Oct - is derived from octa for eight

Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	 ene diene triene
3.	Unsaturated with One triple bond Two triple bond	 yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	CH_3-CH_2-CH_2-CH_3	4	But	ane	Butane
2.	CH_3-CH = CH_2	3	Prop	ene	Propene
3.	CH ≡ CH	2	Eth	yne	Ethyne
4.	CH_2=CH–CH = CH_2	4	Buta*	diene	Butadiene
5.	HC ≡ C – C ≡ CH	4	Buta*	diyne	Butadiyne

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* extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	>C=O	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

a) If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.

b) If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.

c) If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structu-ral formula	No. of C atoms	Root word	Primary suffix	Secondary suffix	IUPAC name	Remarks
1.	CH_3 | CH_2-OH	2	Eth	ane	ol	Ethanol	`e' of prim suffix dropped

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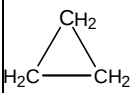
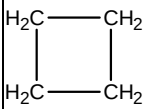
2.	CH_2-OH | CH_2-OH	2	Eth	ane	diol	Ethane diol	`e' of prim suffix not dropped
3.	CH_3 | CH_2 | CHO	3	Prop	ane	al	Propanal	`e' of the prim suffix dropped
4.	CH_3 | CH_2 | CH_2 | COOH	4	But	ane	oic acid	Butanoic acid	`e' of prim suffix dropped

Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

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Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH_3	Methyl
- C_2H_5	Ethyl
CH_3 - CH_2 - CH_2 -	n-propyl
$(CH_3)_2$ CH -	Iso propyl
$(CH_3)_3$ C -	t - Butyl
- NO_2	Nitro
- NH_2	Amino
- NO	Nitroso
$N \equiv N$	Diazo
- OCH_3	Methoxy
- OC_2H_5	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH_3-CH_2-Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH_3-NO_2	1	Meth	ane	-	-	Nitro	Nitro methane

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Saturated Hydrocarbons : Alkanes

General formula : C_nH_{2n+2} **Suffix** : ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH_4	Methane	Methane
2.	$H_3C - CH_3$	Ethane	Ethane
3.	$H_3C - CH_2 - CH_3$	Propane	Propane
4.	$H_3C - CH_2 - CH_2 - CH_3$	n-butane	Butane

Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix-**ane** by- **yl**.

Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH_4	Methane	CH_3 -	Methyl
2.	$CH_3 - CH_3$	Ethane	$CH_3 - CH_2$ -	Ethyl
3.	CH_3-CH_2-CH_3	Propane	CH_3-CH_2-CH_2-	Propyl

Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

a) **iso –** The alkyl group in which a - CH_3 branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH_3 group is called on isoalkyl group.

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Sl.No.	Structure	IUPAC name
1.	$CH_3-CH(CH_3)-$	1-methyl ethyl (iso-propyl)
2.	$CH_3-CH(CH_3)-CH_2-$	2-methyl propyl (iso-butyl)
3.	$CH_3-CH(CH_3)-CH_2-CH_2-$	3-methyl butyl (iso-pentyl)

b) Sec - The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	$CH_3-CH(-)-CH_3$	1 - Methyl ethyl (Sec - propyl)
2.	$CH_3-CH_2-CH(CH_3)-$	1 - methyl propyl (Sec - butyl)
3.	$CH_3-CH_2-CH_2-CH(CH_3)-$	1 - methyl butyl (Sec - pentyl)

c) Tert - (or) t -

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	$CH_3-C(CH_3)_2-$	1,1 – dimethyl ethyl (tert - butyl)
2.	$CH_3-CH_2-C(CH_3)_2-$	1,1 – dimethyl propyl (tert - pentyl)

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Alkenes

General formula : C_nH_{2n} **Suffix : ene**

The common name of alkene is obtained by replacing the ending - **ane** from the name of its parent alkane with - **ylene**.

The IUPAC name of an alkene is obtained by replacing - **ane** of the alkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
CH_3-CH_2- CH= CH_2 (double bond starts at C_1)	1- Butylene	But-1-ene
CH_3-CH = CH-CH_3 (double bond starts at C_2)	2- Butylene	But-2-ene

Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	CH_2=CH-CH_2-	allyl	Prop - 2 - enyl

Alkynes

General formula : C_nH_{2n-2} **Suffix** : - yne

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

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Sl. No.	Structural formula	Common Name	IUPAC name
1.	$HC \equiv CH$	Acetylene	Ethyne
2.	$CH_3 - C \equiv CH$	Methyl acetylene	Propyne
3.	$CH_3 - C \equiv C - CH_3$	Dimethyl acetylene	But-2– yne

Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
CH_3-CH_2-CH_2-Br	n-propyl bromide	1-bromopropane
$CH_3 - CH(I) - CH_3$	Iso-propyl iodide	2-iodopropane
CH_3-CH_2-CH_2-CH_2-Cl	n-butyl chloride	1-chlorobutane
CH_3-CH_2–$CH(Br)$–CH_3	Sec-butyl bromide	2-bromobutane
CH_3–$CH(CH_3)$–CH_2–Cl	Isobutyl chloride	1-chloro-2-methyl propane
$CH_3 - C(CH_3)_2 - I$	ter-butyl iodide	2-iodo-2-methyl propane
CH_2=CH-Cl	Vinyl chloride	Chloroethene
CH_2=CH-CH_2-Cl	Allyl chloride	3-Chloro-1-propene

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Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-**, **di-**, **tri-**hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "**e**" of the alkane is replaced by "**ol**".

Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
CH_3-OH	Methyl alcohol	methanol
CH_3-CH_2-OH	Ethyl alcohol	ethanol
CH_3-CH_2-CH_2-OH	n-propyl alcohol	1-propanol
CH_3 –CH – CH_3 | OH	Isopropyl alcohol	2-propanol
CH_3-CH_2-CH_2-CH_2-OH	n-butyl alcohol	1-butanol
CH_3 – CH_2 –CH – CH_3 | OH	sec-butyl alcohol	2-butanol
CH_3 –CH – CH_2 – OH | CH_3	Isobutyl alcohol	2-methyl-1-propanol
CH_3 | CH_3 – C – OH | CH_3	tert-butyl alcohol	2-methyl-2-propanol
CH_2=CH-CH_2-OH	Allyl alcohol	2-propene-1-ol

Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

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Structural formula	Common name	IUPAC name
CH_2-OH | CH_2-OH	Ethylene glycol	1,2-Ethanediol

Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
CH_2 - OH | CH - OH | CH_2 - OH	Glycerol	1,2,3-propanetriol

Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
Simple ethers		
CH_3-O-CH_3	Dimethyl ether	Methoxymethane
CH_3-CH_2-O-CH_2-CH_3	Diethyl ether	Ethoxyethane
Mixed ethers		
CH_3-O-CH_2-CH_3	Ethyl methyl ether	Methoxyethane
CH_3-O-CH_2-CH_2-CH_3	Methyl n-propyl ether	1-methoxypropane
CH_3 - O - CH - CH_3 | CH_3	Isopropyl methyl ether	2-methoxypropane

0777 023 444

Aldehydes

Aldehydes and ketones are two important classes of compounds containing the carbonyl group $-\underset{\underset{O}{\|}}{C}-$. In aldehydes the $-\underset{\underset{O}{\|}}{C}-$ group is linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula R-CHO.

IUPAC names of aldehydes are obtained by replacing the terminal "**e**" of alkane with "**al**".

Structural formula	Common name	IUPAC name
H-CHO	Formaldehyde	Methanal
CH_3-CHO	Acetaldehyde	Ethanal
CH_3-CH_2-CHO	Propionaldehyde	Propanal
CH_3-CH_2-CH_2-CHO	Butyraldehyde	1-Butanal
$CH_3-CH(CH_3)-CHO$	Isobutyraldehyde	2-Methylpropanal

Ketones

In ketones $-\underset{\underset{O}{\|}}{C}-$ group is united with 2 alkyl groups. These compounds are represented by the general formula.

$$R-\underset{\underset{O}{\|}}{C}-R'$$

Ketones are named by replacing the terminal "**e**" of the corresponding alkane name with "**one**".

Structural formula	Common name	IUPAC name
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$	Acetone (Dimethyl ketone)	Propanone
$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$	Ethylmethyl ketone	Butanone
$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$	Diethyl ketone	3-pentanone

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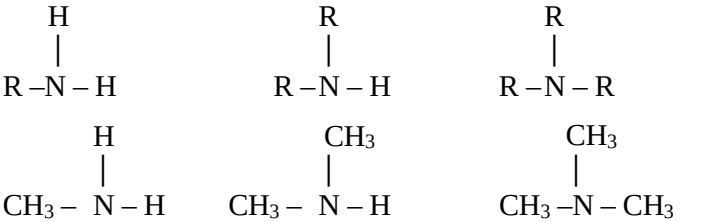
Carboxylic acids

These are represented by the general formula R-COOH. IUPAC name is derived by replacing the terminal "**e**" of the alkane name with "**oic acid**". These compounds are further classified into **mono**- and **di**-carboxylic acids.

Structural formula	Common name	IUPAC name
Monocarboxylic acids		
H-COOH	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
CH_3-CH_2-CH_2-COOH	Butyric acid	Butanoic acid
Dicarboxylic acids		
COOH | COOH	Oxalic acid	Ethanedioic acid
CH_2 < COOH, COOH	Malonic acid	Propanedioic acid
CH_2 – COOH | CH_2 – COOH	Succinic acid	Butanedioic acid

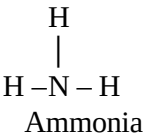
Amines

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.

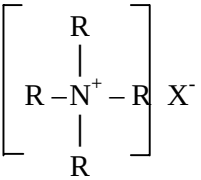


Methylamine (primary amine) | Dimethyl amine (secondary amine) | Trimethyl amine (teritary amine)

0777 023 444



Ammonia



(quarternary salt)

When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

Structural formula	Common	IUPAC name
Primary Amines		
CH_3-NH_2	Methyl amine	aminomethane
CH_3-CH_2-NH_2	Ethyl amine	aminoethane
CH_3-CH_2-CH_2-NH_2	n-propyl amine	1-aminopropane
$CH_3 - CH(NH_2) - CH_3$	Isopropyl amine	2-aminopropane
Secondary Amines		
CH_3-NH-CH_3	Dimethyl amine	(N-methylamino) methane
CH_3-CH_2-NH-CH_2-CH_3	Diethyl amine	(N-ethylamino) ethane
CH_3-NH-CH_2-CH_3	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
Tertiary Amines		
$CH_3 - N(CH_3)_2$	Trimethyl amine	(N,N - dimethyl amino) methane
$C_2H_5 - N(CH_3)_2$	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

0777 023 444

Nitro compounds

These compounds are represented by the general formula RNO_2. IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

	Structural formula	Common/IUPAC name
1.	$CH_3 - NO_2$	Nitromethane
2.	$CH_3 – CH_2 – NO_2$	Nitroethane
3.	$CH_3 – CH_2 – CH_2 - NO_2$	1-Nitropropane
4.	$CH_3 – CH(NO_2) – CH_3$	2-Nitropropane

15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism 2. Stereoisomerism

Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

1. Chain isomerism or Nuclear isomerism

Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

0777 023 444

Examples

$CH_3 - CH_2 - CH_2 - CH_3$ and $CH_3 - CH(CH_3) - CH_3$

n-butane isobutane

$CH_3-CH_2-CH_2-CH_2-OH$ and $CH_3-CH(CH_3)-CH_2-OH$

n-butyl alcohol isobutyl alcohol

2. Position Isomerism

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.

$CH_3 - CH_2 - CH_2 - OH$ and $CH_3 - CH(OH) - CH_3$

1-Propanol 2-Propanol

$CH_3 - CH_2 - CH_2 - Br$ and $CH_3 - CH(Br) - CH_3$

n-propyl bromide Isopropyl bromide

$CH_3-CH_2-CH_2-CH_2-OH$ and $CH_3-CH_2-CH(OH)-CH_3$

n-butyl alcohol Sec - butyl alcohol

$CH_3 - CH(CH_3) - CH_2 - OH$ and $CH_3 - C(CH_3)_2 - OH$

Isobutyl alcohol ter - butyl alcohol

$CH_3 - CH_2 - CH = CH_2$ $CH_3 - CH = CH - CH_3$

1-Butene 2-Butene

0777 023 444

Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

Examples

1. $CH_3 - CH_2 - OH$ and $CH_3 - O - CH_3$

   Ethyl alcohol Dimethyl ether

2. $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3$ and $CH_3 - CH_2 - CHO$

   Acetone Propionaldehyde

3. $CH_3 - CH_2 - COOH$ and $CH_3 - COO - CH_3$

   Propionic acid Methyl acetate

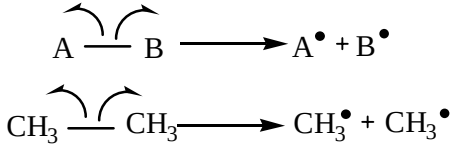
15.6 Fission of bonds

How bond fission occurs?

A covalent bond (σ bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

Homolytic fission

A covalent bond between two atoms A and B may be shown as A· · B or A–B. This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.



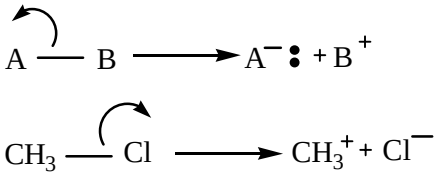
Ethane Methyl free radicals

Heterolytic fission

A covalent bond breaks in such a way that the shared pair of electron

0777 023 444

stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as A^{-}: is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent $\rightarrow$ [intermediate] $\rightarrow$ product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

15.7 Types of Reactions

Substitution or Displacement reactions

Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

a) Nucleophilic substitution reaction (S_N)

When a substitution reaction is brought about by a nucleophile, the reaction is termed as S_N (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1) S_N^1 (substitution, nucleophilic, unimolecular)

$$\underset{\text{tert-butyl chloride}}{(CH_3)_3C\ Cl} + KOH \xrightarrow{\text{aqueous}} (CH_3)_3C\ OH + KCl$$

0777 023 444

(2) S_N^2 (Substitution, nucleophilic, bimolecular)

$$\underset{\text{(Methyl Chloride)}}{CH_3Cl} + KOH \xrightarrow{\text{aqueous}} CH_3OH + KCl$$

b) Electrophilic substitution reaction (S_E)

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (S - stands for substitution and E for electrophile).

c) Free radicals substitution reaction

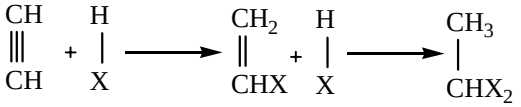
These reactions are initiated by free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \quad \text{(Free radical)}$$

$$\underset{\text{Methane}}{CH_4} + 2Cl\cdot \rightarrow CH_3Cl + HCl$$

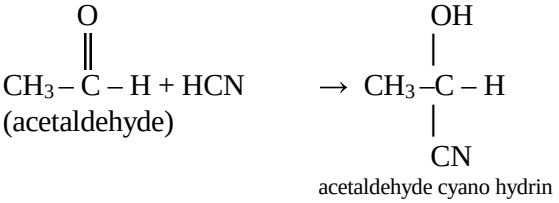
Addition Reactions

All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.

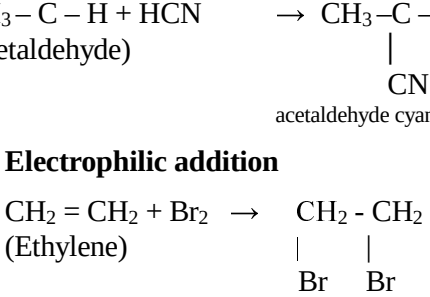


Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

(a) Nucleophilic addition



(b) Electrophilic addition



(c) Free radical addition

$$CH_3 - CH = CH_2 \xrightarrow[H_2O]{HBr} CH_3 - CH_2 - CH_2 - Br$$

Elimination reactions

In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

(a) Unimolecular elimination (E_1)

$$(CH_3)_3C\text{-}Br \xrightarrow[KOH]{alcoholic} (CH_3)_2C{=}CH_2 + H_2O + Br^-$$

2-Methyl propene

(b) Bimolecular elimination (E_2)

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow[KOH]{alcoholic} CH_3 - CH = CH_2 + KBr + H_2O$$

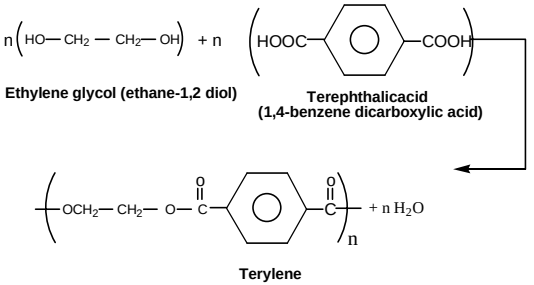
Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

Examples

$$n\ CH_2 = CH_2 \xrightarrow{473K, 1000\ atm} (-\ CH_2 - CH_2\ -)_n$$

Ethylene (Monomer) → Polyethene (Polymer)



0777 023 444

Condensation reactions

When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like H_2O, NH_3, HCl, CO_2, it is called a **condensation** reaction.

Example

Aldol condensation reaction

$$\underset{\text{(acetaldehyde)}}{CH_3\text{-}CHO} + HCH_2 - CHO \xrightarrow{NaOH} \underset{\text{(aldol)}}{CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2\text{-}CHO}$$

Hydrolysis

Esters are hydrolysed by boiling with mineral acids or alkalis.

a) Acid hydrolysis

An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid (H_2SO_4 or HCl) as catalyst.

$$\underset{\text{Ethylacetate}}{CH_3\text{-}COOCH_2\text{-}CH_3} + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{acetic acid}}{CH_3\text{-}COOH} + \underset{\text{Ethyl alcohol}}{CH_3\text{-}CH_2\text{-}OH}$$

The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water.

b) Basic hydrolysis

When an ester is treated with an alkali (NaOH or KOH) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

$$\underset{\text{Ethyl propionate}}{CH_3\text{-}CH_2\text{-}COOC_2H_5} + NaOH \rightarrow \underset{\text{Sodium propionate}}{CH_3\text{-}CH_2\text{-}COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Reduction and oxidation reactions

A reaction which proceeds by the addition of hydrogen is termed

0777 023 444

Reduction and the one that involves the addition of oxygen is called **Oxidation**. For example,

1) Clemmensen Reduction

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.

$$\underset{\text{acetophenone}}{C_6H_5COCH_3} \xrightarrow[\text{HCl}]{\text{Zn/Hg}} \underset{\text{Ethyl benzene}}{C_6H_5 - CH_2 - CH_3}$$

2) Very mild oxidising agent such as $KMnO_4$, causes a spliting of the molecule at the double bond.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O + [O] \rightarrow \underset{\text{Ethylene glycol}}{\begin{array}{l} CH_2 - OH \\ | \\ CH_2 - OH \end{array}}$$

15.7.1 Types of Reagents

Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

(i) Positive electrophiles (or) Ionic electrophiles

(ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	H^+ (proton)	$AlCl_3$
2.	Cl^+ (chloronium)	BF_3
3.	Br^+ (bromonium)	$ZnCl_2$
4.	No_2^+ (Nitronium)	$FeCl_3$
5.	$>C^+$ carbonium	SO_3

0777 023 444

Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH_3	X^- (halide ions)
2.	H_2O	OH^- (hydroxide)
3.	R-OH	RO^- (alkoxide)
4.	$R\text{-}NH_2$	CN^- (cyanide)
5.	$R_3\text{-}N$	$< C^-$ (carbanion)

The differences between these reagents are summarised in the following table.

S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

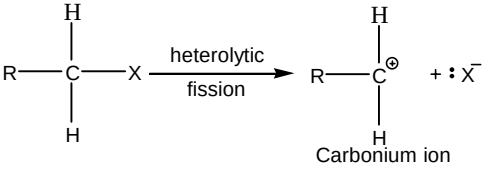
15.7.2 Carbonium ions

Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon

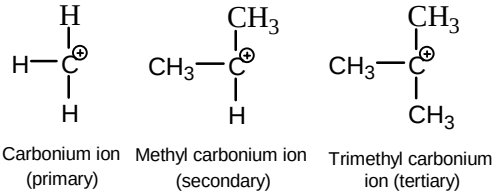
0777 023 444

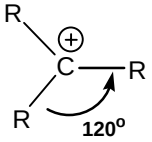
are known as carbonium ions.

For illustration



These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.





The geometry of alkyl carbonium ion

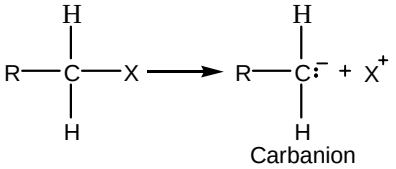
Since the carbon of the carbonium ion is in sp^2 hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

Carbanion

Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

0777 023 444

For illustration



Examples

$CH_3 - CH_2^- :$ methyl carbanion

$CH_3 - CH(CH_3)^- :$ dimethyl carbanion

15.8 Free Radicals

Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

Few examples : $Cl\cdot$, $CH_3\cdot$, $C_6H_5\cdot$

They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

Formation of free radicals

(a) Photochemical fission : When an organic compound is exposed to ultraviolet region it under goes bond fission.

Example : $Cl \cdot \cdot Cl \xrightarrow{uv} Cl\cdot + Cl\cdot$

(b) Thermal fission : All organic compounds on heating yield free radicals.

$$(C_2H_5)_4Pb \xrightarrow{\Delta} Pb + 4C_2H_5\cdot$$

Polar Effects

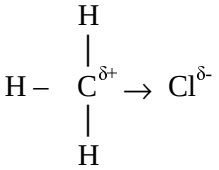
Inductive Effect

If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

0777 023 444

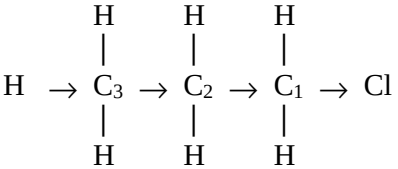
shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.

Consider methyl chloride,



In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2. This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1. This type of electron displacement occuring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by $\rightarrow$ the arrow head pointing towards the more electronegative atom. This effect operates in the case of σ - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

- C_6H_5, ^-OH, -I, -Br, -Cl, -F

Groups having + I effect [electron pumping]

0777 023 444

CH_3 -, CH_3 - CH_2 - , $(CH_3)_2CH$-, $(CH_3)_3C$ -

(Methyl) (Ethyl) Isopropyl tertiarybutyl

Resonance (Mesomeric) Effect

When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.

$$O = C = O$$
(I)

The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO_2 molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

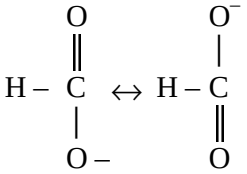
Again, the heat of formation of carbon dioxide is 1592 $kJ.mol^{-1}$ where as on the basis of the above structure it is expected to be approximately 1466 $kJ.mol^{-1}$. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.

$$O^+ \equiv C - O^- \leftrightarrow O = C = O \leftrightarrow {}^-O - C \equiv O^+$$

The difference in energy i.e. 126 $KJ.mol^{-1}$ is regarded as resonance energy.

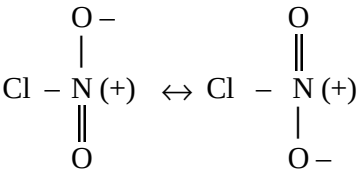
Few other examples

1. Formate ion, $HCOO^-$

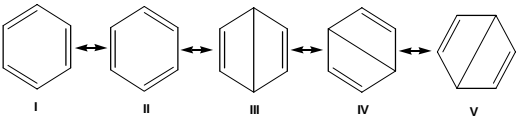


2. Nitryl chloride, NO_2Cl

0777 023 444



3.



Benzene

Questions

A. Write IUPAC name of the following

(a) $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$

(b) $CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_3$

(c) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{OH}{|}}{CH} - CH_3$

(d) $CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_2 - CH_3$

(e) $CH_2 = CH - COCH_2CH_3$

(f) CH_3CH_2CHO

0777 023 444

(g) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - COOH$

(h) $CH_3CH_2OCH_2CH_3$

(i) $CH_3OCH_2CH_2CH_3$

(j) $CH_3 - O - \underset{\underset{CH_3}{|}}{CH} - CH_3$

(k) $CH_3CH_2CH_2CH_2NH_2$

B. Explain briefly on the following

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

SUMMARY

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.

0777 023 444

- Method of writing IUPAC names of different organic compounds are explained with suitable examples.
- All types of organic reactions, like substitution, addition, elimination, condensation, polymerisation, hydrolysis, oxidation and reduction reactions are explained with suitable examples.
- Different types of isomerism and the representations are explained.
- Nature of fission of bonds, reagents, carbonium ions carbanions and free radicals are structurally explained with suitable examples.
- Notable electron displacements in organic chemistry like inductive and mesomeric effect in covalent bond are explained.

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0777 023 444

16. PURIFICATION OF ORGANIC COMPOUNDS

OBJECTIVES

The main objectives of this chapter are to provide

* *Characteristics of organic compounds*
* *Need for purification*
* *Methods of purifying organic substances like crystallisation, distillation, fractional distillation, steam distillation, distillation under reduced pressure and various methods of chromatography.*

16.1 Characteristics of organic compounds

Organic compounds have the following general characteristics.

i) Organic compounds are generally covalent and hence they do not dissolve in water (polar solvents) but dissolve in organic solvents (non-polar solvents) such as ether, alcohol, benzene etc.

ii) Due to maximum catenation and tetravalency of carbon, they have tendency to form long open and closed chain compounds.

iii) They are volatile, inflammable and possess low boiling points and melting points.

iv) Some organic compounds exhibit the phenomenon of polymerisation. For example, ethylene polymerises to poly ethylene.

v) They exhibit isomerism.

vi) They contribute homologous series.

vii) They are non-conductors of electricity.

Need for purification of organic compounds

The organic compounds obtained from natural sources are not pure. They contain a number of other compounds which occur with them. Similarly, the organic compounds prepared in the laboratory are also not pure. They are found to contain other products formed during the reaction. In order to investigate the structure and properties of an organic compound, it should be in the purest form. Hence purification of organic compounds become essential.

0777 023 444

Various methods used for purification and separation of organic compounds are:

i) Crystallisation
ii) Fractional Crystallisation
iii) Sublimation
iv) Distillation
v) Extraction with solvents
vi) Chromatography

16.2 Crystallisation

Crystallisation is carried out in four stages (a) preparation of the solution of the substance in a suitable solvent (b) filtration of the hot solution (c) crystallisation by cooling the hot filtrate (d) isolation and drying of the purified substance.

a) Preparation of the solution : The powdered organic substance is taken in a semi-micro round bottom flask and the solvent is added little by little with constant stirring and heating till the amount added is just sufficient to dissolve the solute, when the solution is just boiled. If the solvent is non-inflammable, heating may be done on the wire gauze, while in the case of inflammable solvents, heating should be done on a water bath.

b) Filtration of the Solution : The hot saturated solution obtained is filtrated through a fluted filter paper placed in a hot water funnel.

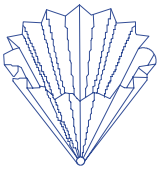


Fig. 16.1 Fluted Filter paper

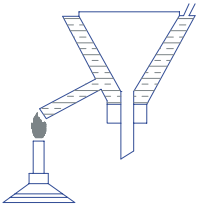


Fig. 16.2 Water funnel

0777 023 444

c) Crystallisation : When the filtration is over, the beaker containing the solution is allowed to cool when pure crystals separate. Sometimes the crystals do not separate due to super cooling of the solution. Crystallisation can be started in such cases by scratching the sides of the vessel containing the solution with a glass rod or seeding with a tiny crystal of the substances.

d) Isolation and drying of the purified crystals : The purified crystals are separated from the mother liquor by filtration using Buchner funnel and a suction pump.

When the whole of the mother liquor has been drained off, the crystals are washed with small amounts of cold solvent thrice. The crystals are then transfered to a porous plate, pressed by using filter paper and then dried by using infra-red light or by keeping in sunlight. If the crystals are coloured, decolourisation is effected by using animal charcoal.

Fractional Crystallisation

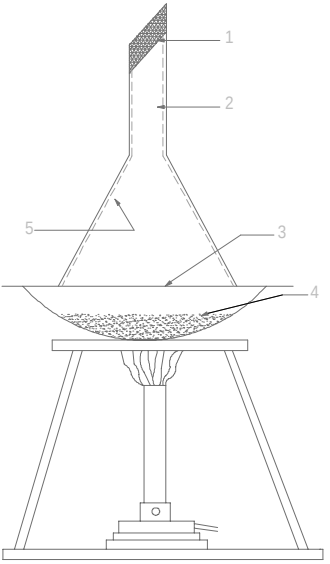
When the solubility of two substances in any solvent is not much different from one another, then the two compounds can be separated by fractional crystallisation, involving a series of repeated crystallisations. For example, when a solution containing two substances A and B is subjected to crystallisation, the slightly less soluble substances (say A) containing a small amount of the other substance (B) crystallises out. The mother liquor when subjected to crystallisation gives crystals of B containing a small amount of A.

Now, if these crystals are subjected to recrystallisation separately and the process is repeated number of times to get pure A and pure B.

16.3 Sublimation

Certain solid substances like Naphthalene or camphor when heated pass directly from solid to the vapour state without melting. The vapours when cooled give back the solid substance. This process is known as sublimation.

0777 023 444



1. Cotton
2. Inverted funnel
3. Perforated asbestos sheet
4. Mixture
5. Sublimate

Fig. 16.3

This process is very helpful in separating a volatile solid from a non-volatile solid. The powdered substance is taken in a China dish and covered with a perforated filter paper and an inverted funnel. The dish is carefully heated on a sand bath.

The vapours passing through the holes in the paper condense on the inner sides of the funnel. The non-volatile impurities remain in the dish.

16.4 Methods for the purification of liquids Distillation

Distillation is used for separating the constituents of a liquid mixture which differ in their boiling points. Depending upon the difference in the boiling points of the constituents, different types of distillation are employed. These are described below.

i) Simple Distillation

Liquids with boiling points widely apart (about 40K and above) can be purified by simple distillation if they do not decompose under ordinary pressure. Simple distillation involves conversion of a liquid into its vapour

0777 023 444

by heating in a distilling flask and then condensation of the vapour into a liquid in the receiver.

Mixtures like the following can be separated by this simple distillation.

a Nitro benzene (b.p 484K) and benzene (b.p.354K)

b. Diethyl ether (b.p.308K) and ethyl alcohol (b.p.351K)

Note : Simple distillation is also helpful in separating non-volatile impurities from liquids.

16.4.1 Fractional Distillation

This method is applicable for the separation and purification of a mixture of two or more miscible liquids whose boiling points lie very close to each other.

This is similar to the ordinary distillation method with the only exception that a fractionating column is introduced in-between the distillation flask and the condenser.

The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation.

The fractionating columns used for the purpose are of different shapes.

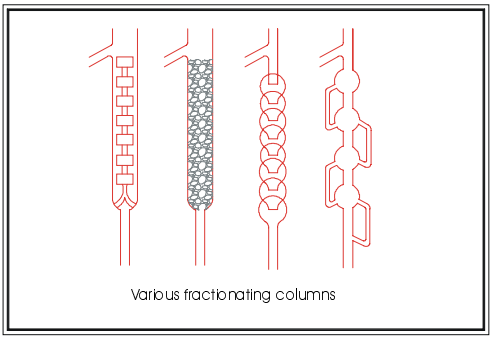


Fig. 16.4

16.4.2 Steam Distillation

In steam distillation impure compounds are distilled in a current of steam. This method is applicable to solids as well as liquids. For purification by steam distillation, an impure compound must satisfy the following conditions:

0777 023 444

i) It should not decompose at the steam temperature.

ii) It should have a fairly high vapour pressure at 373 K.

iii) It should be insoluble in water.

iv) The impurities present should be non-volatile

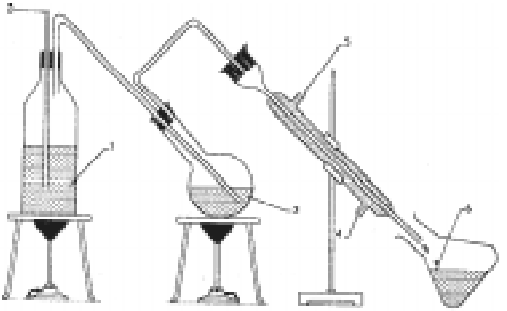


Fig. 16.5

1. Water 2. Protective tube 3. Flask 4. Inlet for water
5. Outlet for water 6. Pure liquid

The apparatus used for steam distillation is shown in the figure (16.5). The impure compound is taken in the round bottomed flask and a small quantity of water is added. The flask is then heated gently. Now steam is bubbled through the contents in the flask. The vapours of the compound mix up with steam and escape into the condenser. The condensate thus obtained is a mixture of water and the organic compound which can be separated.

Theory of steam distillation

Let p_1 represent the vapour pressure of water and p_2 the vapour pressure of the organic liquid. In steam distillation the liquid boils at a temperature at which

$$p_1 + p_2 = \text{Atmospheric Pressure}$$

This temperature must be lower than the normal boiling point of water or the organic liquid. The reason that $p_1 + p_2$ becomes equal to the atmospheric pressure must earlier than p_1 or p_2 alone. Thus in steam distillation, the impure liquid boils at a temperature which is lower than its normal boiling point. Hence, steam distillation serves the same purpose as

0777 023 444

distillation under reduced pressure. However, the former is cheaper but less useful than the latter.

16.4.3 Distillation under reduced pressure

This technique is used for purifying or separating thermally unstable liquid compounds which decompose at their normal boiling points.

Principle : Lowering of pressure on the surface of a liquid lowers its boiling point. As a result, a liquid can be boiled and distilled at a temperature much below the normal boiling point without any decomposition.

Procedure : Distillation under reduced pressure or vacuum is carried out in a specially designed glass apparatus as shown in (Fig.17.6).

The receiver is attached to a vacuum pump to reduce pressure. The pressure is measured with the help of a manometer.

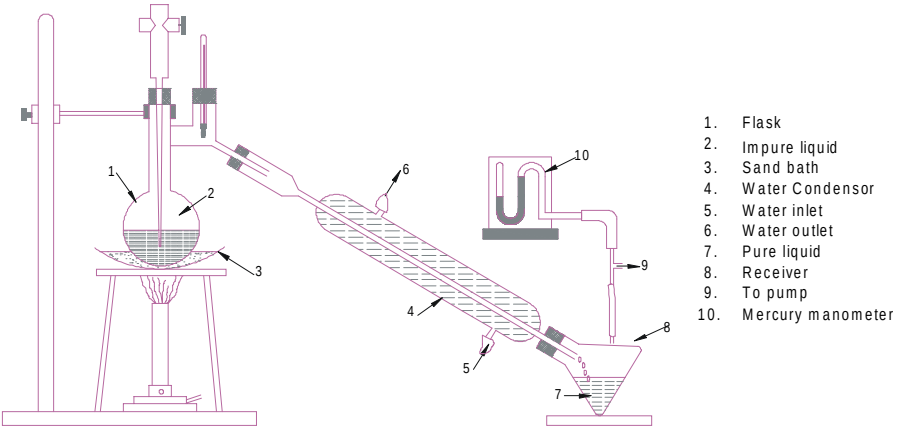


Fig.16.6 Distilation under reduced pressure

Advantages of distillation under reduced pressure

Distillation under reduced pressure has the following advantages:

0777 023 444

i) The compounds which decompose on heating to their boiling points under normal pressure can be purified by distillation under reduced pressure. This is because at a reduced pressure, a liquid would boil at temperature much below its normal boiling point.

ii) In distillation under reduced pressure, a liquid boils at temperature well below the normal boiling point. So, the distillation under reduced pressure is more fuel-economical.

16.4.4 Extraction with solvents

This method is based on the fact that organic substances are more soluble in organic solvents than in water.

The organic substance is extracted from its aqueous solution adopting the following procedure.

a. The aqueous solution containing organic substance is shaken with a suitable organic solvent which dissolves the substance but is immiscible with water. Two layers are formed; the organic layer and aqueous layer.
b. The solvent layer containing the organic substance (organic layer) is separated using a `separating funnel'. The impurities remain in the aqueous layer removed by distillation to obtain the organic substance.
c. The organic solvent is removed by distillation to obtain the organic substance.

16.5 Chromatography

This technique was introduced by M.S.Tswett, a Russian botanist in 1906 when he reported the separation of different coloured constituents of chlorophyll. He achieved it by passing a petroleum ether solution of the chlorophyll present in leaves through a column of calcium carbonate firmly packed into a narrow glass tube. Different components of the pigment got separated into band or zones of different colours.

Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases - a stationary phase and a moving phase. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis is partition.

0777 023 444

Hence, chromatography can be defined as the technique for the separation of a mixture of compounds where the separation is brought about by the differential movement of the individual compounds through a porous medium under the influence of a moving solvent. The technique has now a days undergone tremendous modification and is widely used for the separation and purification of different types of organic compounds.

The different chromatographic techniques used are : column chromatography (CC), thin-layer chromatography (TLC), paper chromatography (PC), gas-liquid chromatography (GLC) and ion-exchange chromatography.

a) Column Chromatography

The simplest chromatographic method is column chromatography. It is carried out in a long glass column having a stop-cock near the bottom. To start the operation, a plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent powder. The tube is packed uniformly with suitable adsorbent. This constitutes what is known as the stationary phase. The commonly employed adsorbents are activated aluminium oxide (alumina), magnesium oxide, silica gel and starch. A loose plug of cotton or glass wool is then placed at the top of the adsorbent column.

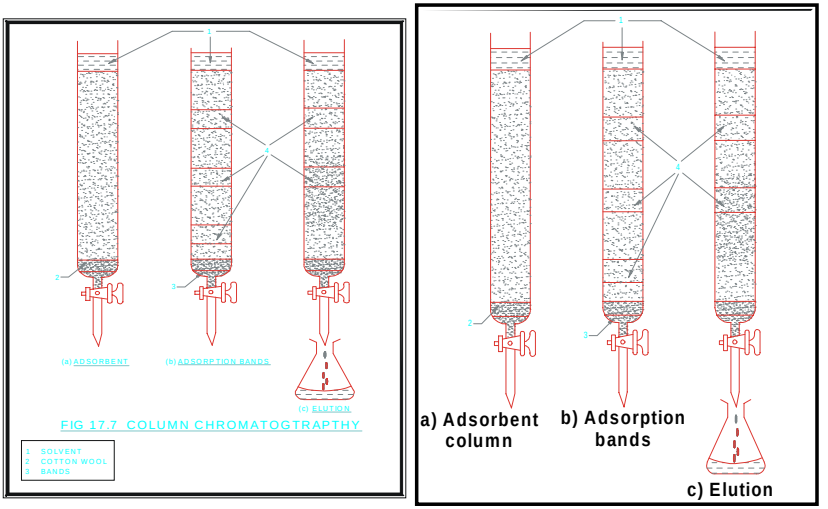


Fig. 16.7 Column chromatography

0777 023 444

The substance to be purified is added, as such if it is a liquid or in the form of its solution in some suitable solvent if it is a solid, at the top of the column and allowed to pass slowly through it. As it passes through the column, the different components of a mixture (Say A, B and C) got adsorbed to different extent and are thus retained by the adsorbent at different levels of the column. The components which are adsorbed very strongly are retained at the top while others are retained at lower levels. In this way different zones or bands are formed in the column which contain different components of a mixture. As soon as the last portion of the substances enter the column, a selected solvent, known as eluent, is added to the column. This acts as moving phase. The elements dissolve out the different components from the various zones selectively and thus `take out' the different bands in the form of fractions which are collected separately.

b) Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent. A thin layer (about 0.2mm thick) of an adsorbent (Silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the solvent (Below 2cm height). As the solvent jar moves up the plate, the components of mixture move up along the plate to different distances depending on this degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retention factor ie., R_f Value.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

c) Paper Chromatography

It is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bound to the cellulose network (inert support) of the paper. The mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds

0777 023 444

between these two liquid phases. The mobile phase travels by capillary action through the paper. Depending upon the way the solvent travels on the paper, there are three types of paper chromatography.

i) Ascending Paper Chromatography : The mobile phase moves upwards on the paper strip in this case.

ii) Descending Paper Chromatography : The mobile phase in this case moves downward on the paper strip.

iii) Circular or radial paper chromatography: The mobile phase moves horizontally along a circular sheet of paper in this case.

In the ascending paper chromatography, the mixture of compounds is applied on the paper as a spot little above the lower end and then this end is dipped in the solvent. When the solvent has risen more than two third length of the paper, then it is removed from the solvent. The paper is dried and is known as chromatogram.

Now the spots for different compounds can be visualised using some suitable chemicals. The ratio of the distance travelled by the compound in a particular solvent to that the distance travelled by the solvent is a constant and is known as retention factor (R_f). This value is used in identifying the compounds.

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solvent}}$$

Type of Chromatography	Stationary Phase	Mobile Phase
1. Column Chromatography	Solid	Liquid
2. Thin Layer Chromatography (TLC)	Solid	Liquid
3. Paper Chromatography	Liquid	Liquid
4. Gas Liquid Phase Chromatography	Liquid	Gas

0777 023 444

Difference between paper chromatography and thin layer chromatography

Paper Chromatography	Thin Layer Chromatography
(i) Separation based on partition	Separation is based on partition, adsorption and ion exchange.
(ii) Stationary phase is the water molecules bound on the paper.	Stationary phase is a layer of silica gel or alumina on glass plate.

Questions

A. Choose the best answer

1. Organic compounds are soluble in
   a) Non-polar Solvents b) Polar solvents c) Water d) HCl
2. Decolourisation of coloured compounds can be effected by using
   a) Animal charcoal b) Carbon c) Coke d) Infra-red rays
3. Compounds having boiling points widely apart 40 K and above can be purified by
   a) Crystallisation b) Simple distillation
   c) Fractional distillation d) Sublimation
4. Nitrobenzene and benzene can be separated by the method of
   a) Steam distillation b) Crystallisation
   c) Fractional crystallisation d) Chromatography
5. Purification of two miscible liquids possessing very close boiling points can be separated using
   a) Fractional distillation b) Sublimation
   c) Simple distillation d) Steam distillation
6. Purification of mixture of compounds can be done by steam distillation only if the impurities are
   a) Non-volatile b) Volatile c) Insoluble in Water d) both a & c
7. When the stationary phase is solid, then the compounds can be separated on the basis of
   a) Adsorption b) Partition c) Both partition and adsorption d) Either
8. Column Chromatography is based on the principle of
   a) Adsorption b) Partition c) Absorption d) Distribution
9. In Ascending paper Chromatography, the solvent moves
   a) Upwards b) Downwards c) Horizontally d) None
10. The existence of wide range of organic compounds is due to their, property of
    a) Extensive catenation b) Lower boiling points
    c) Polymerisation d) Isomerism

0777 023 444

B. Fill in the blanks

1. The Compounds separated and purified by crystallisation can be dried over _____
2. Camphor can be purified by the process of _____ .
3. In simple distillation the compounds should not decompose at _____
4. Water insoluble compounds can be purified by _____ .
5. In T.L.C the stationary phase is a _____ .
6. Chromatographic technique was first introduced by _____ .
7. In paper chromatography, the mobile phase travels by _____action through the paper.
8. The adsorbent used in column Chromatography method is_____ .
9. In Chromatographic technique, the separation of compounds are brought about by _____ movement of the compounds.
10. Paper Chromatography is _____ Chromatography.

C. Write in one or two sentence

1. What are the different stages followed during Crystallisation?
2. Define steam distillation.
3. What are different types of distillation?
4. Give the advantages of distillation under reduced pressure.
5. What are the types of paper chromatography?

D. Explain briefly on the following

1. Explain the method of purifying a solid organic compound.
2. Write short notes on
   a) Fractional crystallisation b) Solvent extraction
3. Explain the purification of compounds by using thin layer chromatography.
4. What are the various principles used in chromatographic separation?
5. Write down the general characteristics of organic compounds.

SUMMARY

All organic compounds must be purified before study. There are various purification methods adopted. Depending on the physical and chemical properties of the organic compounds, purification methods are done. Methods like crystallization, sublimation, distillation, solvent extraction and chromatographic techniques are dealt in detail in this chapter.

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0777 023 444

17. DETECTION AND ESTIMATION OF ELEMENTS

OBJECTIVES

The main objectives of the chart are to provide

* *Detection and estimation of carbon, hydrogen, nitrogen, sulphur and halogens.*
* *The various methods for the detection and estimations are discussed in detail.*

17.1 Qualitative Analysis

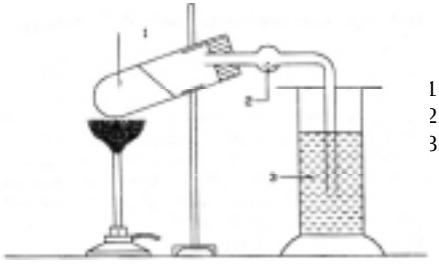
Qualitative analysis of an organic compound involves the detection of various elements present in it. The elements commonly present in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens and sulphur and sometimes phosphorous. The carbon and hydrogen are present in almost all the organic compounds.

A) Detection of carbon and hydrogen

The detection of carbon and hydrogen in an organic compound is done by a single experiment.

A small quantity of pure and dry compound is mixed with about ten times its weight of copper oxide (CuO). The mixture is taken in a hard glass test tube fitted with a delivery tube having a small bulb. The other end of the tube is immersed in freshly prepared lime water. In the bulb of delivery tube, a small amount of anhydrous copper sulphate (white) is placed. The mixture is heated strongly when carbon and hydrogen present are oxidised to carbon dioxide and water respectively.

$$C + 2CuO \rightarrow CO_2 + Cu$$
$$2H + CuO \rightarrow H_2O + Cu$$



1. Organic Compound + Copper (II) oxide
2. Anhydrous copper sulphate
3. Lime water

Fig. 17.1

0777 023 444

Carbon dioxide turns **lime water milky** and the water vapour turns colourless copper sulphate, blue.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

(White ppt)

$$CuSO_4 + 5H_2O \rightarrow CuSO_4 . 5H_2O$$

(colourless) (blue)

Turning of lime water milky and of colourless copper sulphate blue shows the **presence of carbon and hydrogen** respectively.

B. Detection of Oxygen

There is no direct method for the detection of oxygen in organic compounds. It is detected indirectly. For example,

a) If any organic compound on heating in a dry test tube, gives out water vapour, then the presence of oxygen in the organic compound is indicated.

b) If any organic compound is found to contain any oxygen containing functional groups such as - OH, -CHO, -COOH, $-NO_2$ etc., then the compound contains oxygen.

c) If the sum of the percentages of various elements present in the compound is less than 100, then the compound contains oxygen.

C) Detection of nitrogen, sulphur and halogens

All these can be detected by **Lassaigne's Test**.

Lassaigne's Test : The organic compound is taken in an ignition tube. A pea-size sodium metal is added to it and heated to red hot. The hot tube is crushed to powder under a few ml of water in a mortar. The solution is filtered and the filtrate is known as `sodium extract' or **`lassaigne's filtrate'**. The filtrate is used for the detection of the elements.

Nitrogen : During fusion, the carbon and nitrogen of the organic compound combine with sodium metal forming sodium cyanide.

$$Na + C + N \rightarrow NaCN$$

0777 023 444

The unreacted sodium combines with water forming caustic soda, so the solution becomes alkaline.

Test : To the extract, ferrous sulphate solution is added and warmed. Sodium ferrocyanide is formed.

$$FeSO_4 + 2NaCN \rightarrow Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4\ NaCN \rightarrow Na_4[Fe(CN)_6]$$

sodiumferrocyanide

A few drops of **ferric chloride** are added to it and the solution is **acidified with dilute sulphuric acid**. The ferric ions react with sodium ferrocyanide giving a bright blue (prussion blue) coloration

$$3\ Na_4\ [Fe(CN)_6]+4Fe^{+3} \rightarrow Fe_4[Fe(CN)_6]+ 12Na^{+}$$

ferric ferrocyanide
(prussion blue)

Test : If an organic compound contains nitrogen along with sulphur, a blood red colour will be obtained in the above test.

$$Na + C + N + S \rightarrow Na\ CNS$$

$$3NaCNS + FeCl_3 \rightarrow Fe\ (CNS)_3 + 3NaCl$$

(Ferric sulphocyanide)

(blood red colour)

Sulphur

Organic compounds containing sulphur give sulphide on fusion with sodium.

$$2Na + S \rightarrow Na_2S$$

Test : To the Lassaigne's filtrate, sodium nitroprusside is added. **Purple colour** is developed.

$$Na_2S + Na_2\ [Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5\ NOS]$$

sodium nitroprusside purple

0777 023 444

Halogens : In sodium extract, the halogen is present as sodium halide.

$$Na + X \rightarrow NaX \ (X = Cl, Br, I)$$

Test : The extract is acidified with dilute nitric acid and silver nitrate solution is added. Formation of precipitate indicates the presence of halogen.

$$NaX + AgNO_3 \rightarrow AgX \downarrow + NaNO_3$$

The halogen is identified from the **colour** and the **solubility** of the precipitate in ammonium hydroxide.

Sl. No.	Colour of the precipitate	Halogen present	Solubility in ammonium hydroxide
1.	White	chlorine	Easily soluble
2.	Pale yellow	bromine	Sparingly soluble
3.	Yellow	iodine	Insoluble

17.2 Quantitative analysis of organic compounds

Once we have known the various elements present in any organic compound, the next point of interest is to know how much of each element is present in the compound. Determination of the relative proportions (generally as percentages) of various elements present in an organic compound is called **quantitative analysis of that compound**. For quantitative analysis, the percentages of the various elements present in any compound are estimated by suitable chemical methods.

(a) Estimation of carbon and hydrogen (liebig's combustion method)

The estimation of carbon and hydrogen is carried out in one experiment.

A known weight of the organic compound is strongly healed with excess of dry copper oxide in an atmosphere of dry and pure oxygen or air. Carbon of the compound is oxidised to carbon dioxide and hydrogen to water.

0777 023 444

$$C + 2CuO \rightarrow CO_2 \uparrow + Cu$$
$$2H + CuO \rightarrow H_2O \uparrow Cu$$

The CO_2 and H_2O are absorbed by a strong solution of **caustic potash** and **anhydrous calcium chloride** respectively. The percentage of carbon and hydrogen is calculated from the weights of CO_2 and H_2O obtained. These weights are obtained by finding the weights of caustic potash and calcium chloride tubes before and after the experiment.

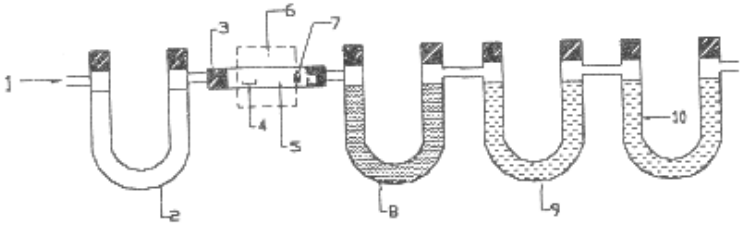


Fig.17.2

1. Oxygen supply 2. Drying tube 3. Glass joints
4. Platinum boat with organic compound 5. CuO
6. Combustion tube 7. Copper coil to remove nitrogen oxide
8. $CaCl_2$ guard tube 9. KOH tube 10. To prevent the incoming CO_2 and H_2O

Calculation

Let, weight of organic compound = wg
Increase in weight of $CaCl_2$ tube
(weight of water formed) = w_1g
Increase in weight of potash bulbs
(weight of carbon dioxide formed) = w_2g

Percentage of carbon

Molecular weight of CO_2 = (12 + 32) = 44
44 g of carbon dioxide contains, carbon= 12 g
w_2g of carbon dioxide contains,

$$= \frac{12}{44} \times w_2 g \text{ carbon}$$

wg of compound contains

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$$= \frac{12}{44} \times w_2 \text{ g of carbon}$$

∴ 100 g of compound contains

$$= \frac{12}{44} \times \frac{w_2}{w} \times 100 \text{ g of carbon}$$

Percentage of carbon in the compound $= \frac{12}{44} \times \frac{w_2}{w} \times 100$

Percentage of hydrogen

Molecular weight of H_2O = (2 + 16) = 18

18 g of water contains, hydrogen = 2 g

w_1 g of water contains, hydrogen $= \frac{2}{18} \times w_1$ g

wg of compound contains

$$= \frac{2}{18} \times w_1 \text{ g of hydrogen.}$$

∴ 100 g of compound contains

$$= \frac{2}{18} \times \frac{w_1}{w} \times 100$$

Example 1

0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g water. Calculate the percentage of carbon and hydrogen in it.

Solution

Weight of organic compound = 0.30 g

Weight of carbon dioxide = 0.88 g

Weight of water = 0.54 g

Percentage of carbon

44 g of carbondioxide contains, carbon = 12 g

0777 023 444

0.88 g of carbon dioxide contains, carbon = $\frac{12 \times 0.88}{44}$ g

0.30 g substance contains, carbon = $\frac{12 \times 0.88}{44}$ g

100 g substance contains

$= \frac{12 \times 0.88}{44} \times \frac{100}{0.30} = 80$ g of carbon

Percentage of carbon = 80

Percentage of hydrogen

18 g of water contains, hydrogen = 2 g

0.54 g of water contains, hydrogen = $\frac{2 \times 0.54}{18}$ g

0.30 g of substance contains hydrogen = $\frac{2 \times 0.54}{18 \times 0.30}$ g

100 g of substance contains = $\frac{2 \times 0.54}{18 \times 0.30} \times 100$ g

= 20 g of hydrogen

Percentage of hydrogen = 20

(b) Estimation of oxygen

Oxygen is commonly estimated by the method of difference. The percentage of all other elements are added together and then subtracted from 100. The balance is the percentage of oxygen.

Example 2

0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O. Find the percentage composition.

Solution

Weight of organic compound = 0.2004 g

Weight of carbon dioxide = 0.2940 g

Weight of water = 0.1202 g

Percentage of carbon

44 g of CO_2 contains, carbon = 12 g

0777 023 444

0.2940 g of CO_2 contains, carbon = $\frac{12 \times 0.2940}{44}$ g

Percentage of carbon = $\frac{12 \times 0.2940}{44} \times \frac{100}{0.2004} = 40.01$

Percentage of hydrogen

18 g of H_2O contains, hydrogen = 2 g

0.1202 of H_2O contains, hydrogen = $\frac{2 \times 0.1202}{18}$

Percentage of hydrogen = $\frac{2 \times 0.1202}{18} \times \frac{100}{0.2004} = 6.66$

Percentage of oxygen is therefore by difference,

= [100 - (40.01 + 6.66)] = 53.33

Estimation of nitrogen

c) Kjeldahl Method

This method is based on the fact that many nitrogenous organic compounds when heated with con. H_2SO_4, are quantitatively converted into ammonium sulphate. The ammonium sulphate so obtained is heated with excess NaOH and the ammonia liberated is absorbed in a known volume of standard acid.

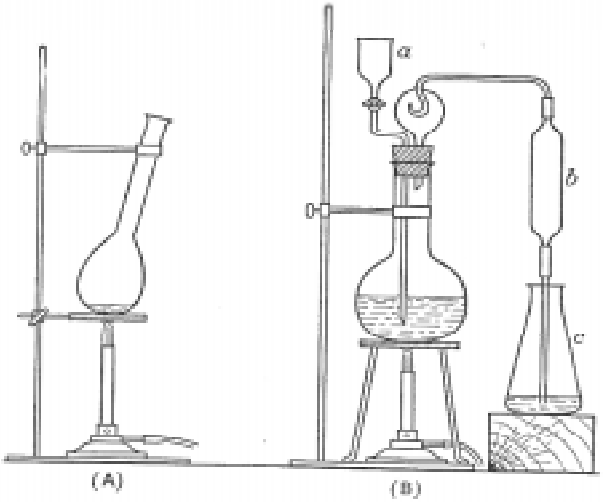

Fig. 17.3 Kjeldahl's method

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From the volume of standard acid used by ammonia and the mass of organic compound taken for the experiment, we can calculate the mass of nitrogen in the compound.

Organic compound $\xrightarrow{H_2SO_4}$ $(NH_4)_2$

SO_4 $\xrightarrow{NaOH}$ NH_3 $\xrightarrow{H_2SO_4}$ $(NH_4)_2\ SO_4$

with nitrogen

Note : 1000 ml 1N acid $\equiv$ 17 g NH_3 $\equiv$ 14 g nitrogen.

Calculation

Mass of the nitrogenous substance = W g

Volume of acid used up by NH_3 = V_1 ml

Normality of acid = N_1

Volume of 1 N acid = V_1 N

$$\text{Mass of nitrogen} = \frac{14 \times V_1 N_1}{1000}$$

$$\text{\% of nitrogen} = \frac{14 \times V_1 N_1 \times 100}{1000 \times w}$$

Example 1

The ammonia evolved from 0.21 g of an organic compound by Kjeldahl method neutralised 15 ml of N/20 sulphuric acid solution. Calculate the percentage of nitrogen.

Weight of organic compound = 0.21 g

$$\text{Normality of acid} = \frac{N}{20}$$

Volume of standard acid neutralised by ammonia = 15 ml

1000 ml of 1N ammonia contains = 14 g of nitrogen

15 ml of ammonia of normality

$$\frac{N}{20} \text{ contains nitrogen} = \frac{14 \times 15 \times 1}{1000 \times 20}$$

0.21 g of compound contains nitrogen

$$= \frac{14 \times 15}{1000 \times 20}$$

100 g of compound contains nitrogen

$$= \frac{14 \times 15 \times 100}{1000 \times 20 \times 0.21} = 5g$$

∴ Percentage of nitrogen = 5

Example 2

0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 ml of N/5 H_2SO_4. The excess acid required 154 ml of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Solution

Volume of N/5 H_2SO_4 solution taken = 100 mL

The volume of N/5 H_2SO_4 neutralised by N/10 NaOH can be obtained as follows :

$$N_{acid} \times V_{acid} = N_{alkali} \times V_{alkali}$$

$$\frac{N}{5} \times V_{acid} = \frac{N}{10} \times 154 \text{ mL}$$

$$V_{acid} = \frac{154}{10} \times 5 \text{ mL}$$

= 77 mL

Therefore,

Volume of N/5 H_2SO_4 used for

neutralising ammonia = (100 - 77) mL

= 23 mL

Then,

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality volume of acid used for neutralising } NH_3}{\text{Mass of the compound taken}}$$

Percentage of nitrogen in the sample

$$= \frac{1.4 \times 1/5 \times 23}{0.35} = 18.4$$

d) Estimation of sulphur

Carius method

A known mass of the organic compound is heated in a sealed tube with fuming nitric acid. The sulphur present in the organic compound will be oxidised to sulphuric acid. The tube is cooled and broken in dilute hydrochloric acid. Then excess of barium chloride solution is added. The precipitate of barium sulphate obtained is filtered, washed, dried and weighed accurately.

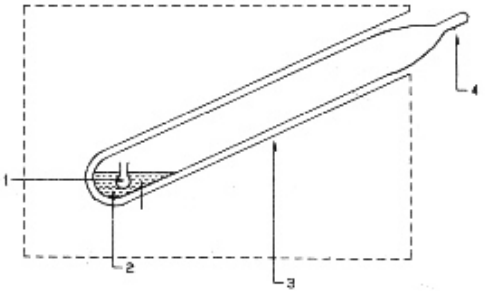

Fig.17.4

1. Organic compound 2. Nitric acid 3. Iron tube 4. Carius tube

0777 023 444

Calculations

Mass of the organic compound = w g

Mass of barium sulphate = w_1 g

233.4 g $BaSO_4$ contains 32 g sulphur

$$\therefore w_1 \text{ g } BaSO_4 \text{ will contain } \frac{32 \times w_1}{233.4} \text{ g sulphur}$$

Percentage of sulphur

$$= \frac{32 \times w_1}{233.4 \times w} \times 100$$

Example

0.316 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of the precipitate of barium sulphate. Determine the percentage of sulphur in the compound.

(Atomic masses : Ba = 137, S = 32, O = 16, C = 12, H = 1).

Solution

Mass of the substance taken = 0.316 g

Mass of $BaSO_4$ formed = 0.466 g

Molecular mass of $BaSO_4$ = 137 + 32 + 64 = 233

Then, mass of S in 0.466 g of $BaSO_4$

$$= \frac{0.466 \times 32}{233} \text{ g}$$

Percentage of S in compound

$$= \frac{0.466 \times 32 \times 100}{233 \times 0.316}$$

$$= 20.25$$

0777 023 444

e) Estimation of halogens

Carius Method

Principle : The organic compound is heated with silver nitrate and fuming nitric acid. The halogen in the organic compound becomes the halide ion and this reacts with silver ion of the silver nitrate solution. The silver halide is precipitated. The precipitate is filtered, washed, dried and then weighed accurately.

Procedure

About 0.2 g of the organic compound is weighed accurately in a small glass tube. The tube is introduced into the Carius tube containing fuming nitric acid and silver nitrate crystals. The upper end of the tube is sealed. The tube is then heated in a furnace for 5 to 6 hours. The organic compound breaks up and the halogen present gives a precipitate of silver halide. The Carius tube is cooled and then broken. The precipitate of silver halide is washed, dried and weighed accurately.

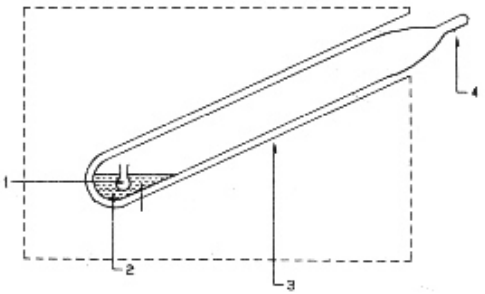

Fig.17.5

1. Organic compound
2. Nitric acid + Silver nitrate
3. Iron tube
4. Carius tube

Calculation

Mass of organic compound = w g

Let the mass of silver halide be w_1 g

143.5 g of silver chloride contains

35.5 g Cl_2

w_1 g of AgCl contains $\frac{35.5 \times w_1}{143.5}$ g of Cl_2

0777 023 444

$$\text{Percentage of chlorine} = \frac{35.5 \times w_1 \times 100}{143.5 \times w}$$

similarly,

Percentage of bromine

$$= \frac{80}{188} \times \frac{w_1}{w} \times 100$$

Percentage of iodine

$$= \frac{127}{235} \times \frac{w_1}{w} \times 100$$

Example

0.15 g of iodoform gave 0.2682 g of AgI. Calculate the percentage of iodine.

Weight of compound = 0.15 g

Weight of silver iodide = 0.2682 g

Molecular weight of silver iodide = 108 + 127 = 235

235 g of silver iodide contains 127 g of iodine

$$0.2682 \text{ g of AgI contains} = \frac{127 \times 0.2682}{235}$$

= 0.144 g iodine

0.15 g of compound contains 0.144 g of iodine

$$100 \text{ g of compound contains} = \frac{100 \times 0.1449}{0.15} = 96.6 \text{ g}$$

∴ Percentage of iodine = 96.6

Problems

Estimation of carbon and hydrogen

1. 0.12 g of an organic compound gave on combustion 0.18 g of water and 0.11 g of CO_2. Calculate the percentage of C and H in the organic compound. [Ans : C = 25%, H = 16.66%]
2. An organic compound contains C, H and O. 0.2475 g of the organic compound yielded on combustion 0.4950 g of CO_2 and 0.2025 g of H_2O. Find the percentage composition of the organic compound. [Ans : C = 54.54%, H = 9.09%, O = 36.37%]

0777 023 444

3. 0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O. Find the percentage composition.
   [Ans : C = 40.01%, H = 6.66%, O = 53.33%]
4. 0.2056 g of an organic compound gave on combustion 0.114 g of H_2O and 0.880 g of CO_2. Find the percentage of hydrogen and carbon in the organic compound. [Ans : C = 93.76%, H = 6.128]
5. On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 of H_2O. Find the percentage composition of the organic compound. [Ans : C = 21.95%, H = 4.58%]

Estimation of nitrogen

1. 1.15 g of an organic compound was analysed by Kjeldahl's method and the ammonia produced was collected in 30 mL of normal HCl solution. The excess of acid consumed 18.4 mL of normal sodium hydroxide solution for back titration. Calculate the percentage of nitrogen in the substance. [Ans : N = 14.12%]
2. 0.80 g of a substance was digested with sulphuric acid and then distilled with an excess of caustic soda. The ammonia gas evolved was passed through 100 ml of 1N H_2SO_4. The excess of the acid required 80 ml of 1N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the organic compound.
   [Ans : N = 35%]
3. 0.36 g of a nitrogeneous organic compound was Kejldahilised and the ammonia liberated was exactly neutralised by 20 ml of 0.3 N H_2SO_4. Calculate the percentage of nitrogen in the compound.
4. 0.257 g of an organic substance was Kjeldahlised and ammonia evolved was absorbed in 50 mL of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization. Determine the percentage of nitrogen in the compound. [Ans : N = 14.6%]
5. During nitrogen estimation present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen neutralised 10 ml of 1 M H_2SO_4. Find the percentage of nitrogen in the compound. [Ans : N = 56%]

Estimation of sulphur

1. 0.4037 g of an organic substance containing sulphur was heated with conc. nitric acid in a carius tube. On precipitation with $BaCl_2$, 0.1963 g of $BaSO_4$ was produced. Determine the percentage of sulphur in the compound. [Ans : S = 7.66%]

0777 023 444

2. 0.316 g of an organic compound gives 0.466 g of barium sulphate by carius method. Calculate the percentage of sulphur?
   [Ans : S = 20.25%]
3. 0.530 g of an organic compound gave 0.90 g of $BaSO_4$ in carius determination of sulphur. Calculate the percentage of sulphur.
   [Ans : S = 23.32%]

Estimation of halogens

1. 0.24 g of an organic compound gave 0.287 g of AgCl in the carius method. Calculate the percentage of chlorine in the compound.
   [Ans : Cl = 25%]
2. In carious method of estimation of halogen 0.15 g of an organic compound gave 0.12 g of AgBr. Find the percentage of bromine in the compound. [Ans : Br = 34.04%]
3. 0.301 g of an organic compound gave 0.282 g of silver bromide by carius method. Find the percentage of bromine. [Ans : Br = 39.83%]
4. 0.196 g of an organic compound gave 0.22 g of CO_2 and 0.0675 g of H_2O. In carius determination, 0.3925 g of the substance gave 0.717 g of dry AgCl. Find the percentage composition of the substance.
   [Ans : C = 30.6%, 4 = 3.8%, Cl = 45.2%, O = 20.4%]
5. 0.25 g of an organic compound was found to produce 0.35 g of AgCl after heating with fuming HNO_3 and $AgNO_3$ in a sealed carius method. Determine the percentage of chlorine in the compound.
   [Ans : Cl = 34.75%]

SUMMARY

This chapter explains various methods of detection and estimation.

The principles behind various methods of detection and estimation are explained.

REFERENCES

1. I.L. Finar organic chemistry Vol.1, ELBS edition.
2. Vogel's Organic quantitative analysis ElBS.

0777 023 444

18. HYDROCARBONS

OBJECTIVES

The main objectives of this chapter is to give

* *knowledge on sources, classification and nomenclature of hydrocarbons.*
* *general methods of preparation of alkanes, alkenes and alkynes and their chemical properties.*

18.1 Classification of Hydrocarbons

Hydrocarbons are made of only carbon and hydrogen. They are obtained mainly from petroleum, natural gas and coal. They are divided into two main categories :

* aliphatic hydrocarbons
* aromatic hydrocarbons

The aliphatic hydrocarbons are further classified into saturated (alkanes), unsaturated (alkenes and alkynes) and alicyclic (cycloalkanes) hydrocarbons.

Aliphatic Saturated Hydrocarbons

These are otherwise called alkanes. Alkanes are often referred to as paraffins. Alkanes show little chemical affinity towards other compounds and are chemically inert to most reagents.

18.2 IUPAC nomenclature

With the exception of the first four compounds (methane, ethane, propane and butane) whose names have historical roots, other alkanes are named from Greek number according to the number of carbon atoms present.

Table 18.1

Number of Carbon atoms	Name	Molecular formula C_nH_{2n+2}
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}

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The suffix `ane' is added to the end of the each name to indicate that the molecule identified is an alkane. Thus, pentane is a five-carbon alkane and hexane is a six carbon alkane and so on. According to IUPAC rules, branched chain alkanes can be named by the following four steps:

Step 1 Finding out the parent hydrocarbon

a. Find the longest continuous carbon chain present in the molecule and use the name of that chain as the parent name.

```
                                  2      1
                                 CH2 — CH3
                                  |
CH3 — CH2 — CH2 — CH — CH3
 6      5      4      3
```

Named as a substituted hexane.

b. If two different chains of equal length are present, select the chain with the larger number of branch points as the parent.

```
          CH3
          |
CH3 — CH — CH — CH2 — CH2 — CH3
 1      2    | 3    4      5      6
            CH2 — CH3
```

3-ethyl-2-methyl hexane
(correct name)
4- is opropylhexane
(wrong name)

The above compound is named as hexane with two substituents and not as hexane with one substituent.

Step 2 Numbering the carbon atoms in the main chain

a. Beginning either from the left or from the right nearer the first branch point, give the number to each carbon atom in the longest chain, you have identified.

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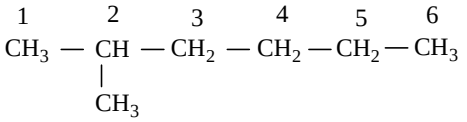
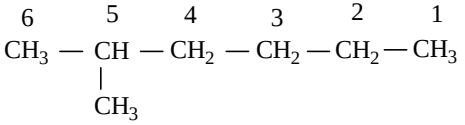


2-methylhexane (correct)

(Not as)

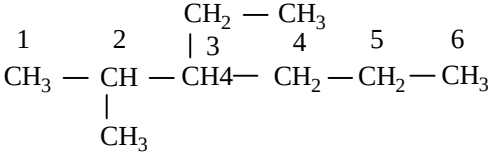


5-methylhexane (wrong)

b. If there are branchings at equal distance from both ends of the parent chain, give numbering from the end which is nearer to the second branch point.

Step 3 Identifying and numbering the substituents

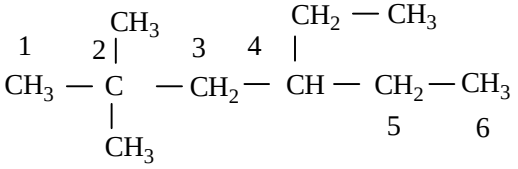
a. Using the correct numbering system, assign a number to each substituent according to its point of attachment to the main chain e.g.



Substituents : On C_2, there is a methyl group, and write it as 2-methyl.

On C_3, there is a ethyl group, and write it as 3-ethyl.

b. If there are two substituents on the same carbon, give them the same number. There must always be as many numbers in the name as there are substituents :



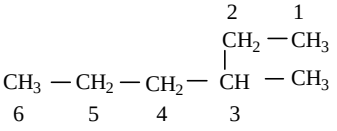
0777 023 444

Substituents : On C_2 there are two methyl groups, they are written as 2,2 dimethyl, on C_4 there is an ethyl group, it is written as 4-ethyl.

Step 4 Final naming

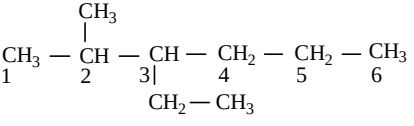
Write out the name as a single word, using hyphens to separate the different prefixes and using commas to separate numbers. If two or more different substituents are present, write them in alphabetical order. If two or more identical substituents are present use one of the prefixes di-, tri-, tetra- and so on. Don't use those prefixes for alphabetising purposes. The following are a few examples adopting the above IUPAC nomenclature.

1)



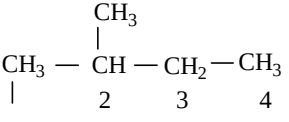
3-methylhexane and not as 2-ethylpentane

2)



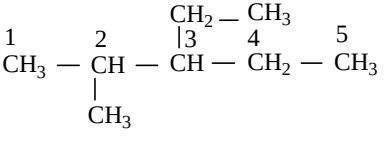
3-ethyl-2-methylhexane (correct)
4-ethyl-5-methylhexane (or) 4-isopropylhexane (wrong)

3)



2-methylbutane

4)



3-ethyl-2- methylbutane

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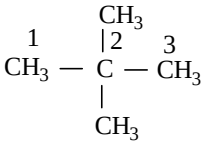
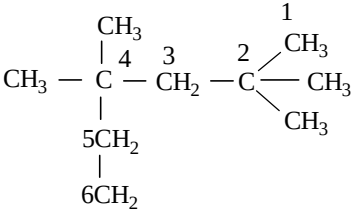
5)



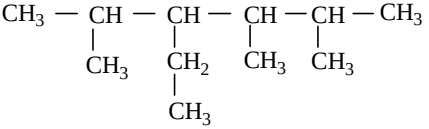
2,2-dimethylpropane

6)



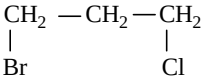
2,2,4,4,-tetramethylhexane

7)



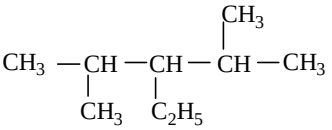
4-ethyl -2, 3-5-
trimethlyhexane

8)



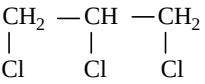
1-bromo-3-chloropropane

9)



3-ethyl1-2,4-dimethylpentane

10)



1,2,3-trichloropropane

0777 023 444

18.3 Sources of alkanes (petroleum)

The major sources of alkanes are natural gas and petroleum deposits, which are derived from the decomposition of marine organic matter. Natural gas consists chiefly of methane but ethane, propane, butane and isobutane are also present. Petroleum is a highly complex mixture of hydrocarbons that must be refined into different fractions to get various lower member hydrocarbons.

Cracking

When higher alkanes are passed through a chamber heated to 400-600°C in the presence of a catalyst (metallic oxides), the products are alkanes with less number of the carbon atoms and this is known as cracking.

18.4 General methods of preparation of alkanes

(i) By catalytic reduction of alkenes

Many alkenes (olefins) may be reduced by passing their vapours with hydrogen over finely divided nickel supported on Kieselguhr at 200-300°C. This reaction is referred to as the Sabatier-Senderens reduction.

$$CH_2 = CH_2 \xrightarrow[H_2]{Ni/300°C} CH_3 - CH_3$$

$$CH_3CH = CH_2 \xrightarrow[H_2]{Ni/300°C} CH_3CH_2CH_3$$

Nickel adsorbs, activates and dissociates molecular hydrogen for addition to olefins.

Finely divided nickel may be replaced by Raney nickel introduced by Raney (1927). It is more active than finely divided nickel. It is active even at room temperature. It is prepared by removing aluminium from Al-Ni alloy using sodiumhydroxide. Olefins can also be hydrogenated at room temperature over platinum or palladium.

Unsaturated edible oils are hydrogenated to Vanaspathi ghee with nickel catalyst at 300°C.

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(ii) Wurtz reaction

An ethereal solution of an alkyl halide is treated with sodium to obtain an alkane.

$CH_3CH_2Br + 2Na + Br - CH_2.CH_3 \rightarrow CH_3(CH_2)_2CH_3 + 2NaBr$

The reaction can be applied to mixed alkyl halides. The products are mixed alkanes.

$$CH_3CH_2Br + 2Na + BrCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH_3$$

(iii) From Grignard reagents

Alkyl magnesium halides (RMgX, X = halogen) are known as Grignard reagents. Alkyl halides (chloride, bromide or iodide) react with magnesium in dry ether to give Grignard reagents. Grignard reagents react with water or dilute acids to give alkanes.

$$CH_3CH_2Br + Mg \xrightarrow{\text{Ether}} CH_3CH_2MgBr$$

$$CH_3CH_2MgBr + H_2O \longrightarrow CH_3CH_3 + MgBr(OH)$$

(iv) By decarboxylation of carboxylic acids

When sodium salts of carboxylic acids are heated with soda lime, alkanes are obtained.

$$CH_3CH_2COONa + NaOH \xrightarrow{CaO\,/\,350°C} CH_3CH_3 + Na_2CO_3$$

Sodalime is a 3:1 mixture of NaOH and CaO. The role of CaO is to fuse sodium hydroxide.

(v) Kolbe's electrolytic method

When a concentrated solution of sodium or potassium salt of carboxylic acid is electrolysed, a higher homologue of the alkane series is obtained. During electrolysis, the anions ($RCOO^-$) migrate towards the anode where they get decomposed to alkanes and carbon dioxide.

$$2RCOOK \xrightarrow{\text{Electrolysis}} 2RCOO^- + 2K^+$$

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At Anode

$$2R-\underset{\underset{O}{\|}}{C}O^- \longrightarrow 2R^\bullet + 2CO_2 + 2e^-$$

$$2R^\bullet \longrightarrow R-R$$

Example

$$2CH_3COONa \longrightarrow 2CH_3COO^- + 2Na^+$$

At Anode

$$CH_3COO^- + CH_3COO^- \longrightarrow \underset{\text{ethane}}{CH_3-CH_3} + 2CO_2 \uparrow$$

(vi) From alcohols

Alcohols on heating with concentrated hydroiodic acid and red phosphorous at 150°C under pressure in a sealed tube get reduced to alkanes.

$$ROH + 2HI \xrightarrow{P/\Delta} RH + H_2O + I_2$$

18.5 Physical Properties

The dipole moment of all alkanes, whether straight or branched-chain is zero. Hence the alkanes have very weak force of attraction (Vanderwaals forces) between them. The Vanderwaals force increases with increase in the area of contact. Hence in the n-alkanes, owing to their large surface area due to their linear structure, the Vanderwaals force is large. In the branched alkanes the molecules tend to become spherical hence they have less surface area and contact, and less Vanderwaals force. As a consequence these, C_1-C_4 hydrocarbons are gases, C_5 - C_{17} liquids, and from C_{18} onwards are solids. The boiling points rise fairly regularly as the number of carbon atoms in the compound increases. Other physical properties such as melting point, density, viscosity etc., also changes, as the chain length of the compound increases.

Account for the following

(i) The boiling point of butane (0°C) is more than 2-methyl propane(-120.0°C).

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(ii) The melting point of n-pentane (-129.7°C) is less than neopentane (-17°C).

Solution

(i) Due to more Vanderwaal's force of butane.

(ii) The melting point of alkanes depends on the packing of the molecules in the crystal lattice. Packing in turn depends on molecular size. As neopentane is spherical in shape it will be better packed in the crystal lattice than n-butane. Hence the melting point of n-butane is less than neopentane.

All of them are colourless. Methane is soluble in water, but others are insoluble. Solubility of methane is due to its small molecular size. Due to its small size it can easily diffuse and dissolve in water. An useful rule in organic chemistry with respect to solubility is that `like dissolves like', e.g., if a compound contains a hydroxyl group, then the best solvents usually contain the hydroxyl groups.

18.5.1 Chemical Properties

(i) Halogenation

Chlorination and bromination of alkanes may be brought about by light, heat or catalysts. In the presence of ultraviolet light ($\lambda < 400$ nm λ = wavelength of light) or at high temperature all the four hydrogen atoms of CH_4 may be substituted. The reaction is of free radical type.

$$CH_4 + Cl_2 \xrightarrow{h\upsilon} CH_3Cl + HCl$$
Methyl chloride

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + HCl$$
Methylene chloride

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} CHCl_3 + HCl$$
Chloroform

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$
Carbon tetrachloride

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Iodides are prepared by treating the chloro- or bromoderivative with sodium iodide in methanol or acetone

$$RCl + NaI \xrightarrow[CH_3OH]{} RI + 2NaCl$$

It is easy to separate the product from NaCl as the later is insoluble in methanol or acetone. This reaction is known as the **Finkelstein** or **Conant-Finkelstein** reaction.

Direct fluorination is usually explosive in nature. The great reactivity of fluorine is due to its low dissociation energy (150.6 kJ mol^{-1}). Also, one of the termination step is $R^{\bullet} + F^{\bullet} \rightarrow RF$. This reaction is very strongly exothermic (447.7 kJ). The energy liberated is larger than that required to break a C-C single bond (347.3 kJ), thereby resulting in the fragmentation of the organic molecule.

(ii) Nitration

Nitration of alkanes is carried out between 150 and 475°C, and the reaction yields a complex mixture of products. The reaction may be of free radical type.

$$CH_3CH_2CH_3 \xrightarrow[400°C]{HNO_3} \begin{array}{l} CH_3CH_2CH_2NO_2 + CH_3\overset{\overset{NO_2}{|}}{C}HCH_3 + \\ CH_3CH_2NO_2 + CH_3NO_2 \end{array}$$

(iii)Oxidation

Alkanes readily burn in excess air to form CO_2 and H_2O.

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$$

At controlled oxygen supply methane forms carbon black used in the manufacturing of ink and black pigments. It is also used as fillers.

Oxidising agents such as $KMnO_4$ readily oxidise isobutane into tertiary butyl alcohol.

$$(CH_3)_3CH + [O] \xrightarrow{KMnO_4} (CH_3)_3COH$$

Molybdenum trioxide oxidises methane to formaldehyde

$$CH_4 + O_2 \xrightarrow{MoO_3} HCHO + H_2O$$

Ag_2O oxidises ethane to acetic acid

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$$2CH_3CH_3 + 3O_2 \xrightarrow{Ag_2O} 2CH_3COOH + H_2O$$

(iv) Isomerization

n-Alkanes can be isomerized into branched chain alkanes when heated with anhydrous aluminium chloride and hydrogen chloride at 300°C. The presence of an alkene impurity is shown to be important to initiate isomerization.

$$CH_3(CH_2)_4CH_3 \xrightarrow{HCl/AlCl_3} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_2CH_3 + CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$$

(v) Aromatization

When alkanes with six or more carbon atoms are passed over hot alumina supported chromium, vanadium or molybdenum oxide, dehydrogenative cyclization to yield aromatic compounds occurs.

$$CH_3(CH_2)_4CH_3 \xrightarrow[500°C,\ 10 - 20\ atm]{Cr_2O_3/Al_2O_3}$$ $+ 4H_2$

Cr_2O_3 is the catalyst, and Al_2O_3 merely disposes Cr_2O_3 on it.

18.6 Alkenes

Alkenes are hydrocarbons that contain carbon-carbon double bond as functional group. They are otherwise known as olefins. Alkenes occur abundantly in nature. Following table contains details of a few simple alkenes.

Table 18.2

Molecular formula	Structural formula	Common name	IUPAC name
C_2H_4	$CH_2 = CH_2$	Ethylene	Ethene
C_3H_6	$CH_3 - CH = CH_2$	Propylene	Propene
C_4H_8	$CH_3-CH_2-CH = CH_2$	Butylene	1 - Butene

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IUPAC Nomenclature : Alkenes are named systematically by following a series of rules similar to those followed for alkanes, with the suffix -ene instead of -ane. The following three basic steps are used.

Step 1 Name the parent hydrocarbon

Find the longest chain containing the double bond and name the compound accordingly using the suffix -ene.

Step 2 Number the carbon atoms in the chain beginning from the end which is nearer the double bond, e.g:

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

Hex-2-ene (or) 2-hexene (correct)
4-hexene (wrong)

If the double bond is equidistant from the two ends, give the number from the end which gives the lowest number to the substituent.

Step 3 If more than one double bond is present, indicate the position of each double bond and use the suffices as -diene, -triene, -tetrene etc.

Example

$$\underset{1}{CH_2} = \underset{2}{\overset{\overset{CH_3}{|}}{C}} - \underset{3}{CH} = \underset{4}{CH_2}$$ 2-methyl-1,3-butadiene

18.7 General methods of Preparation of alkenes

i. By dehydration of alcohols

Alcohols can be dehydrated to olefins by heating with sulphuric acid.

$$CH_3 - CH_2 - OH \xrightarrow[160\text{-}170°C]{H_2SO_4} CH_2 = CH_2$$

The mechanism is as follows

$$CH_3 - CH_2 - OH + H^+ \longrightarrow CH_3CH_2 - \overset{+}{O}H_2$$

$$\xrightarrow{-H_2O} CH_3 - CH_2 \xrightarrow{-H^+} CH_2 = CH_2$$

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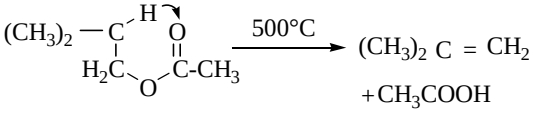
Sulphuric acid is a catalyst. For this reaction H_3PO_4, anhydrous zinc chloride and alumina can also be used as catalysts.

ii. By pyrolysis of esters

Esters with more than one carbon in the alkyl portion of the esters can be pyrolysed to get olefins.



iii. Dehydrohalogenation of alkyl halides

When an alkyl halide is treated with alcoholic potassium hydroxide, hydrogen halide is removed resulting in the formation of an alkene. For example

$$CH_3-CH_2Br \xrightarrow[\text{Dehydrohalogenation}]{\text{Alcoholic KOH}} CH_2=CH_2 + H_2O + KBr$$

iv. Hydrogenation of alkynes

Alkynes on controlled reduction with palladium and hydrogen give alkenes. For example

$$\underset{\text{Acetylene}}{HC\equiv CH} + 2[H] \xrightarrow[\text{Controlled Reduction}]{Pd} \underset{\text{Ethylene}}{CH_2=CH_2}$$

v. By electrolysis of salts of dicarboxylic acids

Alkenes are formed by the electrolysis of the aqueous solutions of potassium salts of dibasic acids of the succinic acid series.

$$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2 + 2KOH + H_2$$

vi. Dehalogenation of vicinal halides

Treatment of vicinal dihalides with zinc dust and ethyl alcohol gives the alkenes.

$$R-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{Zn/C_2H_5OH} R-CH=CH_2 + ZnBr_2$$

0777 023 444

18.8 Physical Properties

The olefins with two to four carbon atoms are gases; five to seventeen liquids, eighteen on wards solids at room temperature and they burn in air with luminous smoky flame.

The exhibit isomerism

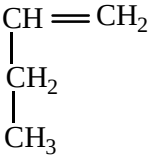
i. Position isomerism : It arises due to position of the double bond in a molecule. Ethene and propene do not show position isomerism, but butene shows.

$CH_3CH_2CH{=}CH_2$ But - 1 - ene

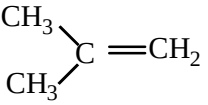
CH_3 - CH = CH -CH_3 But - 2 - ene

ii. Chain isomerism

It is due to branching of the linear chain



But-1-ene

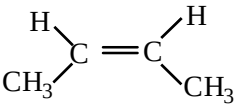


2-Methyl propene-1

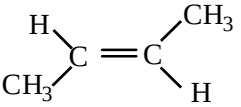
iii. Geometrical Isomerism

When two isomers differ in their spatial arrangement of atoms or groups, they are said to be stereoisomers. This type of isomerism is called stereoisomerism. Types of stereoisomerism : 1. Optical isomerism, 2. Geometrical isomerism

Geometrical isomers are named as cis and trans compounds depending on whether the identical groups are on the same or opposite sides of the bonds.



Cis-isomer



Trans-isomer

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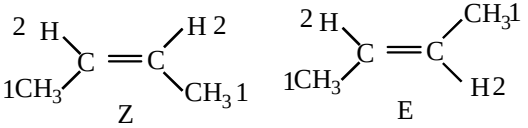
The necessary and sufficient condition for geometrical isomerism is that the two groups or atoms attached to the same carbon must be different. When the two groups or atoms of highest priority are on the same side of the double bond, the isomer is designated as Z (Zusammen in German means together), and when they are on the opposite sides, the isomer is designated as E (Entegen in German meaning opposite). The priority is decided by the atomic number of atoms to which the olefinic carbons are bonded. The sequence rules given by Cahn - Ingold and Prelog are applied.



The atoms with the high atomic number is given the number 1 and other 2.

18.9 Chemical Properties

i. Hydrogenation of alkenes

Alkenes can be readily hydrogenated under pressure in the presence of a catalyst.

$$CH_2{=}CH_2 + H_2 \xrightarrow[\text{Room Temp}]{\text{Pt or Pd}} CH_3{-}CH_3$$

Nickel supported on alumina is effective between 200 and 300°C (Sabatier -senderens reduction). Raney nickel is effective at room temperature and atmospheric pressure.

ii. Addition of halogens

Bromine and chlorine add readily to alkenes to yield dihaloalkanes.

$$CH_2 = CH_2 \xrightarrow{Cl_2} \overset{Cl}{\overset{|}{CH_2}} - \overset{Cl}{\overset{|}{CH_2}}$$

1,2-dichloroethane

$$CH_3 - CH = CH_2 \xrightarrow{Br_2} CH_3 - \overset{Br}{\overset{|}{CH}} - \overset{Br}{\overset{|}{CH_2}}$$

1,2-dibromopropane

In this reaction bromine will be decolourised and this test is used to detect unsaturation.

0777 023 444

iii. Hydrohalogenation

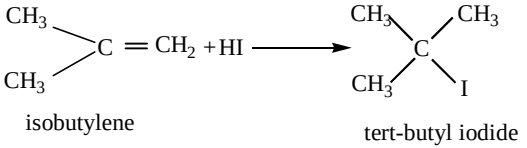
An alkene is converted into the corresponding alkyl halide by HX. The reaction is frequently carried out by passing dry gaseous HX directly into the alkene. For example,

$$\underset{\text{ethylene}}{CH_2 = CH_2} \xrightarrow{\text{dry HCl}} \underset{\text{ethyl chloride}}{CH_3CH_2Cl}$$

Propylene can yield two possible products namely n-propyl iodide or isopropyl iodide with HI, depending upon the orientation of addition. Actually it is found that isopropyl iodide is the only product obtained.

$$\underset{\text{propylene}}{CH_3-CH=CH_2} + HI \longrightarrow \underset{\text{isopropyl iodide}}{CH_3-\underset{\underset{I}{|}}{CH}-CH_3}$$

In the same way, isobutylene can yield either of the two products, isobutyl iodide or tertiary butyl iodide. Here the orientation or addition is such that the tertiary butyl iodide is the only product.



In the above two reactions, though two products are possible, only one of the products is obtained. The Russian chemist Vladimir Markovnikov, explained the reason which is known as Markovnikov's rule, which states that, the negative part of addendum attaches itself to the carbon atom carrying less number of hydrogen atoms.

Carbocations are involved as intermediates in these reactions. Highly substituted carbocation is formed as an intermediate in preference to the less substituted one due to stability.

(Order of stability

3° carbocation > 2° carbocation > 1° carbocation])

Hence in the above two reactions the formation of only one of the products can be accounted on the basis of the stability of the carbocation

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intermediate. When HBr adds to alkene under normal conditions, we know that an intermediate carbocation is formed and Markovnikov's orientation will be observed (electrophilic addition). But in the presence of peroxides the electrophilic addition does not take place and the addition takes place through free radical mechanism.

iv. Hydration

Water can be added to simple alkenes to yield alcohols. This hydration reaction takes place on treatment of the alkene with water in presence of a strong acid-catalyst.

$$\underset{\text{ethylene}}{CH_2 = CH_2} + H_2O \xrightarrow{H^+} \underset{\text{ethyl alcohol}}{CH_3 - CH_2OH}$$

v. Halohydrin formation

Alkenes can add HOCl or HOBr under suitable conditions to yield 1,2 haloalcohols or halohydrins. Halohydrin formation does not take place by direct reaction of an alkene with the reagents (HOCl or HOBr). But the addition is done indirectly by the reaction of the alkene with either Br_2 or Cl_2 in presence of water.

Example

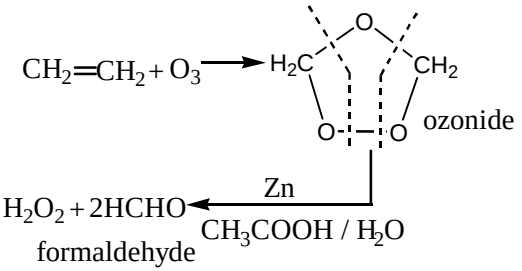
$$\underset{\text{ethylene}}{CH_2 = CH_2} \xrightarrow{Cl_2/H_2O} \underset{\text{Ethylene chlorohydrin}}{CH_2(OH) - CH_2(Cl)}$$

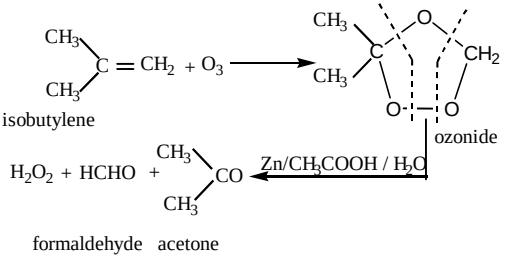
$$\underset{\text{Propylene}}{CH_3 - CH = CH_2} \xrightarrow{Br_2/H_2O} \underset{\text{Propylene bromohydrin}}{CH_3 - CH(OH) - CH_2(Br)}$$

vi. Ozonolysis

Ozone is the most useful double bond cleavage reagent. When added to an alkene first an ozonide intermediate is formed. When the ozonide is further treated with a reducing agent such as zinc metal in acetic acid, it is converted into carbonyl compounds.

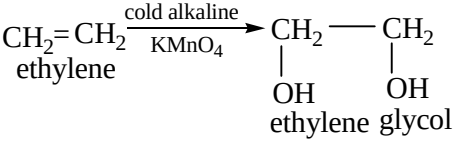
0777 023 444





vii. Hydroxylation

The addition of an -OH group to each of the two alkene carbons can be carried out with alkaline potassium permanganate. This reagent is known as Baeyer's reagent. Ethylene or any alkene decolourises potassium permanganate and this is a test for unsaturation.



viii. Hydroboration

Alkenes readily react with diborane to form trialkyl boranes which on oxidation with alkaline hydrogen peroxide yield primary alcohols.

$$3CH_2{=}CH_2 + (BH_3)_2 \rightarrow 2(CH_3\text{-}CH_2)_3B$$

$$(CH_3\text{-}CH_2)_3B \xrightarrow{H_2O_2} 2CH_3CH_2OH$$

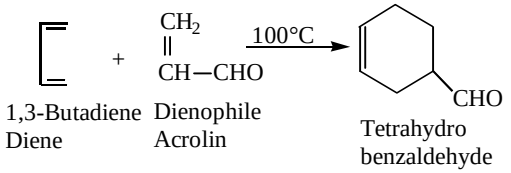
0777 023 444

ix. Epoxidation

When ethylene is mixed with oxygen, under pressure passed over at 200 - 400°C, epoxide is obtained.

$$CH_2 = CH_2 + \tfrac{1}{2}O_2 \xrightarrow[200\text{-}400°C]{Ag} \overset{\diagup O \diagdown}{CH_2 - CH_2}$$

x. Diels - Alder reaction



Polymerisation : A polymer is simply a large molecule built up by many smaller units called "monomers". Conversion of a large number of monomers into a single polymer is known as polymerisation.

When ethylene is heated under pressure in presence of oxygen, a compound of high molar mass known as polyethylene or polythene is formed.

$$nCH_2{=}CH_2 \xrightarrow[\text{under pressure}]{O_2,\ \triangle} \underset{\text{polythene}}{(\text{-}CH_2\text{-}CH_2)_n}$$

18.10 Uses of Alkenes

(i) Ethylene is used for ripening of fruits.

(ii) Ethylene is used to prepare industrial solvents like ethylene dichloride, glycol, dioxan etc.,

(iii) Ethylene and propylene are important industrial organic chemicals. They are used in the synthesis of polymers like polythene, polypropylene, pvc, polystyrene, teflon, orlon, acrilan, polyvinyl acetate, polyvinyl alcohol etc.,

(iv) Ethylene dichloride which is prepared from ethylene is used in the preparation of a synthetic rubber called thiokol.

0777 023 444

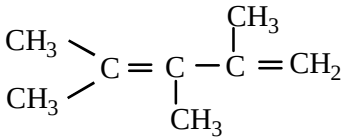
18.10.1 Test for ethylene

(i) Rapid decolourisation of bromine in carbontetrabromide without evolution of hydrogen bromide.

(ii) Decolourisation of cold dilute aqueous potassium permanganate solution.

18.11 Unsaturated compounds with two or more double bonds

If a hydrocarbon contains two double bonds it is called diolefin or alkadiene. Alkadienes have general formula C_nH_{2n-4}. In the chain containing the maximum number of double bonds is chosen as the parent hydrocarbon, and the chain is so numbered as to give the lowest possible numbers to the double bonds.



2,3,4 - Trimethyl penta - 1,3-diene

Preparation of alkadiene

i. Alkadienes with isolated double bonds

$$CH_2{=}CH\ CH_2Cl + Mg \xrightarrow{\text{Ether}} CH_2{=}CH(CH_2)_2CH{=}CH_2 + MgCl_2$$

Hexa 1,5-diene

ii. Alkadienes with cumulative double bonds

By heating 1,2,3-tribromopropane with solid KOH and then treating the resulting 2,3- dibromopropene with zinc dust in methanol.

$$Br\,CH_2\,CH\,Br - CH_2Br \xrightarrow{KOH} Br\,CH_2\,CBr = CH_2$$

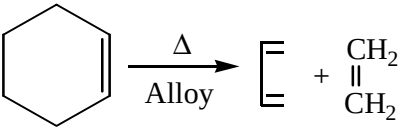
$$\xrightarrow{Zn/CH_3OH} CH_2{=}C{=}CH_2$$

Allene gas

iii. Preparation of alkadienes with conjugated double bonds.

0777 023 444

Buta - 1,3 - diene can be obtained by passing cyclohexene over a heated nichrome wire (an alloy of Ni, Cf and Fe).



Butadiene is used in the manufacture of Buna rubber.

18.12 Alkynes

Alkynes are also called acetylenes. They are hydrocarbons that contain a carbon-carbon triple bond. The first and the most important member of this series is acetylene and hence these are called acetylenes.

IUPAC nomenclature of alkyenes : Alkynes follow the general rule of hydrocarbon nomenclature. The suffix -yne is substituted for `-ane' in the base hydrocarbon name to denote alkyne and the position of the triple bond is indicated by its number in the chain. Numbering begins from the chain end which is nearer the triple bond.

The following table contains details along a few of the simple alkynes.

Table 18.3

Structural formula	Common name	IUPAC name
$CH \equiv CH$	acetylene	ethylene
${}^{3}CH_3{}^{2}C \equiv {}^{1}CH$	methyl acetylene	1-propyne
${}^{4}CH_3{}^{3}CH_2\ {}^{2}C{\equiv}{}^{1}CH$	ethyl acetylene	1-butyne
$CH_3 - C \equiv C - CH_3$	dimethyl acetylene	2-butyne

General methods of preparation

(i) Dehydrohalogenation of vicinal dihalides : Compounds that contain halogen atoms on adjacent carbon atoms are called vicinal dihalides. Alkynes are obtained by treatment of vicinal dihalides with alcoholic KOH followed by treatment with sodamide ($NaNH_2$). For example

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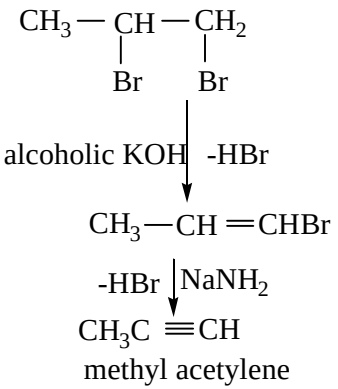
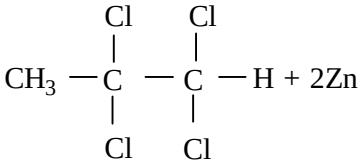
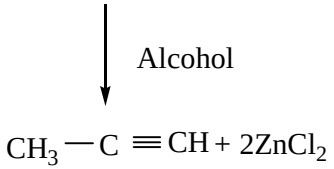


methyl acetylene

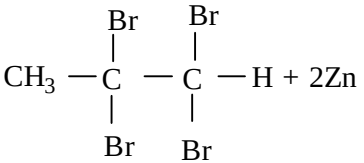
(ii) Dehalogenation of tetrahalides : When 1,1,2,2-tetrahalide is heated with zinc dust in alcohol, alkyne is formed. For example,



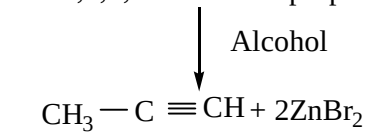
1,1,2,2-tetrachloropropane



methyl acetylene



1,1,2,2-tetrabromopropane



methyl acetylene

0777 023 444

Electrolysis of salts of unsaturated dicarboxylic acids.

$$\begin{array}{l} CH\ \ COOK \\ \| \\ CH\ \ COOK \end{array} \longrightarrow \begin{array}{l} CH \\ \| \\ CH \end{array} + 2CO_2 + 2KOH + H_2$$

18.13 Physical properties of alkynes

Alkynes have physical properties that are essentially the same as those of alkanes and alkenes. They are insoluble in water but quite soluble in organic solvents like benzene, carbon tetrachloride, ether etc. They are less dense than water. Their boiling points and melting points show a regular increase with increasing carbon number and the usual effects of chain branching are also observed.

18.14 Reactions of alkynes

Alkynes contain carbon-carbon triple bond. One of them is strong carbon-carbon sigma (σ) bond and the other two are weak carbon-carbon pi (π) bonds. Alkynes undergo addition reactions with other compounds due to the cleavage of these weak pi (π) bonds.

(i) Addition of hydrogen : Alkynes are easily converted to alkanes by addition of hydrogen in the presence of metal catalyst like nickel, platinum or palladium.

Example

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow{Ni/H_2} \underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{Ni/H_2} \underset{\text{Ethane}}{CH_3 - CH_3}$$

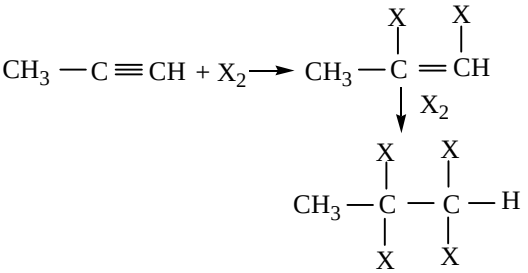
$$\underset{\text{Methyl acetylene}}{CH_3 - C \equiv CH} \xrightarrow{Ni/H_2} \underset{\text{Propylene}}{CH_3 - CH = CH_2}$$

$$\downarrow Ni/H_2$$

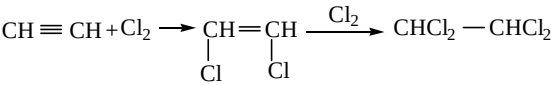
$$\underset{\text{propane}}{CH_3 - CH_2 - CH_3}$$

(ii) Addition of halogens : Two molecules of halogens add to alkynes in two steps forming dihalides and then tetrahalides

0777 023 444



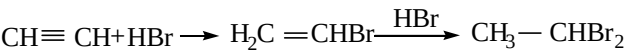
Direct combination of C_2H_2 with chlorine may explode and this is prevented by using a metal chloride catalyst.



Acetylene 1,2-dichloroethylene 1,1,2,2-tetrachloroethane

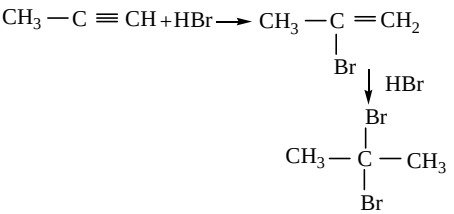
(iii) Addition of halogen acids : Halogen acids add to alkynes in the same way as in alkenes and give the expected addition product. Halogen acids add to symmetrical alkynes in two stages. After one molecule of the acid is added to a symmetrical alkyne, the product is an unsymmetrical derivative of alkene. The addition of a second molecule of the acid takes place in accordance with Markonikov's rule.

Example



1,1-dibromoethan

The addition of halogen acid to unsymmetrical alkynes follows Markonikov's rule both in the first and second steps.



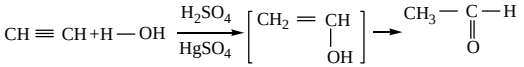
2,2-dibromopropane

Peroxides have the same effect on the addition of hydrogen bromide to alkynes as in alkenes.

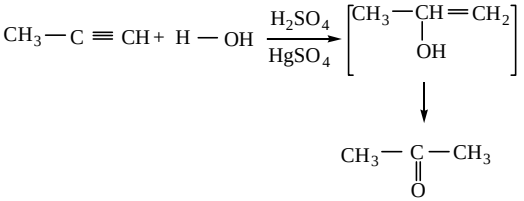
0777 023 444

(iv) Addition of water : When alkynes are passed into dilute sulphuric acid in presence of mercuric sulphate as catalyst at 60°C one molecule of water is added to the alkyne resulting in the formation of either an aldehyde or a ketone.

Example

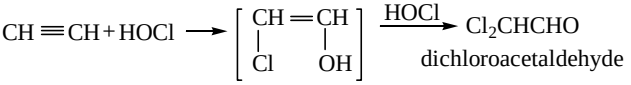


Acetaldehyde



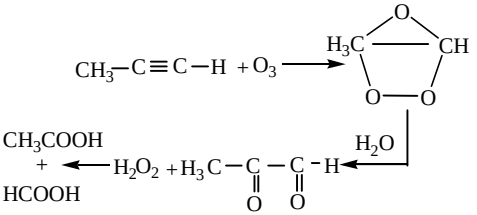
Acetone

(v) Addition of HOCl : When acetylene is passed into hypochlorous acid solution, dichloroacetaldehyde is formed.

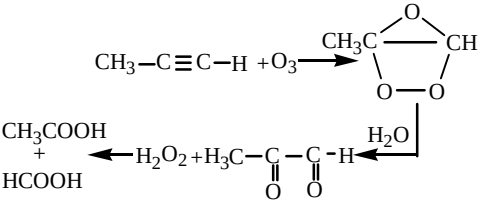


dichloroacetaldehyde

(vi) Addition of ozone : Alkynes react with ozone to give ozonides. These ozonides get decomposed with water to yield diketones. Diketones are oxidised to acids by hydrogen peroxide produced in the reaction.



Acetylene is an exception as it gives both glyoxal and formic acid with ozone.



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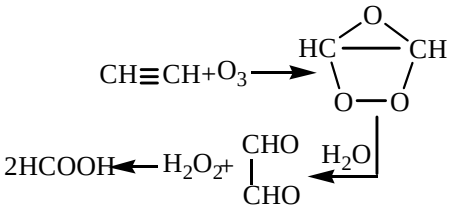


(vii) Reactions of acidic hydrogen : The most striking difference between alkenes and alkynes is that terminal alkynes are weakly acidic. In alkyenes sp hybridization is taking place in carbon atoms and so they exhibit. 50% s character. Hence an alkyne attracts the electrons towards itself and therefore the terminal H can be removed as H^+. When acetylene is passed into ammoniacal silver nitrate solution silver acetylide (white) is precipitated respectively.

Example

$$CH \equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC \equiv CAg \downarrow + 2NH_4NO_3 + 2H_2O$$

Sliver-acetylide

$$CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \xrightarrow{Cu_2Cl_2} CuC \equiv CCu \downarrow + 2NH_4Cl + 2H_2O$$

Copper acetylide

Dry copper and silver acetylides are very sensitive to shock and may explode violently. However, they can be decomposed by nitric acid to regenerate alkynes. This type of reaction is possible with only terminal alkynes. Non-terminal alkynes will not give this reaction.

$$CH_3-CH_2-C\equiv CH + AgNO_3 \xrightarrow{NH_4OH} CH_3-CH_2-C\equiv CAg$$

(1-butyne)

(A terminal alkyne)

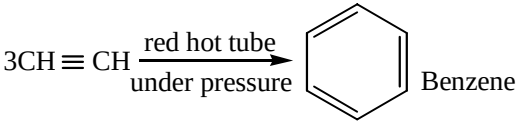
$$CH_3-C\equiv C-CH_3 + AgNO_3 \xrightarrow{NH_4OH} \text{No reaction}$$

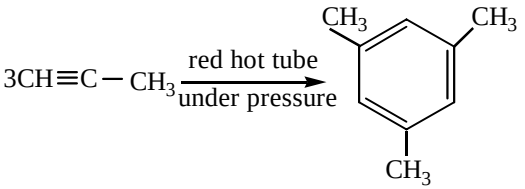
(A non-terminal alkyne)

Thus this reaction can be used to differentiate terminal alkynes and non-terminal alkynes.

0777 023 444

(viii) Polymerisation : When alkynes are passed through red hot iron tube under pressure they polymerise to aromatic compounds. For example acetylene polymerises to benzene and propylene polymerises to mesitylene.





Mesitylene or
1,3,5-trimethyl
benzene

18.14.1 Tests for acetylene

(i) Acetylene decolourises bromine water.

(ii) Acetylene decolourises alkaline potassium permanganate solution

(iii) With ammoniacal solution of cuprous chloride it gives a red precipitate of cuprous acetylide.

(iv) With ammoniacal solution of silver nitrate it gives a white precipitate of silver acetylide. The tests (iii) and (iv) will not be answered by ethylene and these two tests can be used to distinguish ethylene from acetylene.

18.14.2 Uses of alkynes

(1) Acetylene is used as a starting material for manufacture of industrially important compounds like acetaldehyde, acetone and benzene.

(2) Acetylene is used in oxyacetylene torch used for welding and cutting metals.

(3) Westron, a solvent which is tetrachloro derivative of acetylene is prepared from acetylene.

(4) Acetylene is used as a starting material for the manufacture of PVC, polyvinyl acetate and synthetic rubber.

0777 023 444

Questions

A. Choose the correct answer

1) Alkanes can be represented by the formula
   a) C_nH_{2n+2} c) C_nH_{2n-2}
   b) C_nH_{2n} d) C_nH_{2n-3}
2) Alkenes are represented by the formula
   a) C_nH_{2n+2} c) C_nH_{2n-2}
   b) C_nH_{2n} d) C_nH_{2n-3}
3) Alkynes are represented by the formula
   a) C_nH_{2n+2} c) C_nH_{2n-2}
   b) C_nH_{2n} d) C_nH_{2n-3}
4) The type of substitution reaction that takes place when methane is treated with Cl_2 in presence of light
   a) ionic c) nucleophilic
   b) electrophilic d) radial
5) When n-hexane is passed over hot alumina supported chromium, vanadium or molybdenum oxide the compound formed is
   a) cyclopentaene c) toluene
   b) cyclohexane d) benzene
6) When the identical groups are on the same or opposite sides of the bonds in alkenes the isomerism is called as
   a) chain isomerism b) geometrical isomerism
   c) position isomerism d) optical isomerism
7) Diels-Alder reaction is the reaction between
   a) diene and dienophile
   b) electrophile and nucleophile
   c) oxidant and reductant
   d) none.
8) Unsaturated compounds with two double bonds are called as
   a) diene c) olefins
   b) alkadiene d) paraffins.
9) The hybridization of carbons in ethylene is
   a) sp^2 c) sp^3
   b) sp d) dsp^2

0777 023 444

10) Alcohols can be dehydrated to olefins using
   a) H_2SO_4 c) Pd
   b) $SOCl_2$ d) Zn/Hg
11) When alkyl halides are treated with alcoholic KOH, the products are
   a) olefins c) alcohols
   b) alkanes d) aldehydes
12) Witting reaction is used to prepare
   a) an alkene c) an alkane
   b) an alkyne d) none of the above.
13) Electrolysis of potassium succinate gives
   a) ethylene c) acetylene
   b) ethane d) none of the above.

B. Fill up the blanks

1) In alkanes, the carbon atoms are connected by _____ bonds.
2) Treatment of 1,2-dibromopropane with zinc and ethanol gives _____.
3) Cis But-2-ene is an _____ isomer.
4) Addition of HCl to an olefin follows _____ rule.
5) An alkene reacts with ozone to form
6) CaC_2 on hydrolysis gives
7) Ethylenedibromide on treatment with KOH gives
8) Electrolysis of sodium maleate gives

C. Explain briefly on the following

1) Mention any five chemical properties of alkanes.
2) Discuss the general methods of preparing alkanes.
3) What is hydroboration?
4) What is ozonolysis?
5) What is witting reaction?
6) What is polymerisation?
7) How is ethylene hydrated?
8) What is the action of ozone on acetylene.
9) What happens when acetylene is passed through red-hot tube?

0777 023 444

19. AROMATIC HYDROCARBONS

OBJECTIVES

The main objectives of this chapter are to provide

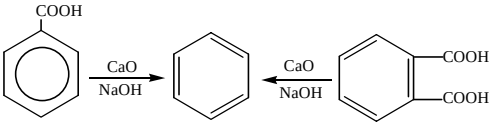
- *Details of nomenclature of aromatic hydrocarbons.*
- *Detail discussion on structure of benzene*
- *Explanatory note on aromaticity*
- *A discussion on orientation in aromatic electrophilic substitution*
- *General methods of preparation of benzene homologues*
- *Some examples for electrophilic substitution and some preliminary discussion of poly cyclic aromatic hydrocarbons.*

Natural sources like resins, balsams, aromatic oils etc., contain aliphatic compounds, and also a group of compounds with pleasant odour. These odorous compounds were arbitrarily classified as aromatic (Greek : aroma : pleasant smell). Most of the simple aromatic compounds were found to contain six carbon atoms. Further when aromatic compounds were subjected to various methods of treatment, they often produced benzene or a derivative of benzene. Hence these aromatic compounds are called benzenoid compounds.

Benzene, C_6H_6, was first isolated by Faraday (1825) from cylinders of compressed illuminating gas obtained from the pyrolysis of whale oil. In 1845, benzene was found in coal-tar by Hofmann, and this is still a source of benzene and its derivatives. Benzene was first synthesised by Berthelot (1870) by passing acetylene through a red-hot tube.

$$3C_2H_2 \longrightarrow C_6H_6 + \text{Other products.}$$

It may be prepared in the laboratory by decarboxylation of aromatic acids.



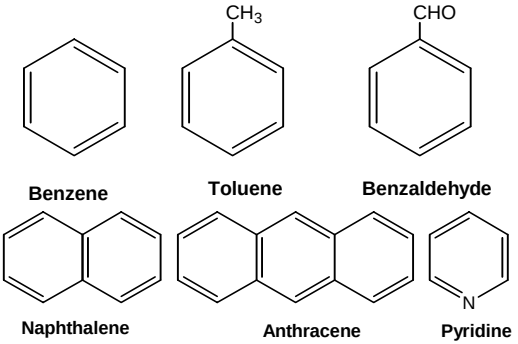
In the early days of organic chemistry the word aromatic was used to describe fragrant substances such as benzaldehyde, toluene etc. It was soon realised that substances grouped as aromatic behaved in a chemically different manner from other organic compounds. Today, we use the term aromatic to refer to benzene and its structural homologues. In this section,

0777 023 444

aromatic compounds showing chemical properties quite different from that of aliphatic compounds are dealt with.

Many compounds isolated from natural sources are aromatic in part. In addition to benzene, toluene and benzaldehyde, complex compounds such as the female steroidal harmone estrone and the well known analgesic, morphine have aromatic rings. Many synthetic drugs used medicinally are also aromatic in part.

Benzene is the first member in the aromatic series of compounds. The whole series of compounds which contain one or more benzene rings in their molecules are called aromatic compounds. Certain heterocyclic compounds like pyridine which do not have benzene rings also come under this classification.



Commercial preparation of benzene from coal tar

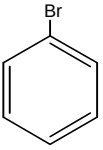
The two main sources of aromatic hydrocarbons are coal and petroleum. Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together. When coal is heated to 1000°C in the absence of air, thermal break down of coal molecules occur and a mixture of volatile products called "coaltar" distills off. The coaltar forms the source of many organic compounds. Further distillation of coaltar yields benzene, toluene, xylene, naphthalene and a host of other aromatic compounds.

19.1 Nomenclature of aromatic compounds

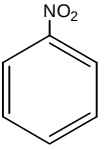
Aromatic compounds acquired a large number of common, nonsystematic names. Although the use of such names is discouraged, IUPAC rules allow for some of the more widely used ones to be retained. eg. methyl benzene is familiarly known as toluene, hydroxy benzene as phenol, aminobenzene as aniline and so on. Mono substituted benzene

0777 023 444

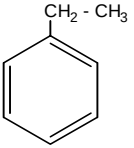
derivatives are systematically named in the same manner as other hydrocarbons with benzene as the parent name.



Bromobenzene

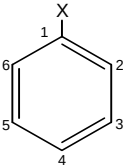


Nitrobenzene

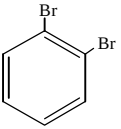


Ethyl benzene

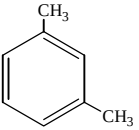
Disubstituted benzene derivatives are named using one of the prefixes ortho, meta or para. In a benzene ring there are six carbon atoms and they can be numbered as follows :



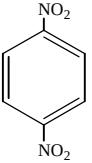
The 2 and 6 positions or the adjacent positions are known as ortho-positions. 3 and 5 or the alternate positions are known as meta-positions and the only one 4th position is known as para- position.



o-dibromobenzene or $_{1,2}$-dibromobenzene



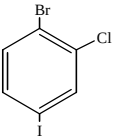
m-xylene or m-dimethylbenzene or $_{1,3}$-dimethylbenzene



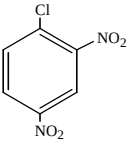
p-dinitro benzene (or) 1,4-dinitro benzene

Benzene with more than two substituents must be named by numbering the position of each substituent on the ring. The numbering should be done in such a way that the lowest possible numbers are given to the substituents and the substituents are listed alphabetically.

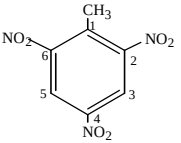
Example



1-bromo-2-chloro-4-iodo-benzene



1-chloro-2,4-dinitro benzene



2,4,6 -Trinitro Toluene

0777 023 444

19.1.1 Aromaticity

Compounds which contain benzene rings or a condensed system of benzene rings have the following properties which are not shown by the analogous aliphatic and alicyclic compounds.

- They readily undergo substitution reactions.
- They are thermally stable.
- They resist addition and oxidation reactions.
- With respect to benzene the enthalpy of hydrogenation, the enthalpy change, when one mole of an unsaturated compound is hydrogenated is much smaller (-208.5kJ mol^{-1}) than the corresponding calculated value for hypothetical 1,3,5 - cyclohexatriene (-359.1 -kJ mol^{-1})

These distinguishing properties led to seek an explanation and define the term aromaticity.

Aromaticity in other related systems

The modern theory of aromaticity was introduced by Huckel in the year 1937. Delocalized electronic cloud and coplanar structure the compound are important for aromaticity. Any polynuclear compound, heterocyclic rings or cyclic ions may be aromatic if they are planar and have 4n + 2 (n = 0,1,2,3 etc) delocalized π electrons in a closed shell. Thus to be aromatic, a molecule must have 2(n=0), 6(n=1), 10 (n=2)..... π electrons.

19.1.2 Orientation in aromatic electrophilic substitution

Orientation in aromatic electrophilic substitution reactions of benzene aims at locating the position of the incoming substituent with respect to the one that is already present. The substituent which is already present in the ring directs the incoming group either to ortho and para or to meta position, and changes the reaction rate higher or lower than benzene.

If a substituent directs the incoming group to ortho and para positions, it is called ortho, para - directing, and if it directs to meta position it is called meta-directing. The substituents that increase the rate of substitution compared to benzene are called activating and those decreasing the rate are called deactivating. The activating groups increase the rate by increasing the electron density of ring, but the deactivating groups decrease the rate by decreasing the electron density of the ring.

Ortho and Para Directing Groups

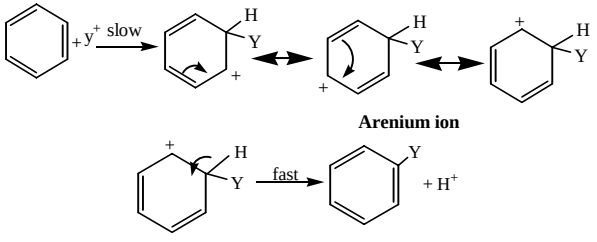
R, OH, OR, NH_2, NHR, $NHCOCH_3$, Cl, Br, I, F, SH etc.

0777 023 444

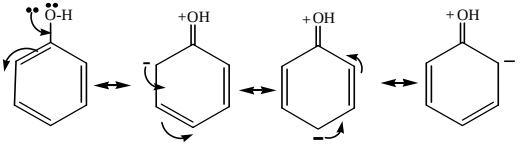
Meta-Directing Groups

NO_2, CHO, COOH, COOR, SO_3H, CN, NH_3^+ etc. The directive influence of these groups are found to be predominant but not exclusive. Halogens behave in a different way, they are ortho, para-directing but deactivating as they withdraw electronic cloud from the ring.

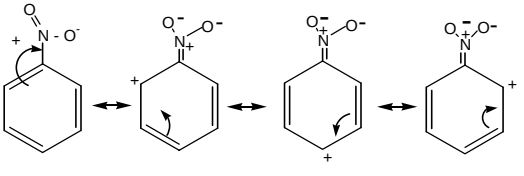
The orientation and activating or deactivating influence of the substituents can be explained based on the resonance and inductive effect of the substituents on the stability of the intermediate arenium ions formed in electrophilic substitution reactions as shown below.



With ortho and para directing groups, for example, OH, there is increased negative charge on the ortho and para positions as shown below. Hence electrophilic substitution predominantly occurs at these positions.



With meta directing groups positive charge is created on the ortho and para positions, but the meta positions are free of such charges, and hence these positions are more reactive than the ortho and para position.



19.2 General methods of preparation of benzene and its homologous series

(i) From aromatic acids : When sodium salt of aromatic acids are heated with sodalime, the corresponding aromatic hydrocarbon is formed.

0777 023 444

Example

$$\underset{\text{Sodium benzoate}}{C_6H_5COONa} \xrightarrow[\Delta]{NaOH + CaO} \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

(ii) When phenol is dry distilled with zinc dust benzene is formed.

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[Zn]{\text{dry distillation}} \underset{\text{Benzene}}{C_6H_6} + ZnO$$

(iii) Wurtz-Fittig reaction : The derivatives of benzene can be prepared by a reaction known as Wurtz-Fittig reaction. When a mixture of aryl halide and an alkyl halide is treated with metallic sodium the derivatives of benzene are formed.

Example

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + 2Na + \underset{\text{Methyl bromide}}{BrCH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaBr$$

(iv) Friedel-Craft's reaction : Benzene reacts with alkyl halides in presence of anhydrous aluminium chloride as catalyst to form alkyl benzenes.

Example

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow[AlCl_3]{\text{anhydrous}} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

19.2.1 Commercial preparation of benzene

From Petroleum

Naphtha obtained by fractional distillation of petroleum is passed over platinum supported on alumina catalyst, benzene, toluene and other homologous of benzene are produced.

This process is now used for the large scale production of benzene and its homologous (toluene xylene). Benzene is separated from the resulting mixture by solvent extraction and by fractional distillation. 90% of commercial benzene is obtained from petroleum.

0777 023 444

19.3 Physical Properties

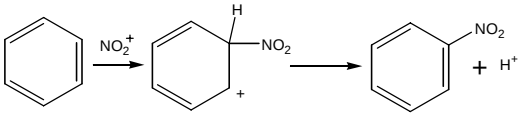
They are colourless liquids or solids with characteristic. They are insoluble in water but are miscible in all proportions with organic solvents such as ethanol, ether etc. They are inflammable, and burn with sooty flame. They are toxic and carcinogenic in nature. The boiling points increase with increase in molecular weight, but their melting points do not exhibit regular gradation Melting point seems to depend on molecular symmetry than on molecular weight.

19.4 Chemical Properties : Reactions of aromatic compounds

Aromatic compounds readily undergo electrophilic substitution reactions. The reactions are normally irreversible and the products formed are kinetically controlled. Sulphonation of aromatics is reversible and at high temperature thermodynamically stable products predominate. There are three steps in electrophilic substitution on aromatics. In the first step an electrophile is produced, in the second step the electrophile attacks the aromatic ring to give an arenium ion, and in the third step the arenium ion gives out a proton to form the final product.

(1) Nitration

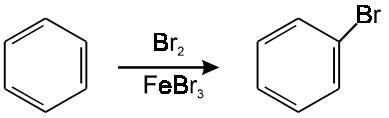
It is carried out in most of the cases with concentrated sulphuric acid and nitric acid. The temperature is between 30-40°C. HNO_3 acid gives nitronium ion after protonation.



NO_2^+ is an electrophile. It attacks the benzene to give an arenium ion, and the later gives out a proton to yield nitrobenzene.

(ii) Halogenation

Benzene can be halogenated with chlorine and bromine in the presence of Lewis acid which, assists polarization of the attacking halogen molecule, thereby making it more reactive.



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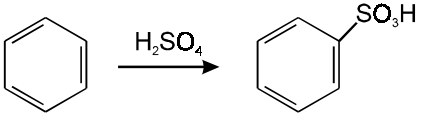
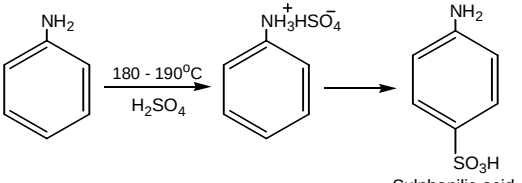
Fluorine reacts vigorously with aromatic hydrocarbons even in the absence of catalyst, however, iodine is very un reactive even in the presence of a catalyst.

(iii) Sulphonation

Aromatic compounds react with concentrated sulphuric acid to give arene sulphonic acid. The electrophile is SO_3. Although it does not have positive charge, it is a strong electrophile. This is because the octet of electrons around the sulphur atom is not reached.



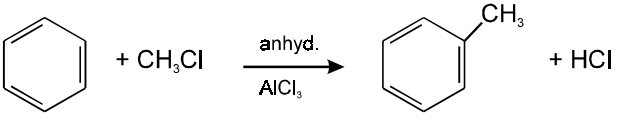
Aniline reacts with sulphuric acid to give a salt, which on strong heating rearranges to sulfanilic acid.



Sulphanilic acid

(iv) Friedel Crafts Alkylation

It is an important reaction to prepare alkyl aromatics. Alkylation of aromatic hydrocarbon is achieved using alkylhalide and aluminium trihalide (Lewis Acid).

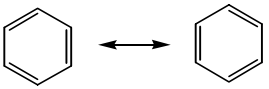


Toluene

19.5 Resonance in benzene

1) The phenomenon in which two or more structures can be written for substance which involve identical position of atoms is called resonance. A double headed arrow (↔)used to represent the resonance hybrid.

0777 023 444



2) Structure of benzene is a single, unchanging hybrid structure that combines the characteristics of both resonance forms.
3) Resonance structures differ only in the position of their electrons. Different resonance structures of a substance need not be equivalent.
4) The resonance hybrid is more stable than any individual resonance structure.
5) More the resonance structures for a molecule more stable the molecule is.

19.6 Structure of benzene

The unusual stability of benzene was a great puzzle in the early days.

1) Although benzene with the molecular formula, C_6H_6 indicates the presence of unsaturation and the Kekule's structure proposes three carbon-carbon double bonds, it does not show any of the characteristic behaviour of alkenes.
2) For example, alkenes react readily with potassium permanganate to give cleaved products, undergo addition reactions with acids followed by hydrolysis to give alcohols and react with HCl to give saturated alkyl chlorides. However benzene does not exhibit any of the above reactions.
3) In the presence of platinum benzene reacts with hydrogen to give cyclohexane, six membered ring. This proves that benzene is a hexagonal molecule with three double bonds.
4) However, benzene reacts with bromine in the presence of iron to give substituted C_6H_5Br rather than the possible addition product of $C_6H_6Br_2$. Further only one monobromo substitution product was formed. No isomers of C_6H_5Br was identified.
5) On further reaction with bromine three isomeric disubstituted products. $C_6H_4Br_2$ are formed. On the basis of these results Kekule proposed that benzene consists of ring of carbon atoms with alternate single and double bonds.

0777 023 444

6) The structure can readily account for the formation of a single mono substituted product and three disubstituted isomers (o-, m- and p-) since all six carbon atoms and all six hydrogen atoms are equivalent.

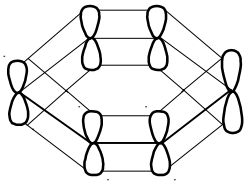
7) X-ray and electron diffraction studies inidicated that all carbon-carbon bonds are of equal length 1.39 Å which is in between that of a single bond (1.54 Å) and that of a double bond (1.34 Å).

8) Localised chemical bonding may be defined in which the electrons are shared by two nuclei only. The delocalised chemical bonding is one in which electrons are shared by more than two nuclei. Certain compounds contain one or more bonding orbitals that are not restricted to two atoms, but spread over three or more atoms. Such bonding is said to be delocalised bonding.

9) Benzene is a flat hexagonal molecule with all carbons and hydrogen lying in the same plane with a bond angle of 120°. Each carbon atom has sp^2 hybridisation.

10) The sp^2 hybrid orbitals of carbon overlap with each other and with 's' orbitals of six hydrogen atoms forming six sigma (σ) C-H bonds and six sigma (σ) C-C bonds.

11) There are six p orbitals perpendicular to the plane containing six carbon atoms. Since all the six p orbitals are parallel to each other in benzene and are equivalent, it is not possible to define three localised alkene type pi (π) bonds, in which a p orbital overlaps with only one neighbouring p orbital. In benzene each p orbital overlaps equally well with both neighbouring p orbitals leading to a picture of benzene in which the six pi (π) electrons are completely delocalised around the ring. Thus benzene has two clouds of electrons one above and one below the ring. This is represented as follows.



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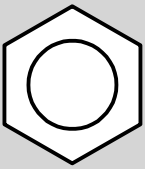
The delocalisation of π orbitals in benzene

12) Thus the structure of benzene is now represented with either a full or a dotted circle to indicate the equivalence of all carbon-carbon bonds.

or

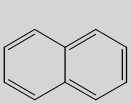


19.7 Uses

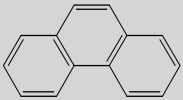
1. Benzene is used as a solvent for the extraction of fats and oils.
2. It is used as fuel along with petrol.
3. It is used for the production of maleic anhydride

19.8 Polynuclear aromatic hydro carbons

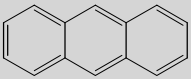
They have two or more fused aromatic rings. They have at least two adjacent carbons shared by aromatic rings. Some examples of these compounds which are carcinogenic.



naphthalene



phenanthrene



Anthracene

Questions

A. Choose the best answer :

1. Aromatic compounds are
   a) benzenoid compounds b) non-benzenoid compounds
   c) aliphatic compounds d) alicyclic compounds
2. Benzene was first isolated by
   a) Huckel b) Faraday c) Hofmann d) Barthelot
3. Benzene undergoes
   a) addition reactions b) oxidation reactions
   c) polymerisation reactions d) electrophilic substitution reactions

0777 023 444

4. The modern theory of aromaticity was introduced by
   a) Faraday c) Hofmann
   b) Huckel d) Berthelot
5. Any compound can be aromatic if they have _____ delocalised π electrons.
   a) 4n + 2 b) 4n + 1 c) 4n d) 4n - 2
6. The function of $FeCl_3$ in chlorination of benzene is to produce
   a) Cl b) Cl^+ c) Cl^- d) C
7. The ortho and para directing groups are
   a) activating group b) deactivating group c) both d) none
8. The purpose of adding conc. H_2SO_4 in nitration of benzene is to produce
   a) NO_2 b) NO_2^- c) NO_2^+ d) NO_3^-
9. An example of polycyclic aromatic hydrocarbon
   a) pyridine b) pyrole c) naphthalene d) cyclohexane
10. The compound which is used as a solvent for the extraction of fats and oils
   a) naphthalene b) benzene c) cyclohexane d) butane

B. Fill in the blanks

1. Many synthetic drugs used are _____ in part.
2. The _____ forms the source of many organic compounds.
3. The modern theory of aromaticity was introduced by _____.
4. Ortho and para directing groups are called as _____ groups.
5. Meta directing groups are called as _____ groups.
6. Alkyl substituted benzenes are prepared by _____ reaction.
7. Naphtha obtained by fractional distillation of _____ is passed over platinum.
8. Aromatic compounds readily undergo _____ substitution reactions.
9. _____ reacts vigorously with aromatic hydrocarbons even in the absence of catalyst.
10. In the presence of _____ benzene reacts with hydrogen to give cyclohexane.

0777 023 444

C. Explain briefly on the following

1. How is benzene is prepared commercially?
2. Explain the term aromaticity.
3. Write a note an activating groups in benzene.
4. How would you convert the following?
   a) sodium benzoate to benzene
   b) phenol to benzene
   c) benzene to toluene
5. Write briefly on resonance in benzene.

SUMMARY

- Aromatic compounds are called as benzenoid compounds.
- Benzene is the first member in the aromatic series of compounds.
- Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together.
- Delocalized electronic cloud and coplanarity of the compound are important for aromaticity.
- Aromatic compounds readily undergo electrophilic substitution reactions.

REFERENCES

1. Organic Chemistry, I.L. Final volume 1, ELBS Edition.
2. Organic Chemistry, Morrison and Boyd.

0777 023 444

20. ORGANIC HALOGEN COMPOUNDS

OBJECTIVES

The main objectives of this chapter are

* *to highlight the medicinal importance of certain halogenated compounds.*
* *to understand the physical and chemical properties of the organic halogen compounds.*
* *to give brief account of classification and nomenclature of these compounds.*
* *to discuss mechanisms of substitution and elimination reactions which are important to halogen compounds.*
* *to provide students more exposure to named organic reactions.*
* *to raise the capability of students to design new synthetic routes for interested target materials.*
* *to provide proof that how much important these compounds are as intermediates in the synthesis of wide variety of organic compounds.*

In organic halogen compounds F, Cl, Br and I are bonded to the carbons of the aliphatic, aromatic and aralkyl hydrocarbons. Many organic halogen compounds occur in nature and some of them have medicinal value. Chloromycetin is a naturally occurring halogen compound used in the treatment of typhoid fever. Thyroxine is yet another one used in the treatment of goitre. There are many synthetic organic halogen compounds few of which are important in health care and medicine. Two such compounds to cite are chloroquine and halothane. The former is used in the treatment of malaria and the later is used as an anaesthetic during surgery. There are also compounds which are important in agriculture and industry, as intermediates in the synthesis of wide variety of other organic compounds.

20.1 Classification of halogen compounds

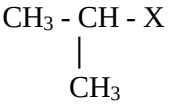
Depending on the type of halogen present, the halohydrocarbons are classified as follows.

Based on the number of alkyl groups bonded to the carbon that carries the halogen, the classification may be as follows.

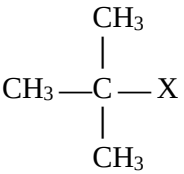
0777 023 444

Primary halides CH_3CH_2 - X

Secondary halides



Tertiary halides



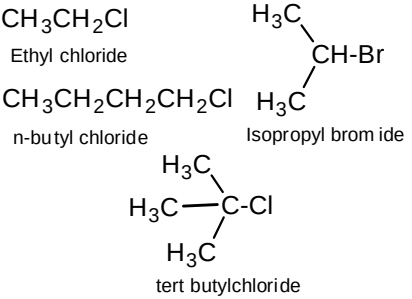
Where X = Halogen

In the primary halides, the carbon bonded to the halogen is connected to one alkyl group, in the secondary halides two alkyl groups in the tertiary halides three alkyl groups.

20.2 Nomenclature of alkyl halides : common and IUPAC

In this section the nomenclature of alkyl halides alone is presented, and the same for aryl halides and aralkyl halides are presented in their respective sections.

The common names of the monohalogen derivatives are derived by naming the alkyl group first and the halogen second.



If two halogen atoms are bonded to the same carbon, they are named as the alkylidene halides. CH_3CHBr_2 Ethylidene bromide. If the two halogen atoms are bonded to adjacent carbons, they are named as the dihalides of the alkenes from which they are formed.

0777 023 444

$$CH_2 = CH_2 + Cl_2 \rightarrow \begin{array}{c} CH_2 - CH_2 \\ | \quad\quad | \\ Cl \quad\quad Cl \end{array}$$

Ethylene dichloride

$$CH_3CH = CH_2 + Cl_2 \rightarrow \begin{array}{c} CH_3CH - CH_2 \\ | \quad\quad | \\ Cl \quad\quad Cl \end{array}$$

Propylene dichloride

Trihalomethane and tetrahalomethanes are named as haloforms and carbon tetra halides respectively.

Example

Write the common names of the following halides

a) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$ b) $CH_3\,CH_2\,CH\,Cl_2$

c) $CH_2 - \overset{\overset{I}{|}}{\underset{\underset{I}{|}}{C}} - CH_3$

d) $CH\,Br_3$ e) CCl_4

Solution

a. Isobutyl bromide b. Propylidene chloride

c. Propylidene iodide d. Bromoform

e. Carbon tetra chloride.

More complex halogen compounds are named according to IUPAC system.

i. If any halogen is at the end of the chain, the carbon bearing the halogen is to be given the number 1.

ii. If the halogen is present in the second or third carbon, numbering is to be started from that side of the chain which gives the least number for carbon bonded to halogen.

0777 023 444

iii. When two different halogens are present, the carbon bonded to higher atomic number halogen is to be given priority.

iv. The names of the halogens and other substituents are to be arranged alphabetically.

$CH_3CH_2CH_2Br$ 1 - Bromobutane

$$\begin{array}{cccc} CH_2 & CH & CH & CH_3 \\ | & | & | & \\ Br & Cl & Cl & \end{array}$$ 1-Bromo-2,3- dichlorobutane

$$CH_3 - \overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2CH_3$$ 2 - Bromo-2-methylbutane

Example

Write the IUPAC names of the following halides.

a. $CH_2Br.CHCl.CH_2CH_2Cl$

b. $CH_3CCl_2.CHBr.CH_3$

c. $CH_3 - \underset{\underset{CH_3}{|}}{CBr} - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3$

Solution

a. 1 - Bromo - 2,4 - dichlorobutane

b. 2 - Bromo - 3,3 - dichlorobutane

c. 2-Bromo-3-chloro-2,4-dimethylpentane

20.3 General methods of preparation

i. From alcohols : Preparation of alkyl halides from alcohols involves replacement of the hydroxyl group with halogen. It is done by using halogen acids.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} RCH_2Cl + H_2O$$

$$R - \underset{\underset{R}{|}}{CH} - OH + HCl \rightarrow R - \underset{\underset{R}{|}}{CHCl} + H_2O$$

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH + HCl \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-Cl + H_2O$$

$ZnCl_2$ is the Lewis acid catalyst. It is required for both primary and secondary alcohols as they are not rapidly reacting. Tertiary alcohols do not require this reagent as they are more reactive.

ii. From alkenes : Alkenes reacts with halogen acids to give alkyl halides. The addition of HCl occurs with first proton and second with halogen.

$$CH_2 = CH_2 + H^+ \rightarrow CH_3\,CH_2^+$$

$$CH_3\,CH_2^+ + Cl^- \rightarrow CH_3CH_2Cl$$

Hence $CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$

HBr and HI are added in a similar manner

When a hydrogen halide is added to an unsymmetrical olefin, the position of the halogen in the product is predicted by Markovnikoff's rule : It states that when a hydrogen halide is added to an unsymmetrical olefin, the negative part of it is added to the carbon that carries least number of hydrogens.

$$CH_3.CH = CH_2 + HCl \rightarrow CH_3\,\underset{\underset{Cl}{|}}{CH} - CH_3$$

It is based on the stability of the carbonium ion formed after the addition of the proton. The order of the stability of the carbonium ion is

tertiary carbonium ion > secondary carbonium ion > primary carbonium ion

The stability of the carbonium ion depends on the extent to which the degree of the positive charge is decreased. In the tertiary carbonium ion the positive charge is more decreased by inductive effect and hyper conjugation and hence its degree of positive charge is more decreased than the secondary and primary carbonium ions.

0777 023 444

iii. From hydrocarbons

By treating alkanes with chlorine (or bromine) at room temperature in the presence of light, chloroalkanes are obtained. The reaction follows a free radical mechanism.

Chlorine molecule decomposes into chlorine atoms by absorption of light and the atoms then react with hydrocarbons.

$$Cl_2 \xrightarrow[\text{light}]{h\upsilon} Cl^{\bullet} + Cl^{\bullet}$$

$$CH_3CH_2 - H + Cl^{\bullet} \rightarrow CH_3CH_2^{\bullet} + HCl$$

$$CH_3CH_2^{\bullet} + Cl_2 \rightarrow CH_3CH_2Cl + Cl^{\bullet}$$

$$ClCH_2CH_3 + Cl^{\bullet} \rightarrow ClCH_2CH_2\,Cl + HCl$$

It is a chain reaction with the formation of several products. The reaction may be stopped by absorption of the chlorine atoms on the wall, or by reaction if two chlorine atoms to form a chlorine molecule.

iv. Hunsdiecker or Borodine - Hunsdiecker reaction

Silver carboxylates in carbon tetrachloride are decomposed by chlorine or bromine to form alkyl halide.

$$CH_3CH_2COO\,Ag + Br_2 \rightarrow CH_3CH_2Br + CO_2 + AgBr$$

Bromine is better than chlorine as the later gives poor yield.

v. By halogen exchange : Finkelstein reaction

Alkyl iodides are prepared by treating the corresponding chloride or bromide with a solution of sodium iodide in acetone. The exchange of halogen between alkyl halide and sodium iodide occurs.

$$RCl + NaI \xrightarrow{\text{Acetone}} RI + NaCl$$

$$RBr + NaI \xrightarrow{\text{Acetone}} RI + NaBr$$

Alkyl fluorides are obtained by treating alkyl chloride or bromide with metallic fluoride, such as AgF or SbF_3. It is the Swarts reaction.

$$CH_3\,CH_2\,Br + AgF \rightarrow CH_3CH_2F + AgBr.$$

0777 023 444

vi. Preparation of dihalogens

$CH_3COCH_3 + PCl_5 \rightarrow CH_3CCl_2.CH_3,$

$CH \equiv CH + 2HBr \rightarrow CH_3CHBr_2$

$CH_3CH = CH_2 \xrightarrow{Br_2} CH_3CHBr\ CH_2Br$

20.4 Properties

20.4.1 Physical properties

The lower members CH_3Cl, CH_3Br and CH_3CH_2Cl are gases. CH_3I and the majority of higher members are sweet-smelling liquids. For a given alkyl group the boiling point of halides increases with increase in the atomic weight of the halogens.

Halide	CH_3F	CH_3Cl	CH_3Br	CH_3I
B.P (°C)	-78	-24	4.0	92

It is due to increase in the Vanderwaals force with increase in the molecular size (molecular weight).

For a given halide, the boiling point increases with the length of the alkyl chains.

Halide	CH_3Cl	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$
B.P (°C)	-22	12.5	47

It is due to increase in the Vanderwaals force with increase in the chain length. In a similar manner the boiling point of isomeric alkyl halides decreases in the order as shown below.

Halide	B.P (°C)
$CH_3CH_2CH_2CH_2Cl$	21.5
$CH_3.CH_2CH(Cl) - CH_3$	68
$(CH_3)_3C\text{-}Cl$	51

Organic halides are insoluble in water, as they are unable to form strong hydrogen bonds with water. They are less inflammable than the

0777 023 444

hydrocarbons. It is due to dilution of oxygen during combustion by the released halogen. Carbon tetrachloride is used in fire extinguishers and as solvent. Tri- and tetrachloroethylenes are widely used as solvents, and they are good solvents for fats and oils. They do not catch fire easily.

20.5 Nucleophilic substitution reactions

The alkyl halides are important reagents in organic synthesis. The halogen can be displaced by other groups by which variety of other organic compounds can be prepared. The reaction can be written as

$$\underset{\text{nucleophile}}{Y^- + RX} \rightarrow \underset{\text{substrate}}{RY} + \underset{\text{product, leaving group}}{X^-}$$

The nucleophile may be negatively charged or a neutral species with a lone pair of electrons.

Nucleophiles : OH^-, RO^-, HS^-, NO_2^-, CN^- etc.
Neutral : H_2O, NH_3 CH_3NH_2 etc.

The R-X bond is polar with partial positive charge on carbon as shown below. It is due to more electronegativity of halogen than carbon.

$$CH_3 - \overset{\delta+}{C}H_2 - \overset{\delta-}{X}$$

The nucleophile attacks on the carbon (CH_2) and displaces the leaving group. This reaction can occur by the following mechanisms.

20.6 Mechanism of nucleophilic substitution reactions

When a substitution reaction involves the attack of a nucleophile, the reaction is referred to as S_N (S-stands for substitution and N for nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.

$$\underset{\text{nucleophile}}{R - X + OH^-} \rightarrow \underset{\text{leaving group}}{R - OH + X^-}$$

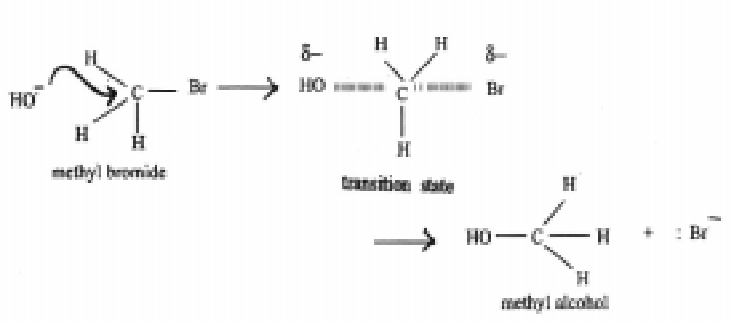
The nucleophilic substitution reactions are divided into two classes : (1) S_N2 reactions (2) S_N1 reactions.

S_N2 reactions : S_N2 stands for bimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends on the

0777 023 444

concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as S_N2.

Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction is represented below.



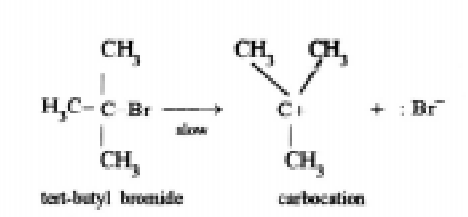
The hydroxide ion approaches the substrate carbon from the side opposite to the bromine atom. This is backside attack. This is because both hydroxide ion and the bromine atom are electron rich. They stay as far apart as possible. The transition state may be pictured as a structure in which both OH and Br are partially bonded to the substrate carbon. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. In the transition state the three C-H bond lie in one plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds.

S_N1 reactions: S_N1 stands for unimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate (alkyl halide), the reaction is first order and is represented as S_N1.

Consider the hydrolysis of tertiary butyl bromide. The reaction consists of two steps.

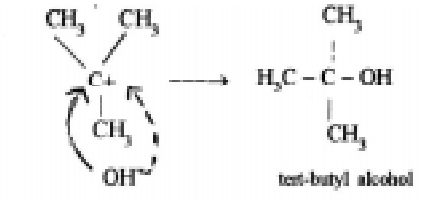
Step 1: The alkyl halide ionises to give the carbocation (carbonium ion). This step is the slow rate determining step.

0777 023 444



The carbocation is planar. This is because the central positively charged carbon atom is sp^2 hybridised.

Step 2 : The nucleophile can attack the planar carbocation from either side to give tertiary butyl alcohol.



Primary alkyl halides undergo hydrolysis by S_N2 mechanism. The tertiary alkyl halides undergo hydrolysis by S_N1 mechanism. Secondary alkyl halides may undergo hydrolysis by both S_N1 and S_N2 mechanism.

20.7 Mechanism of elimination reaction

Elimination reactions are reverse of addition reactions. Here atoms or group attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a double bond. Example, dehydrohalogenation of alkyl halides with alcoholic alkalis.

$$R\text{–}CH_2\text{–}CH_2\text{–}X \xrightarrow[\text{alcoholic alkali}]{OH^-} R\text{–}CH{=}CH_2 + H_2O + X^-$$

These reactions are divided into two classes

1) E2 reaction2) E1 reactions

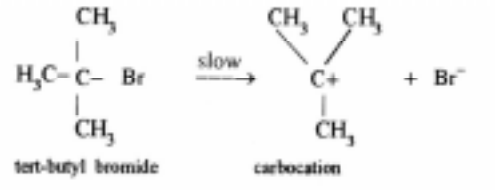
E2 reactions: E2 stands for bimolecular elimination. When the rate of an elimination reaction depends on the concentration of substrate and nucleophile, the reaction is second order and is represented as E2. E2 is a one step process in which the abstraction of the proton from the beta

0777 023 444

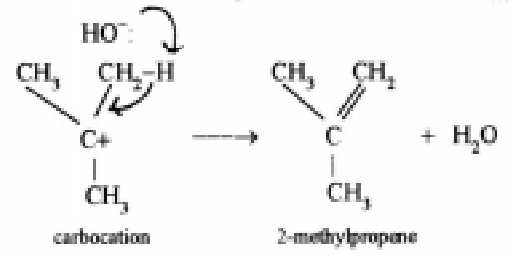
carbon and expulsion of the halide ion from the alpha carbon occur simultaneously. The mechanism is shown below :

E1 reactions: E1 stands for unimolecular elimination. when the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 reactions are two step processes.

Step 1 : The alkyl halide ionise to give the carbocation.



Step 2 : The nucleophile (OH^-) abstracts a proton and forms an alkene.



Uses of alkyl halides

1) Alkyl chlorides such as trichloromethane (chloroform) and tetra chloromethane (carbon tetrachloride) are widely used as industrial solvents. 2) Chloroform is used as anaesthetic 3) Iodoform is used as an antiseptic 4) Carbon tetrachloride is used as a fire extinguisher 5) dichlorodifluoromethane (a freon) is used as a refrigerant 6) Alkyl halides are used for the preparation of Grignard reagents.

0777 023 444

20.8 Aryl halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic ring, the compound is called aryl halide. Example,

chlorobenzene

The halogen atom may be linked to carbon atom in the side chain of an aromatic hydrocarbon. Such a compound is called aralkyl halide. Example,

benzyl chloride

20.8.1 General methods of preparation, properties and uses of aryl halides

The methods of preparation of chlorobenzene can be taken as general methods of preparation of aryl halides.

1. Direct halogenation : Aryl chlorides and aryl bromides are generally prepared from arenes by action with chlorine or bromine in presence of a catalyst such as $FeCl_3$ or $FeBr_3$.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$$

2. Decomposition of diazonium salts : Aryl halides can be prepared by the decomposition of aryldiazonium salts in the presence of appropriate metal halides.

0777 023 444

$$C_6H_5N_2^+Cl^- \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5Cl + N_2$$

$$C_6H_5N_2^+Cl^- \xrightarrow[HBr]{Cu_2Br_2} C_6H_5Br + N_2$$

20.9 General properties :

The molecule of an aryl halide is made of (i) an aromatic ring and (ii) halogen atom directly bonded to the ring. The reactions of aryl halides are, therefore, due to the aromatic ring and the halogen atom.

Reactions involving the halogen atom : Nucleophilic aromatic substitution : 1) Aryl halides do not readily undergo nucleophilic substitution reactions, as those of alkyl halides. The reason for such low reactivity is given below. One reason is that the C-X bond in aryl halides is short and strong compared to that of alkyl halides. Another reason is that the aromatic ring is a centre of high electron density because of the delocalised π electrons. However nucleophilic substitution of halogen of aryl halides can take place under vigorous conditions. Example,

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{623K} \underset{phenol}{C_6H_5OH} + NaCl$$

$$C_6H_5Cl + 2NH_3 \xrightarrow[50\ atm]{523K} \underset{aniline}{C_6H_5NH_2} + NH_4Cl$$

$$\underset{cuprous\ cyanide}{C_6H_5Cl + CuCN} \xrightarrow[pyridine]{523K} \underset{phenyl\ cyanide}{C_6H_5CN} + CuCl$$

2) Wurtz-Fittig reaction : Aryl halides react with alkyl halides when heated with sodium in ether solution to form alkylbenzene.

$$C_6H_5Br + 2Na + C_2H_5Br \xrightarrow{ether} \underset{ethyl\ benzene}{C_6H_5{-}C_2H_5} + 2NaBr$$

3) Fittig reaction : In the absence of alkyl halides, aryl halides in ether solution react with sodium to give biaryl compounds in which two benzene rings are bonded together.

$$C_6H_5Br + 2Na + BrC_6H_5 \rightarrow C_6H_5 - C_6H_5 \text{Biphenyl}$$

0777 023 444

4) Reduction : When reduced with nickel-aluminium alloy in the presence of sodium hydroxide, aryl halides give the corresponding arenes.

$$C_6H_5Cl + 2[H] \xrightarrow[NaOH]{Ni-Al} C_6H_6 + HCl$$

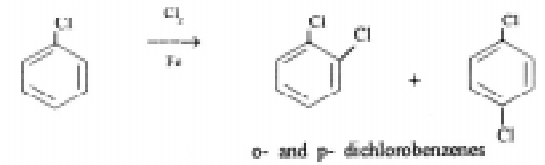
5) Formation of Grignard reagents : Aryl bromides and iodides form Grignard reagents when refluxed with magnesium powder in dry ether. Aryl chlorides do so in presence of tetrahydrofuran (THF) instead of ether.

$$C_6H_5Cl + Mg \xrightarrow{THF} C_6H_5MgCl$$

6) Reactions involving the aromatic ring: Electrophilic aromatic substitution reactions

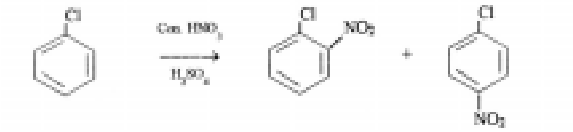
Aryl halides undergo the typical electrophilic aromatic substitution reactions like halogenation, nitration, sulphonation and alkylation. Here the halogen of the aryl halide directs the electrophilic reagents to ortho and para positions. The electrophilic substitution reactions of aryl halides are illustrated by taking the example of chlorobenzene.

i. Chlorination



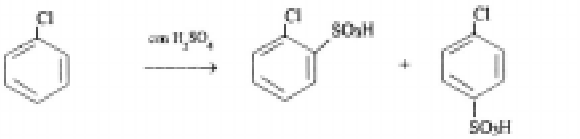
o- and p- dichlorobenzenes

ii. Nitration



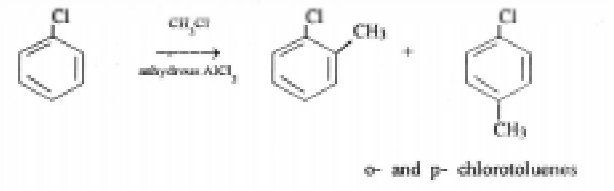
o- and p-nitrochlorobenzes

iiii. Sulphonation



o- and p- chlorobenzenesulphonic acids

iv. Alkylation



v. Formation of DDT : Chlorobenzene reacts with trichloroacetaldehyde (chloral) in the presence of concentrated sulphuric acid to give p-p'-dichloro diphenyltrichloroethane (DDT). It is an effective insecticide.

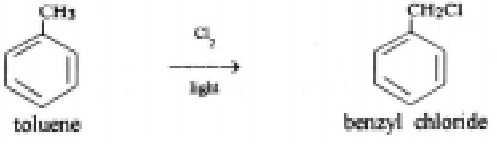
20.10 Uses of aryl halides :

Chlorobenzene is used for the preparation of phenol and nitrochlorobenzenes which are erequired for the manufacture of azo and sulphur dyes; DDT and BHC (benzenehexachloride) which are insecticides.

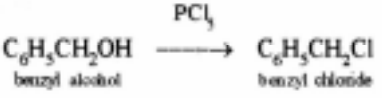
Side-chain halogenated compounds or aralkyl halides

A typical example of this class of compounds is benzyl chloride which can be prepared as follows:

1. Side chain halogenation is favoured by high temperature and light. It occurs in the absence of halogen carriers. For example, benzyl chloride is prepared by chlorination of boiling toluene in light.



2. It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.



0777 023 444

Properties

i) Reduction of aralkyl halides

Reduction of benzyl chloride with Zn-Cu couple gives toluene.

$$C_6H_5CH_2Cl \xrightarrow{\text{Zn-Cu}} C_6H_5CH_3$$

ii) Oxidation

Benzyl chloride on oxidation with alkaline potassium permanganate gives benzoic acid.

On mild oxidation with $Cu(NO_3)_2$ gives benzaldehyde.

$$C_6H_5CH_2Cl \xrightarrow{[O]} C_6H_5 - CHO$$

20.11 Grignard reagents

Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,

CH_3Li C_2H_5MgI

$(C_2H_5)_2Zn$ $Pb(C_2H_5)_4$

Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

General formula and nomenclature : Their general formula can be written as RMgX where R=alkyl or aryl group and X=Cl, Br or I. Examples, CH_3MgBr and CH_3CH_2MgBr.

Nomenclature : Grignard reagents are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,

CH_3MgI methylmagnesium iodide

CH_3CH_2MgBr ethylmagnesium bromide

CH_3Li methyllithium

$(CH_3CH_2)_4Pb$ tetraethyllead

0777 023 444

20.11.1 Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anyhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflex condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. this is used as such in all the reactions.

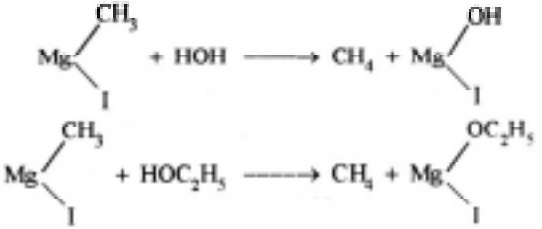
$$CH_3I + Mg \xrightarrow[\text{ether}]{\text{dry}} CH_3MgI$$

20.12 Synthetic uses of methylmagnesium iodide

Grignard regents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

1. Preparation of alkanes

Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.

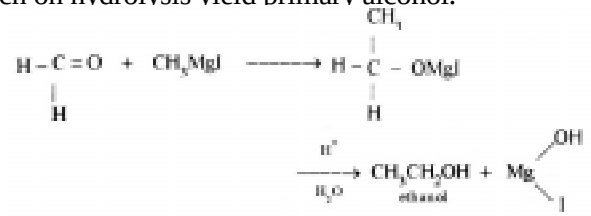


2. Preparation of primary alcohols

Formaldehyde reacts with methylmagnesium iodide to give addition

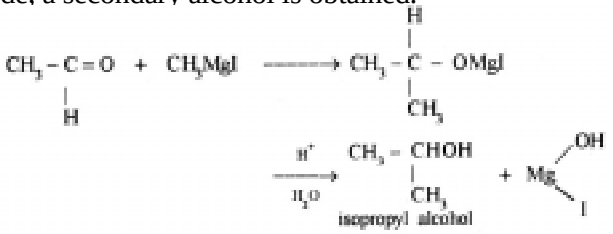
0777 023 444

product which on hydrolysis yield primary alcohol.



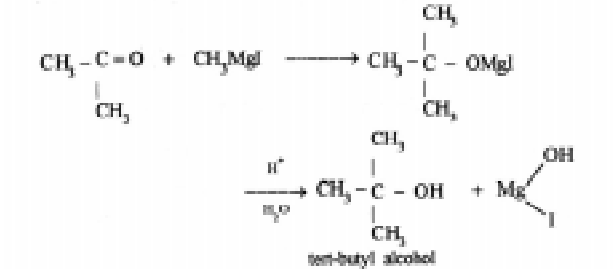
3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



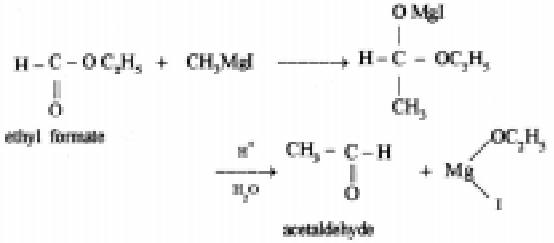
4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.



5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.



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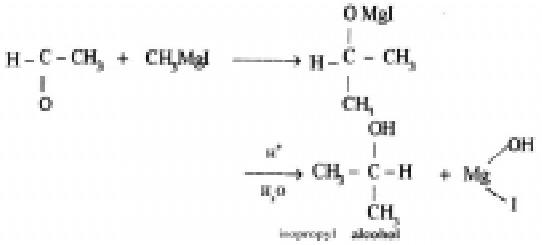
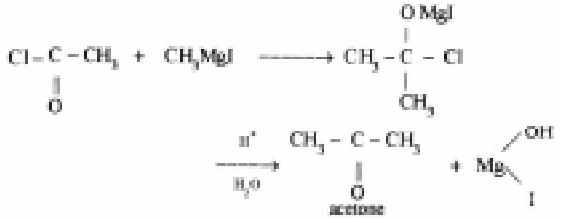
A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



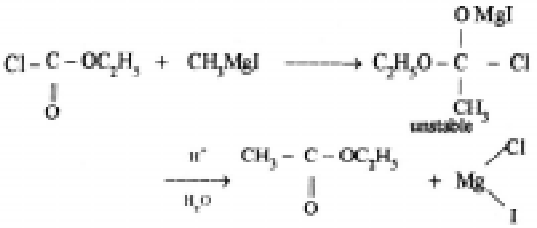
6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



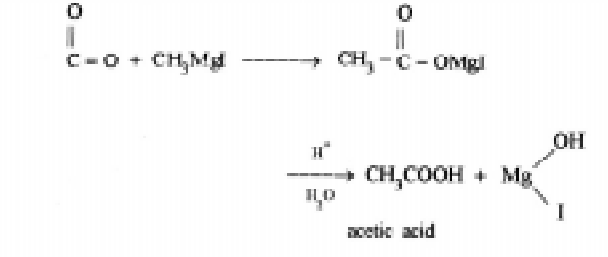
7. Preparation of esters

Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



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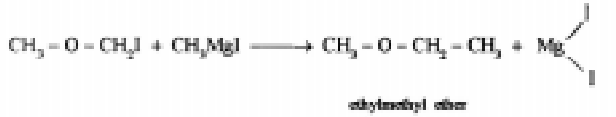
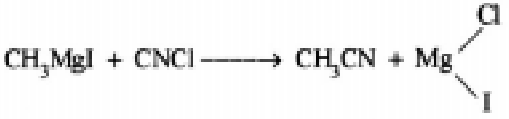
9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.



methyl cyanide or acetonitrile

Questions

A. Choose the correct answer

1. The IUPAC name of

$$CH_3.\underset{\underset{Br}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2} - \overset{\overset{CH_3}{|}}{CH} - CH_3 \text{ is}$$

   a. 2-Bromo-3-chloro-4-methylpentane
   b. 2-Methyl-3-chloro-4-bromopentane
   c. 2-Bromo-3-chloro-3-isopropyl propane
   d. 2,4-Dimethyl-4-Bromo-3-chloro butane.

2. For reacting with HCl, the alcohol which does not require $ZnCl_2$ is
   a. $CH_3\,CH_2\,OH$ b. $CH_3 – CH_2\,CH_2\,OH$
   c. $CH_3 – \underset{\underset{CH_3}{|}}{CH}\,OH$ d. $C\,(CH_3)_3\,C\text{-}OH$.

3. For converting alcohols into alkyl halides, the best reagent is
   a. PCl_3 b. PCl_5 c. $SOCl_2$ d. None of the above

4. The olefin, which is not important for Markovni Koff's addition of HCl, is
   a. Propene b. But-1-ene c. 2-Methyl-propene d. Ethylene

5. The S_N1 reaction of alkyl halides is not affected by the nature of the
   a. alkyl group b. the halogen c. medium d. nucleophile

0777 023 444

20. ORGANIC HALOGEN COMPOUNDS

OBJECTIVES

The main objectives of this chapter are

* *to highlight the medicinal importance of certain halogenated compounds.*
* *to understand the physical and chemical properties of the organic halogen compounds.*
* *to give brief account of classification and nomenclature of these compounds.*
* *to discuss mechanisms of substitution and elimination reactions which are important to halogen compounds.*
* *to provide students more exposure to named organic reactions.*
* *to raise the capability of students to design new synthetic routes for interested target materials.*
* *to provide proof that how much important these compounds are as intermediates in the synthesis of wide variety of organic compounds.*

In organic halogen compounds F, Cl, Br and I are bonded to the carbons of the aliphatic, aromatic and aralkyl hydrocarbons. Many organic halogen compounds occur in nature and some of them have medicinal value. Chloromycetin is a naturally occurring halogen compound used in the treatment of typhoid fever. Thyroxine is yet another one used in the treatment of goitre. There are many synthetic organic halogen compounds few of which are important in health care and medicine. Two such compounds to cite are chloroquine and halothane. The former is used in the treatment of malaria and the later is used as an anaesthetic during surgery. There are also compounds which are important in agriculture and industry, as intermediates in the synthesis of wide variety of other organic compounds.

20.1 Classification of halogen compounds

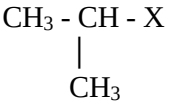
Depending on the type of halogen present, the halohydrocarbons are classified as follows.

Based on the number of alkyl groups bonded to the carbon that carries the halogen, the classification may be as follows.

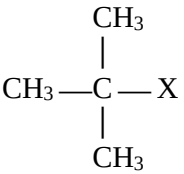
0777 023 444

Primary halides CH_3CH_2 - X

Secondary halides



Tertiary halides



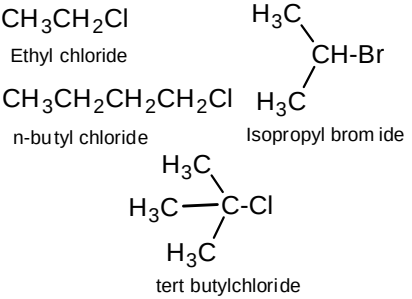
Where X = Halogen

In the primary halides, the carbon bonded to the halogen is connected to one alkyl group, in the secondary halides two alkyl groups in the tertiary halides three alkyl groups.

20.2 Nomenclature of alkyl halides : common and IUPAC

In this section the nomenclature of alkyl halides alone is presented, and the same for aryl halides and aralkyl halides are presented in their respective sections.

The common names of the monohalogen derivatives are derived by naming the alkyl group first and the halogen second.



If two halogen atoms are bonded to the same carbon, they are named as the alkylidene halides. CH_3CHBr_2 Ethylidene bromide. If the two halogen atoms are bonded to adjacent carbons, they are named as the dihalides of the alkenes from which they are formed.

0777 023 444

$$CH_2 = CH_2 + Cl_2 \rightarrow \underset{Cl}{\underset{|}{CH_2}} - \underset{Cl}{\underset{|}{CH_2}}$$

Ethylene dichloride

$$CH_3CH = CH_2 + Cl_2 \rightarrow \underset{Cl}{\underset{|}{CH_3CH}} - \underset{Cl}{\underset{|}{CH_2}}$$

Propylene dichloride

Trihalomethane and tetrahalomethanes are named as haloforms and carbon tetra halides respectively.

Example

Write the common names of the following halides

a) $CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH_2Br$ b) $CH_3CH_2CHCl_2$

c) $CH_2 - \underset{I}{\underset{|}{\overset{I}{\overset{|}{C}}}} - CH_3$

d) $CHBr_3$ e) CCl_4

Solution

a. Isobutyl bromide b. Propylidene chloride

c. Propylidene iodide d. Bromoform

e. Carbon tetra chloride.

More complex halogen compounds are named according to IUPAC system.

i. If any halogen is at the end of the chain, the carbon bearing the halogen is to be given the number 1.

ii. If the halogen is present in the second or third carbon, numbering is to be started from that side of the chain which gives the least number for carbon bonded to halogen.

0777 023 444

iii. When two different halogens are present, the carbon bonded to higher atomic number halogen is to be given priority.

iv. The names of the halogens and other substituents are to be arranged alphabetically.

$CH_3CH_2CH_2Br$ 1 - Bromobutane

$$\begin{array}{cccc} CH_2 & CH & CH & CH_3 \\ | & | & | & \\ Br & Cl & Cl & \end{array}$$ 1-Bromo-2,3- dichlorobutane

$$CH_3 - \overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2CH_3$$ 2 - Bromo-2-methylbutane

Example

Write the IUPAC names of the following halides.

a. $CH_2Br.CHCl.CH_2CH_2Cl$

b. $CH_3CCl_2.CHBr.CH_3$

c. $CH_3 - \underset{\underset{CH_3}{|}}{CBr} - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3$

Solution

a. 1 - Bromo - 2,4 - dichlorobutane

b. 2 - Bromo - 3,3 - dichlorobutane

c. 2-Bromo-3-chloro-2,4-dimethylpentane

20.3 General methods of preparation

i. From alcohols : Preparation of alkyl halides from alcohols involves replacement of the hydroxyl group with halogen. It is done by using halogen acids.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} RCH_2Cl + H_2O$$

$$R - \underset{\underset{R}{|}}{CH} - OH + HCl \rightarrow R - \underset{\underset{R}{|}}{CHCl} + H_2O$$

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH + HCl \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-Cl + H_2O$$

$ZnCl_2$ is the Lewis acid catalyst. It is required for both primary and secondary alcohols as they are not rapidly reacting. Tertiary alcohols do not require this reagent as they are more reactive.

ii. From alkenes : Alkenes reacts with halogen acids to give alkyl halides. The addition of HCl occurs with first proton and second with halogen.

$$CH_2 = CH_2 + H^+ \rightarrow CH_3\,CH_2^+$$

$$CH_3\,CH_2^+ + Cl^- \rightarrow CH_3CH_2Cl$$

Hence $CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$

HBr and HI are added in a similar manner

When a hydrogen halide is added to an unsymmetrical olefin, the position of the halogen in the product is predicted by Markovnikoff's rule : It states that when a hydrogen halide is added to an unsymmetrical olefin, the negative part of it is added to the carbon that carries least number of hydrogens.

$$CH_3.CH = CH_2 + HCl \rightarrow CH_3\,\underset{\underset{Cl}{|}}{CH} - CH_3$$

It is based on the stability of the carbonium ion formed after the addition of the proton. The order of the stability of the carbonium ion is

tertiary carbonium ion > secondary carbonium ion > primary carbonium ion

The stability of the carbonium ion depends on the extent to which the degree of the positive charge is decreased. In the tertiary carbonium ion the positive charge is more decreased by inductive effect and hyper conjugation and hence its degree of positive charge is more decreased than the secondary and primary carbonium ions.

0777 023 444

iii. From hydrocarbons

By treating alkanes with chlorine (or bromine) at room temperature in the presence of light, chloroalkanes are obtained. The reaction follows a free radical mechanism.

Chlorine molecule decomposes into chlorine atoms by absorption of light and the atoms then react with hydrocarbons.

$$Cl_2 \xrightarrow[\text{light}]{h\upsilon} Cl^{\bullet} + Cl^{\bullet}$$

$$CH_3CH_2 - H + Cl^{\bullet} \rightarrow CH_3CH_2^{\bullet} + HCl$$

$$CH_3CH_2^{\bullet} + Cl_2 \rightarrow CH_3CH_2Cl + Cl^{\bullet}$$

$$ClCH_2CH_3 + Cl^{\bullet} \rightarrow ClCH_2CH_2\,Cl + HCl$$

It is a chain reaction with the formation of several products. The reaction may be stopped by absorption of the chlorine atoms on the wall, or by reaction if two chlorine atoms to form a chlorine molecule.

iv. Hunsdiecker or Borodine - Hunsdiecker reaction

Silver carboxylates in carbon tetrachloride are decomposed by chlorine or bromine to form alkyl halide.

$$CH_3CH_2COO\,Ag + Br_2 \rightarrow CH_3CH_2Br + CO_2 + AgBr$$

Bromine is better than chlorine as the later gives poor yield.

v. By halogen exchange : Finkelstein reaction

Alkyl iodides are prepared by treating the corresponding chloride or bromide with a solution of sodium iodide in acetone. The exchange of halogen between alkyl halide and sodium iodide occurs.

$$RCl + NaI \xrightarrow{\text{Acetone}} RI + NaCl$$

$$RBr + NaI \xrightarrow{\text{Acetone}} RI + NaBr$$

Alkyl fluorides are obtained by treating alkyl chloride or bromide with metallic fluoride, such as AgF or SbF_3. It is the Swarts reaction.

$$CH_3\,CH_2\,Br + AgF \rightarrow CH_3CH_2F + AgBr.$$

0777 023 444

vi. Preparation of dihalogens

$CH_3COCH_3 + PCl_5 \rightarrow CH_3CCl_2.CH_3,$

$CH \equiv CH + 2HBr \rightarrow CH_3CHBr_2$

$CH_3CH = CH_2 \xrightarrow{Br_2} CH_3CHBr\ CH_2Br$

20.4 Properties

20.4.1 Physical properties

The lower members CH_3Cl, CH_3Br and CH_3CH_2Cl are gases. CH_3I and the majority of higher members are sweet-smelling liquids. For a given alkyl group the boiling point of halides increases with increase in the atomic weight of the halogens.

Halide	CH_3F	CH_3Cl	CH_3Br	CH_3I
B.P (°C)	-78	-24	4.0	92

It is due to increase in the Vanderwaals force with increase in the molecular size (molecular weight).

For a given halide, the boiling point increases with the length of the alkyl chains.

Halide	CH_3Cl	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$
B.P (°C)	-22	12.5	47

It is due to increase in the Vanderwaals force with increase in the chain length. In a similar manner the boiling point of isomeric alkyl halides decreases in the order as shown below.

Halide	B.P (°C)
$CH_3CH_2CH_2CH_2Cl$	21.5
$CH_3.CH_2CH(Cl) - CH_3$	68
$(CH_3)_3C\text{-}Cl$	51

Organic halides are insoluble in water, as they are unable to form strong hydrogen bonds with water. They are less inflammable than the

0777 023 444

hydrocarbons. It is due to dilution of oxygen during combustion by the released halogen. Carbon tetrachloride is used in fire extinguishers and as solvent. Tri- and tetrachloroethylenes are widely used as solvents, and they are good solvents for fats and oils. They do not catch fire easily.

20.5 Nucleophilic substitution reactions

The alkyl halides are important reagents in organic synthesis. The halogen can be displaced by other groups by which variety of other organic compounds can be prepared. The reaction can be written as

$$\underset{\text{nucleophile}}{Y^- + RX} \rightarrow \underset{\text{substrate}}{RY} + \underset{\text{product, leaving group}}{X^-}$$

The nucleophile may be negatively charged or a neutral species with a lone pair of electrons.

Nucleophiles : OH^-, RO^-, HS^-, NO_2^-, CN^- etc.
Neutral : H_2O, NH_3 CH_3NH_2 etc.

The R-X bond is polar with partial positive charge on carbon as shown below. It is due to more electronegativity of halogen than carbon.

$$CH_3 - \overset{\delta+}{C}H_2 - \overset{\delta-}{X}$$

The nucleophile attacks on the carbon (CH_2) and displaces the leaving group. This reaction can occur by the following mechanisms.

20.6 Mechanism of nucleophilic substitution reactions

When a substitution reaction involves the attack of a nucleophile, the reaction is referred to as S_N (S-stands for substitution and N for nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.

$$\underset{\text{nucleophile}}{R - X + OH^-} \rightarrow \underset{\text{leaving group}}{R - OH + X^-}$$

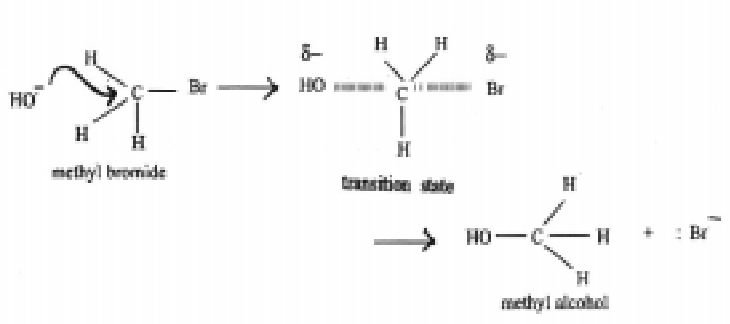
The nucleophilic substitution reactions are divided into two classes : (1) S_N2 reactions (2) S_N1 reactions.

S_N2 reactions : S_N2 stands for bimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends on the

0777 023 444

concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as S_N2.

Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction is represented below.



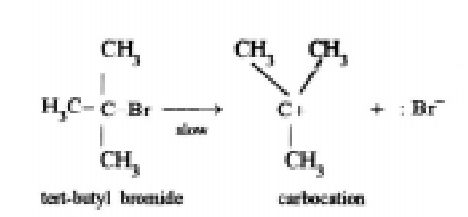
The hydroxide ion approaches the substrate carbon from the side opposite to the bromine atom. This is backside attack. This is because both hydroxide ion and the bromine atom are electron rich. They stay as far apart as possible. The transition state may be pictured as a structure in which both OH and Br are partially bonded to the substrate carbon. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. In the transition state the three C-H bond lie in one plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds.

S_N1 reactions: S_N1 stands for unimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate (alkyl halide), the reaction is first order and is represented as S_N1.

Consider the hydrolysis of tertiary butyl bromide. The reaction consists of two steps.

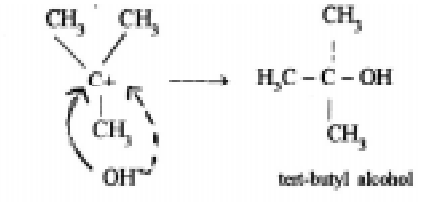
Step 1: The alkyl halide ionises to give the carbocation (carbonium ion). This step is the slow rate determining step.

0777 023 444



The carbocation is planar. This is because the central positively charged carbon atom is sp^2 hybridised.

Step 2 : The nucleophile can attack the planar carbocation from either side to give tertiary butyl alcohol.



Primary alkyl halides undergo hydrolysis by S_N2 mechanism. The tertiary alkyl halides undergo hydrolysis by S_N1 mechanism. Secondary alkyl halides may undergo hydrolysis by both S_N1 and S_N2 mechanism.

20.7 Mechanism of elimination reaction

Elimination reactions are reverse of addition reactions. Here atoms or group attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a double bond. Example, dehydrohalogenation of alkyl halides with alcoholic alkalis.

$$R\text{–}CH_2\text{–}CH_2\text{–}X \xrightarrow[\text{alcoholic alkali}]{OH^-} R\text{–}CH{=}CH_2 + H_2O + X^-$$

These reactions are divided into two classes

1) E2 reaction2) E1 reactions

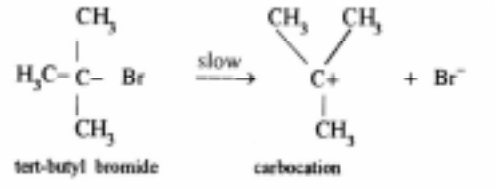
E2 reactions: E2 stands for bimolecular elimination. When the rate of an elimination reaction depends on the concentration of substrate and nucleophile, the reaction is second order and is represented as E2. E2 is a one step process in which the abstraction of the proton from the beta

0777 023 444

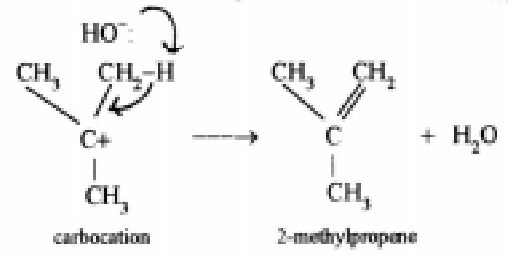
carbon and expulsion of the halide ion from the alpha carbon occur simultaneously. The mechanism is shown below :

E1 reactions: E1 stands for unimolecular elimination. when the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 reactions are two step processes.

Step 1 : The alkyl halide ionise to give the carbocation.



Step 2 : The nucleophile (OH^-) abstracts a proton and forms an alkene.



Uses of alkyl halides

1) Alkyl chlorides such as trichloromethane (chloroform) and tetra chloromethane (carbon tetrachloride) are widely used as industrial solvents. 2) Chloroform is used as anaesthetic 3) Iodoform is used as an antiseptic 4) Carbon tetrachloride is used as a fire extinguisher 5) dichlorodifluoromethane (a freon) is used as a refrigerant 6) Alkyl halides are used for the preparation of Grignard reagents.

0777 023 444

20.8 Aryl halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic ring, the compound is called aryl halide. Example,

chlorobenzene

The halogen atom may be linked to carbon atom in the side chain of an aromatic hydrocarbon. Such a compound is called aralkyl halide. Example,

benzyl chloride

20.8.1 General methods of preparation, properties and uses of aryl halides

The methods of preparation of chlorobenzene can be taken as general methods of preparation of aryl halides.

1. Direct halogenation : Aryl chlorides and aryl bromides are generally prepared from arenes by action with chlorine or bromine in presence of a catalyst such as $FeCl_3$ or $FeBr_3$.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$$

2. Decomposition of diazonium salts : Aryl halides can be prepared by the decomposition of aryldiazonium salts in the presence of appropriate metal halides.

0777 023 444

$$C_6H_5N_2^+Cl^- \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5Cl + N_2$$

$$C_6H_5N_2^+Cl^- \xrightarrow[HBr]{Cu_2Br_2} C_6H_5Br + N_2$$

20.9 General properties :

The molecule of an aryl halide is made of (i) an aromatic ring and (ii) halogen atom directly bonded to the ring. The reactions of aryl halides are, therefore, due to the aromatic ring and the halogen atom.

Reactions involving the halogen atom : Nucleophilic aromatic substitution : 1) Aryl halides do not readily undergo nucleophilic substitution reactions, as those of alkyl halides. The reason for such low reactivity is given below. One reason is that the C-X bond in aryl halides is short and strong compared to that of alkyl halides. Another reason is that the aromatic ring is a centre of high electron density because of the delocalised π electrons. However nucleophilic substitution of halogen of aryl halides can take place under vigorous conditions. Example,

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{623K} \underset{phenol}{C_6H_5OH} + NaCl$$

$$C_6H_5Cl + 2NH_3 \xrightarrow[50\ atm]{523K} \underset{aniline}{C_6H_5NH_2} + NH_4Cl$$

$$\underset{cuprous\ cyanide}{C_6H_5Cl + CuCN} \xrightarrow[pyridine]{523K} \underset{phenyl\ cyanide}{C_6H_5CN} + CuCl$$

2) Wurtz-Fittig reaction : Aryl halides react with alkyl halides when heated with sodium in ether solution to form alkylbenzene.

$$C_6H_5Br + 2Na + C_2H_5Br \xrightarrow{ether} \underset{ethyl\ benzene}{C_6H_5{-}C_2H_5} + 2NaBr$$

3) Fittig reaction : In the absence of alkyl halides, aryl halides in ether solution react with sodium to give biaryl compounds in which two benzene rings are bonded together.

$$C_6H_5Br + 2Na + BrC_6H_5 \rightarrow C_6H_5 - C_6H_5 \text{Biphenyl}$$

0777 023 444

4) Reduction : When reduced with nickel-aluminium alloy in the presence of sodium hydroxide, aryl halides give the corresponding arenes.

$$C_6H_5Cl + 2[H] \xrightarrow[NaOH]{Ni-Al} C_6H_6 + HCl$$

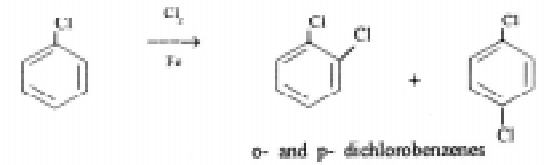
5) Formation of Grignard reagents : Aryl bromides and iodides form Grignard reagents when refluxed with magnesium powder in dry ether. Aryl chlorides do so in presence of tetrahydrofuran (THF) instead of ether.

$$C_6H_5Cl + Mg \xrightarrow{THF} C_6H_5MgCl$$

6) Reactions involving the aromatic ring: Electrophilic aromatic substitution reactions

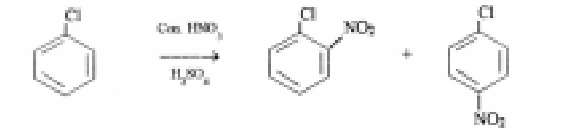
Aryl halides undergo the typical electrophilic aromatic substitution reactions like halogenation, nitration, sulphonation and alkylation. Here the halogen of the aryl halide directs the electrophilic reagents to ortho and para positions. The electrophilic substitution reactions of aryl halides are illustrated by taking the example of chlorobenzene.

i. Chlorination



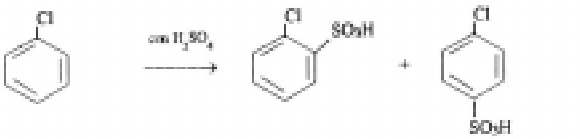
o- and p- dichlorobenzenes

ii. Nitration



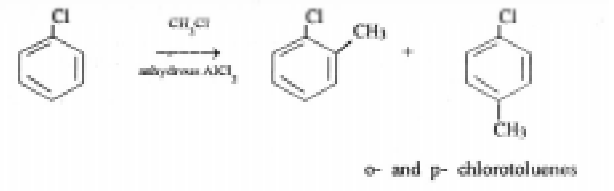
o- and p-nitrochlorobenzes

iiii. Sulphonation



o- and p- chlorobenzenesulphonic acids

iv. Alkylation



v. Formation of DDT : Chlorobenzene reacts with trichloroacetaldehyde (chloral) in the presence of concentrated sulphuric acid to give p-p'-dichloro diphenyltrichloroethane (DDT). It is an effective insecticide.

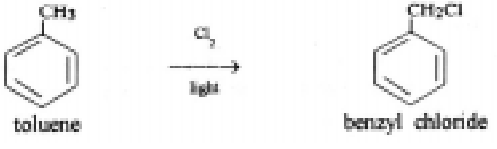
20.10 Uses of aryl halides :

Chlorobenzene is used for the preparation of phenol and nitrochlorobenzenes which are erequired for the manufacture of azo and sulphur dyes; DDT and BHC (benzenehexachloride) which are insecticides.

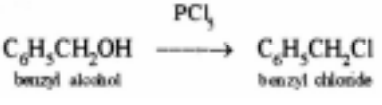
Side-chain halogenated compounds or aralkyl halides

A typical example of this class of compounds is benzyl chloride which can be prepared as follows:

1. Side chain halogenation is favoured by high temperature and light. It occurs in the absence of halogen carriers. For example, benzyl chloride is prepared by chlorination of boiling toluene in light.



2. It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.



0777 023 444

Properties

i) Reduction of aralkyl halides

Reduction of benzyl chloride with Zn-Cu couple gives toluene.

$$C_6H_5CH_2Cl \xrightarrow{\text{Zn-Cu}} C_6H_5CH_3$$

ii) Oxidation

Benzyl chloride on oxidation with alkaline potassium permanganate gives benzoic acid.

On mild oxidation with $Cu(NO_3)_2$ gives benzaldehyde.

$$C_6H_5CH_2Cl \xrightarrow{[O]} C_6H_5 - CHO$$

20.11 Grignard reagents

Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,

CH_3Li C_2H_5MgI

$(C_2H_5)_2Zn$ $Pb(C_2H_5)_4$

Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

General formula and nomenclature : Their general formula can be written as RMgX where R=alkyl or aryl group and X=Cl, Br or I. Examples, CH_3MgBr and CH_3CH_2MgBr.

Nomenclature : Grignard reagents are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,

CH_3MgI methylmagnesium iodide

CH_3CH_2MgBr ethylmagnesium bromide

CH_3Li methyllithium

$(CH_3CH_2)_4Pb$ tetraethyllead

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20.11.1 Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anyhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflex condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. this is used as such in all the reactions.

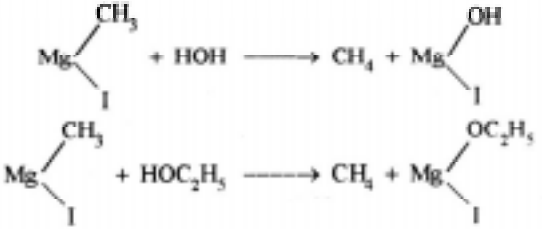
$$CH_3I + Mg \xrightarrow[\text{ether}]{\text{dry}} CH_3MgI$$

20.12 Synthetic uses of methylmagnesium iodide

Grignard regents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

1. Preparation of alkanes

Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.



2. Preparation of primary alcohols

Formaldehyde reacts with methylmagnesium iodide to give addition

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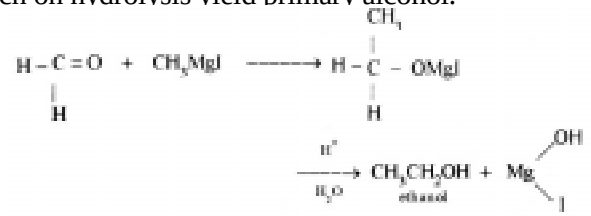
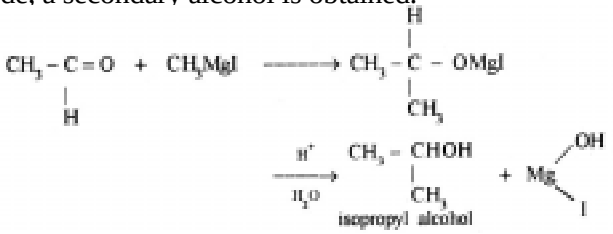
product which on hydrolysis yield primary alcohol.



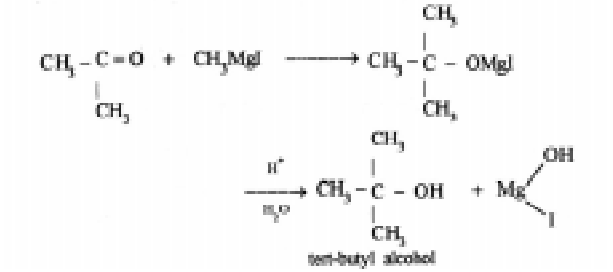
3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



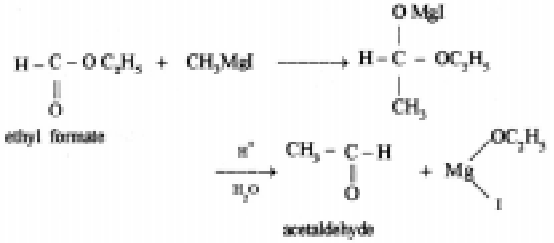
4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.



5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.



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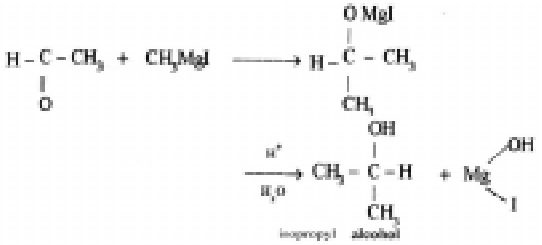
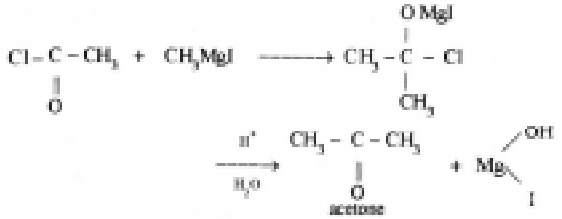
A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



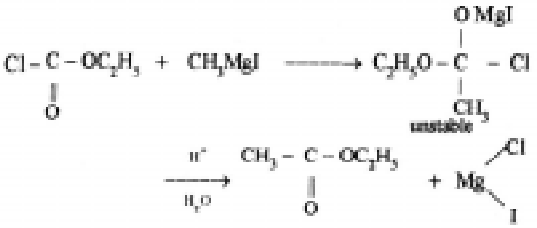
6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



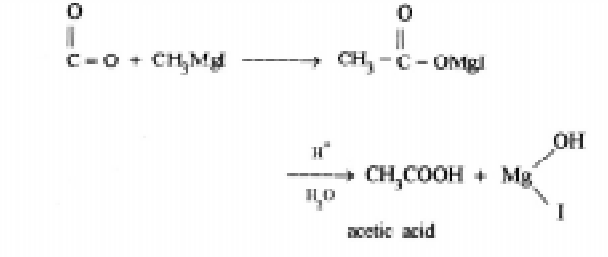
7. Preparation of esters

Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



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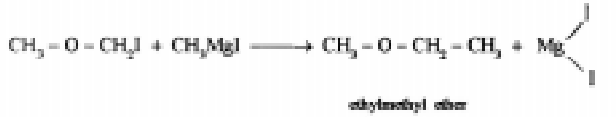
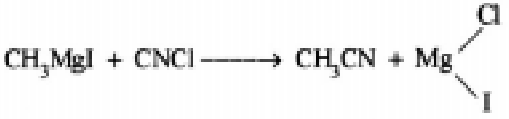
9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.



methyl cyanide or acetonitrile

Questions

A. Choose the correct answer

1. The IUPAC name of

$$CH_3.\underset{\underset{Br}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2} - \overset{\overset{CH_3}{|}}{CH} - CH_3 \text{ is}$$

   a. 2-Bromo-3-chloro-4-methylpentane
   b. 2-Methyl-3-chloro-4-bromopentane
   c. 2-Bromo-3-chloro-3-isopropyl propane
   d. 2,4-Dimethyl-4-Bromo-3-chloro butane.

2. For reacting with HCl, the alcohol which does not require $ZnCl_2$ is
   a. $CH_3\,CH_2\,OH$ b. $CH_3 – CH_2\,CH_2\,OH$
   c. $CH_3 – \underset{\underset{CH_3}{|}}{CH}\,OH$ d. $C\,(CH_3)_3\,C\text{-}OH$.

3. For converting alcohols into alkyl halides, the best reagent is
   a. PCl_3 b. PCl_5 c. $SOCl_2$ d. None of the above

4. The olefin, which is not important for Markovni Koff's addition of HCl, is
   a. Propene b. But-1-ene c. 2-Methyl-propene d. Ethylene

5. The S_N1 reaction of alkyl halides is not affected by the nature of the
   a. alkyl group b. the halogen c. medium d. nucleophile

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B. Fill in the blanks

1. Markonikoff's rule is followed for the addition of HCl to.....
2. In Swarts reaction metallic fluorides are added to.....
3. Hoffman's rule is applicable to elimination .....
4. Chloropicrin is prepared by adding nitric acid to.....

C. Write in one or two sentence

1. What are Lewis acids?
2. What is an electrophilic addition?
3. What is Hunsdiecker reaction?
4. What is Finkelstein reaction?
5. What is Swarts reaction?

D. Explain briefly on the following

1. Discuss S_N1 mechanism
2. Discuss S_N2 mechanism
3. Discuss E1 elimination
4. Discuss E2 elimination
5. What are the uses of alkyl halides?
6. What are the general reactions of aryl halides.
7. What are aralkyl halides ? How are they prepared?
8. What are Grignard reagents? Discuss its synthetic uses.
9. Discuss the general methods of preparation of alkyl halides.

SUMMARY

- Organic halogen compounds are classified into alkyl, aryl and aralkylhalides.
- Alkyl halides are very good synthetic compounds from which various compounds are synthesised.
- In Aryl halides chloro group is ortho and meta directing.
- If a halogenoalkane is reacted with magnesium metal in dry ethoxyethane, a Grignard reagent is the product - these act as nucteophiles and are commonly used to form new carbon-carbon bonds.

REFERENCES

1. Organic Chemistry IL Finar ELBS
2. Organic Chemistry by Morrison and Boyd.