MAA OMWATI DEGREE COLLEGE, HASSANPUR (PALWAL)

NOTES

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SUBJECT : Organic Chemistry

CLASS : B.Sc 2nd Sem

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Alkenes

Introduction

- **Alkenes are the unsaturated hydrocarbons having the general formula** C_nH_{2n}. They are characterised by the presence of a $>C=C<$ (Carbon-carbon double bond) in their molecules. The Carbon-carbon double bond is also referred to as the **ethylenic or the olefinic bond.**
- **Alkenes are also referred to as olefins :** Since ethylene, the first member of the alkene series reacts with chlorine to give an oily product of the constitution $C_2H_4Cl_2$. Hence, ethylene is also referred to as the olefiant gas (i.e. oil forming). Hence, the alkene series commencing from ethylene began to be referred as olefins.

Structure of Alkenes

- The structure of ethylene, the simplest alkene is being discussed here.
- The two C-atoms of ethylene are sp^2–hybridised.
- Each C-atom uses its three hybrid orbitals in the formation of three sigma (σ) bonds: One C – C σ bond formed by the head-on-overlap of sp^2 hybrid orbital of one C-atom with that of the other and two C – H σ bonds formed by the overlap of sp^2-hybrid orbital of C–atom with 1s-orbital of H-atom.
- The σ–bond skeleton of ethylene molecules is as shown below :

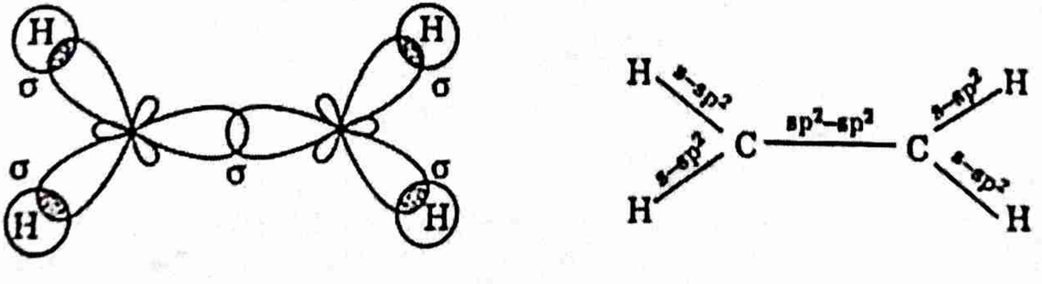


Fig. 1.1. : σ-bonded skeleton of ethylene

- As a result of sp^2-hybridisation of C-atoms, the ethylene molecule is flat and all the C – and H-atoms lie in the same plane, i.e., they are coplanar.

Nomenclature

There are two systems of nomenclature :

I. **The Common System**

The common names of the alkenes are derived from the corresponding alkanes by replacing the suffix 'ane' by 'ylene'. *i.e.,*

$$\text{Alkane} \xrightarrow[+\text{ylene}]{-\text{ane}} \text{Alkylene}$$

In case of isomeric alkenes, the position of the double bond is indicated by the prefixes α –, β–, γ – etc.

II. **The IUPAC Nomenclature**

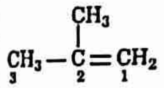
(a) **IUPAC Nomenclature of Simple Alkenes**

The longest chain containing the double bond is chosen as the parent alkane and the IUPAC name is derived by replacing the suffix. 'ane' of the corresponding alkane by 'ene', *i.e.,*

$$\text{Alkane} \xrightarrow[+\text{ene}]{-\text{ane}} \text{Alkene}$$

The carbon chain is then numbered in a manner such that the position of the double bond gets the lowest possible number. This position number is then written just before the prefix-ene or simply before the name of the parent alkene.

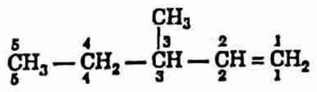
The common and IUPAC names of some alkenes are summarised in the table given below :

Formula	Name of the corresponding alkane	Common Name	IUPAC Name
$>CH_2$ (A divalent radical)	Methane	Methylene	Methene
$CH_2 = CH_2$	Ethane	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propane	Propylene	Propene
$CH_3 - CH_2 - CH = CH_2$	Butane	α-Butylene	1–Butene or But-1-ene
CH_3-$CH = CH - CH_3$	Butane	β-Butylene	2-Butene or But-2-ene
 $\overset{3}{CH_3} - \overset{CH_3}{\overset{\vert}{\underset{2}{C}}} = \underset{1}{CH_2}$	Isobutane	Isobutylene	2-Methyl-1-propene *or* 2-Methyl prop-1-ene
$CH_3 - CH_2 - CH_2 - CH = CH_2$	Pentane	α-Pentylene	1-Pentene or Pent-1-ene
$CH_3 - CH_2 - CH = CH - CH_3$	Pentane	β-Pentylene	2-Pentene or Pent-2-ene
$CH_3 - CH_2 - CH_2 - CH_2 - CH = CH_2$	Hexane	α-Hexylene	1-Hexene or Hex-1-ene.

(b) **IUPAC Nomenclature of Alkenes with Substituents**

(i) The position of substituent is indicated by the number of the C-atom to which it is attached. Note that while numbering, the position of the double bond gets preference over the substituents.

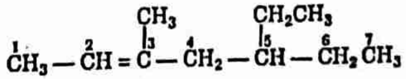
For example,



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

3-Methyl pent-1-ene

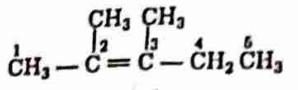
(ii) If different types of substituents are attached to the parent chain, then while naming the alkene are arranged in an alphabetical order along with their respective position numbers. For example,



$$\overset{1}{CH_3} - \overset{2}{CH} = \overset{CH_3}{\overset{\vert 3}{C}} - \overset{4}{CH_2} - \overset{CH_2CH_3}{\overset{\vert 5}{CH}} - \overset{6}{CH_2}\overset{7}{CH_3}$$

5–Ethyl–3–methyl hept–2–ene.

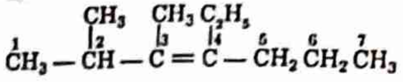
(iii) If the same substituent is repeated twice, thrice etc., then the prefixes di, tri, tetra ....etc. are used with the name of the substituent. For example,



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

2, 3–Dimethyl pent–2–ene

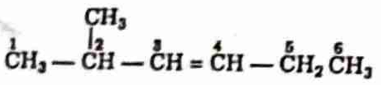
(iv) Note that while deciding the alphabetical order of various simple substituents, the prefixes di, tri, tetra, etc. are not considered. For example,



$$\overset{1}{CH_3}-\overset{CH_3}{\overset{|}{\overset{2}{CH}}}-\overset{CH_3}{\overset{|}{\overset{3}{C}}}=\overset{C_2H_5}{\overset{|}{\overset{4}{C}}}-\overset{5}{CH_2}\overset{6}{CH_2}\overset{7}{CH_3}$$

4–Ethyl–2, 3–dimethylhept–3–ene

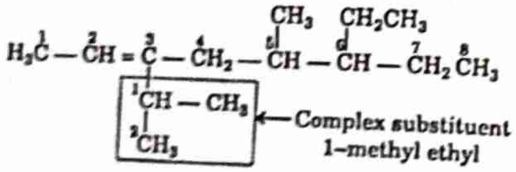
(v) If the double bond is at equal distance from either end, then the numbering of the parent chain is done in a manner such that the substituents get the lowest possible number. For example,



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

2-Methyl hex-3-ene
(and not 5-Methyl hex-3-ene)

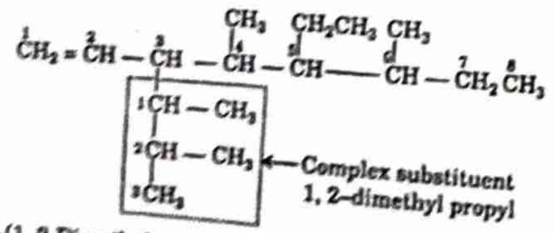
(vi) If a complex substituent is attached to the parent chain, its name is written in brackets along with its position number. For example,



$$H_3\overset{1}{C}-\overset{2}{CH}=\underset{\boxed{\overset{1}{C}H-CH_3 \\ \overset{2}{C}H_3}}{\overset{3}{C}}-\overset{4}{CH_2}-\overset{CH_3}{\overset{|}{\overset{5}{CH}}}-\overset{CH_2CH_3}{\overset{|}{\overset{6}{CH}}}-\overset{7}{CH_2}\overset{8}{CH_3}$$

6–Ethyl–5–methyl–3–(1–methyl ethyl) Oct–2–ene

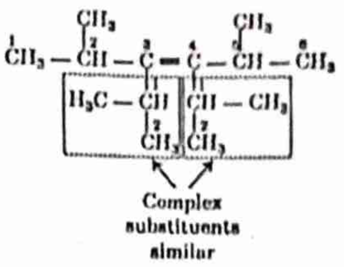
(vii) Note that while deciding the alphabetical order of various substituents, the first letter of the complete name of the complex substituent is considered including the prefixes di, tri, etc....while, such prefixes are not considered for simple substituents. For example,



$$\overset{1}{CH_2}=\overset{2}{CH}-\underset{\boxed{\overset{1}{C}H-CH_3 \\ \overset{2}{C}H-CH_3 \\ \overset{3}{C}H_3}}{\overset{3}{CH}}-\overset{CH_3}{\overset{|}{\overset{4}{CH}}}-\overset{CH_2CH_3}{\overset{|}{\overset{5}{CH}}}-\overset{CH_3}{\overset{|}{\overset{6}{CH}}}-\overset{7}{CH_2}\overset{8}{CH_3}$$

3 – (1, 2-Dimethyl propyl) — 5 – ethyl – 4, 6-dimethyl oct–1–ene)
Here, the alphabetical order of various substituents is : dimethyl propyl, ethyl and methyl respectively.

(viii) If more than one similar complex substituents are attached to the parent chain, then the prefixes bis, tris etc. are used instead of di, tri, etc. before the name of the complex substituent.
For example,



$$\overset{1}{CH_3}-\overset{CH_3}{\overset{|}{\overset{2}{CH}}}-\underset{\boxed{H_3C-\overset{1}{C}H \\ \overset{2}{C}H_3}}{\overset{3}{C}}=\underset{\boxed{\overset{1}{C}H-CH_3 \\ \overset{2}{C}H_3}}{\overset{4}{C}}-\overset{CH_3}{\overset{|}{\overset{5}{CH}}}-\overset{6}{CH_3}$$

2, 5–Dimethyl – 3, 4 – bis (1 – methyl ethyl) hex–3–ene

(e) **Alkenyl groups :** Just as alkyl groups are obtained after the *removal of one* H-atom from alkane for example,

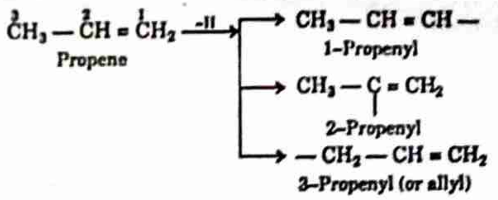
$$\underset{\text{Methane}}{CH_4} \xrightarrow{-H} \underset{\text{Methyl group}}{-CH_3}$$

$$\text{(i.e. Alkane} \xrightarrow[+yl]{-ane} \text{Alkyl)}$$

Similarly, the monovalent unsaturated groups obtained by the removal of one H-atom from an alkene are termed as alkenyl groups. They are named by replacing the terminal '*e*' of the parent alkene by '*yl*' i.e.,

$$\text{Alkene} \xrightarrow[+yl]{-e} \text{Alkenyl}$$

For example, $\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{-H} \underset{\text{Ethenyl (or vinyl)}}{-CH=CH_2}$



$$\underset{\text{Propene}}{\overset{3}{CH_3}-\overset{2}{CH}=\overset{1}{CH_2}} \xrightarrow{-H} \begin{cases} \underset{\text{1-Propenyl}}{CH_3-CH=CH-} \\ \underset{\text{2-Propenyl}}{CH_3-\underset{|}{C}=CH_2} \\ \underset{\text{3-Propenyl (or allyl)}}{-CH_2-CH=CH_2} \end{cases}$$

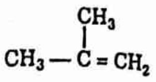
Isomerism In Alkenes

(a) **Structural Isomerism :** Except the first two members *i.e.* ethylene and propylene, all other alkenes exhibit chain isomerism as well as position isomerism. C_4H_8 (Butene)

For example, C_4H_8 exists in three structural isomeric forms :

$CH_3-CH_2-CH=CH_2$
1-Butene
Ⓐ

$CH_3-CH=CH-CH_3$
2-Butene
Ⓑ


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$
2-Methyl propene
Ⓒ

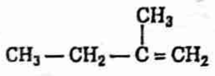
Ⓐ and Ⓑ are positional isomers

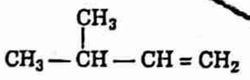
While, Ⓐ and Ⓒ; Ⓑ and Ⓒ are chain isomers.

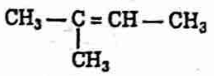
As the number of C-atoms increases, the member of possible isomeric forms increases. For example, C_5H_{10} (Pentene) exists in five structural isomeric forms :

$CH_3-CH_2-CH_2-CH=CH_2$
1-Pentene

$CH_3-CH=CH-CH_2CH_3$
2-Pentene


$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$
2-Methyl-1-butene


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH=CH_2$$
3-Methyl-1-butene


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$$
2-Methyl-2-butene

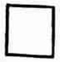
Alkenes also exhibit **ring-chain isomerism with Cycloalkanes.** For example,

$CH_3-CH=CH_2$
Propene


Cyclopropane

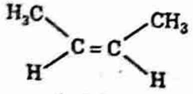
(Both have formula C_3H_6)

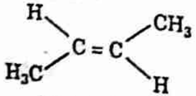
$CH_3-CH=CH-CH_3$
Butene


Cyclobutane

(Both have formula C_4H_8)

(b) **Geometrical Isomerism :** As the rotation around carbon-carbon double bond is strongly hindered, the relative positions of various groups attached to doubly bonded C–atoms gets fixed in space, thus giving rise to geometrical isomerism (or cis-trans isomerism.) The essential condition for an alkene to show geometrical isomerism is that each of the two doubly bonded C—atoms must be attached to two unlike groups. For example, 2–Butene exists in the following two forms :


cis-2-butene

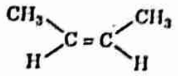
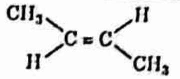
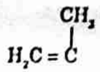
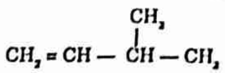
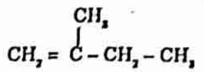
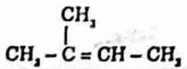

trans-2-butene

Relative Stabilities of Alkenes

- Heat of hydrogenation is an important index for determining the relative stabilities of alkenes.
- Heat of hydrogenation may be defined as the amount of heat evolved when one mole of an unsaturated compound is completely hydrogenated.
- Lesser the value of heat of hydrogenation, more stable is the alkene.

The values of heats of hydrogenation for various alkenes are listed in the table below :

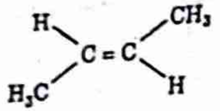
Table : Heats of hydrogenation of alkenes

Alkene	Structure	Heat of hydrogenation (kJ mol⁻¹) ΔH
Ethene	$CH_2=CH_2$	137.2
Propene	$CH_3-CH=CH_2$	125.9
1-Butene	$CH_3-CH_2-CH=CH_2$	126.8
cis-2-Butene		119.6
trans-2-Butene		115.4
2-methyl-1-propene	 $\overset{CH_3}{\overset{\vert}{H_2C=C}}$	118.8
1-Pentene	$CH_2=CH-CH_2CH_2CH_3$	125.9
3-Methyl-1-butene	 $CH_2=CH-\overset{CH_3}{\overset{\vert}{CH}}-CH_3$	126.8
2-Methyl-1-butene	 $CH_2=\overset{CH_3}{\overset{\vert}{C}}-CH_2-CH_3$	119.2
2-Methyl-2-butene	 $CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_3$	112.5

From the above table, following points may be noted :

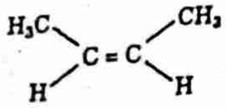
(i) Heat of hydrogenation of a trans-alkene is less as compared to that of a cis-alkene, *i.e.*, **a trans-alkene is more stable as compared to the cis-isomer. For example,** compare cis- and trans 2 –butene.

Reason : Since the two bulky groups are far apart from each other in a tra isomer, thus there is less crowding and less Vander Waal's strain in a trans-iso as compared to the cis-isomer. This accounts for the greater stability of the tra alkene.



trans-2-butene

ΔH(kJ/mole) : 115.4

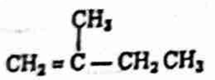


cis-2-butene

119.6

(ii) **Greater the number of alkyl groups attached to doubly bonded C–atoms, greater is the stability of the alkene.**

For example, compare :



$$CH_2 = \overset{\displaystyle CH_3}{\overset{|}{C}} - CH_2\,CH_3$$

2-Methyl-1-butene

ΔH(kJ/mole) : 119.2

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

2-Methyl-2-butene

112.5

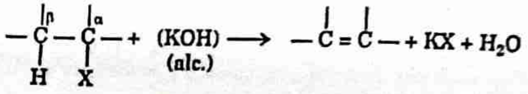
Reason : This is because greater the extent of substitution, greater is the number of α–H atoms available for hyperconjugative interaction and hence greater is the stability.

Thus, the general order of relative stabilities is

$CH_2 = CH_2 < RCH = CH_2 < R_2C = CH_2, RCH = CHR < R_2C = CHR < R_2C = CR_2$

Methods of Preparation of Alkenes

1. **By dehydrohalogenation of alkyl halides :** Alkyl halides when heated with alcohol solution of potassium hydroxide eliminate a hydrogen and a halogen atom from the adjacent C–atoms to give an alkyl halide.



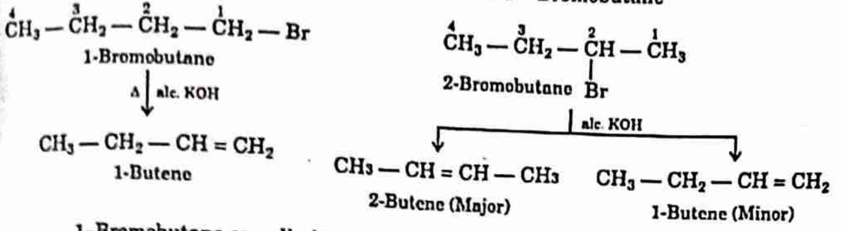
$$-\underset{H}{\overset{|\beta}{\underset{|}{C}}}-\underset{X}{\overset{|\alpha}{\underset{|}{C}}}- + \underset{(alc.)}{(KOH)} \longrightarrow -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

(X = Cl, Br or I)

e.g. $\underset{n\text{-propyl chloride}}{CH_3 - CH_2 - CH_2Cl} + \underset{(alc.)}{KOH} \longrightarrow \underset{\text{Propene}}{CH_3 - CH = CH_2} + KCl + H_2O$

- **Orientation of dehydrohalogenation in case of unsymmetrical alkenes : Saytzeff Rule** In case of unsymmetrical alkenes where the hydrogen can be eliminated from either of the adjacent C–atoms a mixture of isomeric alkenes is formed. In such cases, Saytzeff rule helps to predict the orientation of dehydrohalogenation and thus the major product. **Saytzeff rule states that in case of unsymmetrical alkenes, elimination of H–atom occurs from that C–atom which has less number of H–atoms, thus leading to the formation of highly substituted alkene as the major product.**

For example, compare 1 – Bromobutane and 2 – Bromobutane



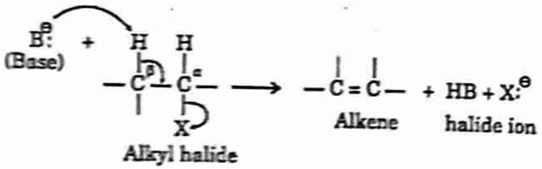
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-Br$ (1-Bromobutane) $\xrightarrow[\Delta]{alc.\ KOH}$ $CH_3-CH_2-CH=CH_2$ (1-Butene)

$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}(Br)-\overset{1}{CH_3}$ (2-Bromobutane) $\xrightarrow{alc.\ KOH}$ $CH_3-CH=CH-CH_3$ (2-Butene (Major)) + $CH_3-CH_2-CH=CH_2$ (1-Butene (Minor))

1-Bromobutane can eliminate a H–atom only in one direction, *i.e* from C–2, to give only one product, *i.e.* 1–Butene. But 2–Bromobutane is an example of unsymmetrical alkene, as it can eliminate a H–atom from two directions, *i.e.* either from C – 1 or C–3, to give 2 types of products : 2–Butene and 1 – Butene. In this case, Saytzeff rule predicts that 2–Butene will be the major product as it is more highly substituted and hence a more stable alkene as compared to 1–Butene.

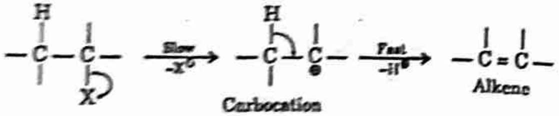
- **Mechanism :** Dehydro-halogenation can take place by either of the following two mechanisms :

(i) **E_2 mechanism (Bi-molecular elimination mechanism) :** It is a single step concerted process involving the abstraction of a H–atom from the β–C–atom by the base and simultaneous expulsion of the halide ion from the α–C–atom, leading to the formation of an alkene. The reaction involves the removal of a hydrogen and halogen atom situated in trans position with respect to each other as shown below :



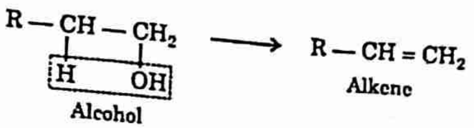
This mechanism is also termed as β–elimination or 1, 2–elimination. The mechanism follows second order kinetics as the rate of reaction depends upon the concentration of alkyl halide as well as that of the base ($\overset{\ominus}{OH}$ Ions). Most of the **Primary alkyl halides undergo dehydrohalogenation by E_2 mechanism.**

(ii) **E_1 mechanism :** It is a two step process involving the loss of a halide ion from an alkyl halide to give a carbocation in the slow, rate determining step, followed by the loss of a proton from the carbocation to give alkene in the fast second step of the mechanism,



The mechanism follows **first order kinetics** as the rate of reaction is found to depend upon the concentration of alkyl halide only. **Most secondary and tertiary alkyl halides undergo dehydrohalogenation by E_1 mechanism.**

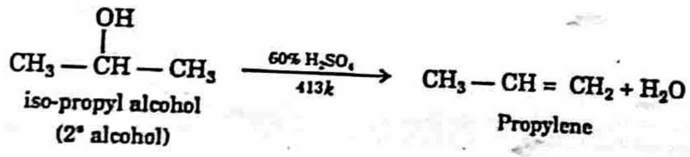
By dehydration of alochols : Alcohols upon heating with acids, undergo dehydration to give alkenes.



The relative case of dehydration of various alcohols follows the order :
Tertiary > Secondary > Primary
The reaction conditions employed thus depend upon the nature of alcohol taken. For example, while 1° alcohols undergo dehydration with 95% H_2SO_4 at 443–453 K, dehydration of 2° and 1° alcohols occurs with dil. H_2SO_4 and at lower temperatures.

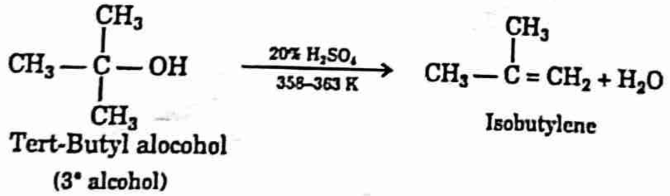
$CH_3-CH_2-OH \xrightarrow[433-443\ K]{95\%\ H_2SO_4} CH_2=CH_2+H_2O$

Ethyl alcohol (1° alcohol) — Ethylene



$CH_3-\underset{}{\overset{OH}{CH}}-CH_3 \xrightarrow[413k]{60\%\ H_2SO_4} CH_3-CH=CH_2+H_2O$

iso-propyl alcohol (2° alcohol) — Propylene

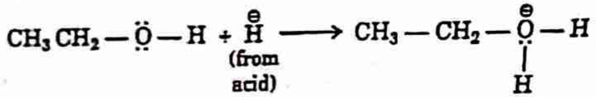


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358-363\ K]{20\%\ H_2SO_4} CH_3-\overset{CH_3}{C}=CH_2+H_2O$

Tert-Butyl alocohol (3° alcohol) — Isobutylene

- **Mechanism of dehydration :** Dehydration of alcohols to alkenes procee via the following steps :

Step 1 : Protonation of alcohol

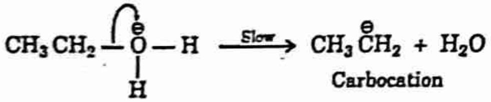


$$CH_3CH_2-\ddot{O}-H + \overset{\ominus}{H} \longrightarrow CH_3-CH_2-\overset{\ominus}{O}(H)-H$$

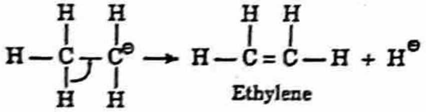
(from acid)

Protonated alcohol (Oxonium ion)

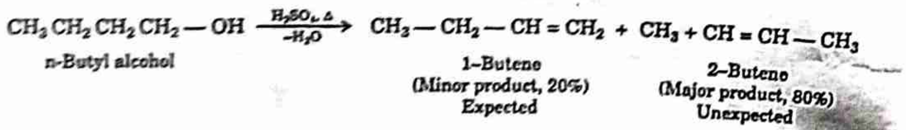
Step 2 : Loss of water to give rise to a carbocation.



Step 3 : Elimination of a proton to form alkene.

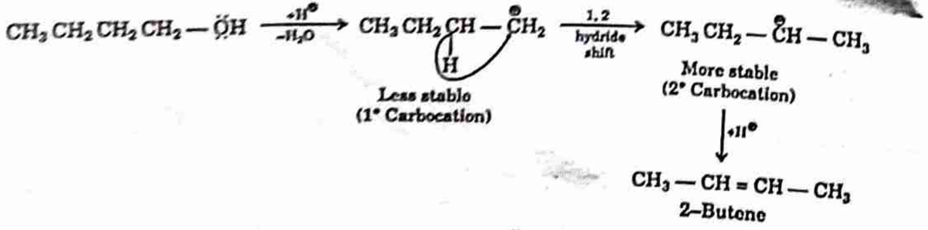


- The above mechanism suggests the formation of a carbocation as an intermediate. Now since the order of stability of carbocations follows the sequence : 3° > 2° > 1°, hence the case of dehydration also follows the sequence : 3° Alcohols > 2° Alcohols > 1° Alcohols
- Also, note that if the carbocation formed is such that it can rearrange to give rise to more stable carbocation by a 1, 2–hydride or 1,2–alkyl shift; then formation of unexpected products can be observed. For example, *n*–butyl alcohol gives the unexpected 2–Butene as the major product and not 1-Butene as expected from the structure. This may be easily explained by the rearrangement of 1° carbocation to the more stable carbocation as shown :



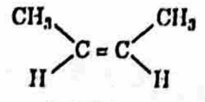
$$CH_3CH_2CH_2CH_2-OH \xrightarrow[-H_2O]{H_2SO_4,\Delta} CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3$$

n-Butyl alcohol; 1–Butene (Minor product, 20%) Expected; 2–Butene (Major product, 80%) Unexpected

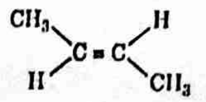


Physical Properties of Alkenes

1. **Physical State :** With the exception of ethylene which has a faint sweet odour, all other members are odourless and colourless. Alkenes containing two to four C–atoms are colourless gases, those having five to eighteen C–atoms are liquids, while alkenes having more than eighteen C–atoms are solids.
2. **Solubility :** Alkenes are insoluble in water but soluble in polar solvents like ether, CCl_4, benzene, etc.
3. **Melting Points :**
   - The melting points show a regular increase with the increase in molecular mass.
   - **Alkenes have slightly higher melting points as compared to alkanes.**
   - **Reason :** This is due to the presence of a double bond in alkenes which is more polarizable than the single bond and allows the formation of induced dipoles in alkenes, which are responsible for stronger intermolecular forces of attraction and hence higher melting points in alkenes.
   - **Trans-alkenes have higher melting points as compared to cis-alkenes.** For example,



cis-2-Butene
m.pt.= 134 K



trans-2-Butene
m.pt.= 167 K

Reason : The trans-form being more symmetrical than the cis-form, fits better into the crystal lattice, leading to close packing in the solid state. Hence, trans-alkenes have higher m.pt. as compared to the corresponding cis-isomer.

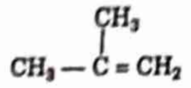
4. **Boiling Points :**

- The branched alkenes have lower boiling points than straight chain alkenes

For example,

$CH_3-CH_2-CH=CH_2$

1–Butene
B.pt.= 267 K



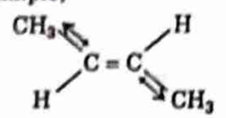
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

Isobutylene
B.pt.= 266 K

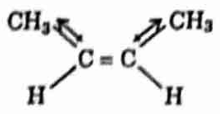
Reason : With increased branching, surface area decreases and so do the Vander Waal's forces of attraction, resulting in the lower of boiling points.

- **Cis-alkenes have higher boiling points than the corresponding trans-alkenes.**

For example,



trans-2-butene
$\mu = 0$
B.pt.= .274 K



cis-2-butene
$\mu = 0.25D$
B.pt.= 277 K

Cis-alkenes are more polar than trans-alkenes where the oppositely oriented dipoles cancel out each other. Hence, cis-alkenes have higher b.pts. than the corresponding trans-isomers.

By pyrolysis of quaternary ammonium hydroxides (Hofmann Elimination) : Quaternary ammonium hydroxides when heated to 400 *k* or above, undergo Hofmann elimination to give alkenes. The quaternary ammonium hydroxides required for the purpose are obtained by treating an amine with excess of methyl iodide (also known as exhaustive methylation) followed by reaction with moist silver oxide.

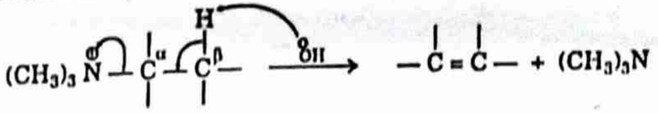
$$\underset{\text{Ethyl amine}}{CH_3CH_2-NH_2} + \underset{\substack{\text{Methyl iodide}\\ \text{(excess)}}}{3\,CH_3I} \longrightarrow [CH_3CH_2\overset{\oplus}{N}(CH_3)_3]\,I^{\ominus}$$

$$\downarrow \text{Moist } Ag_2O$$

$$\underset{\substack{\text{Ethyl trimethyl}\\ \text{amm. hydroxide}}}{[CH_3CH_2\overset{\oplus}{N}(CH_3)_3]\,\overset{\ominus}{O}H}$$

$$[CH_3CH_2\overset{+}{N}(CH_3)_3]\bar{O}H \xrightarrow{\Delta} \underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{Trimethylamine}}{(CH_3)_3N} + H_2O$$

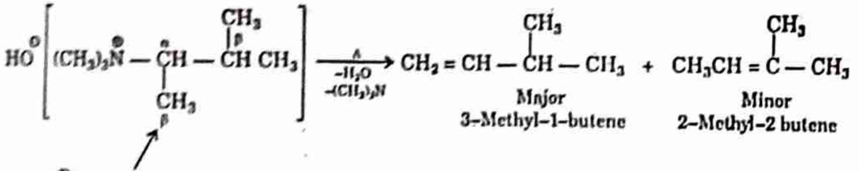
- **Mechanism :** Hofmann elimination is also an example of β –elimination reaction and involves the removal of a proton from a β-carbon w.r.t. the N-atom of the quaternary ammonium group.



In contrast to dehydro-halogenation of alkyl halides which occurs by a similar mechanism and gives rise to more substituted alkene as per Saytzeff Rule Hofmann elimination gives rise to the alkene which is least substituted.

Reason being that the base $\overset{\ominus}{O}H$ preferably abstracts a proton from the least hindered position.

For exmple,



$$\overset{\ominus}{HO}\left[(CH_3)_3\overset{\oplus}{N}-\underset{\underset{\beta}{CH_3}}{\overset{\alpha}{C}H}-\overset{\overset{CH_3}{|\beta}}{C}H\,CH_3\right]\xrightarrow[-H_2O\ -(CH_3)_3N]{\Delta}\underset{\text{3-Methyl-1-butene}}{\underset{\text{Major}}{CH_2=CH-\overset{\overset{CH_3}{|}}{C}H-CH_3}}+\underset{\text{2-Methyl-2 butene}}{\underset{\text{Minor}}{CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_3}}$$

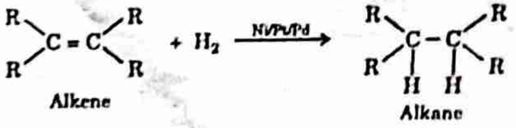
Base removes proton from this less hindered β–carbon

Chemical Reactions of Alkenes

Addition reactions across the C = C bond are the characteristic reactions of alkenes. Most of them involve attack by electrophilic reagents. Some of them are discussed as follows :

(I) **Catalytic hydrogenation – Formation of Alkenes :** Alkenes add on a molecules of hydrogen in the presence of finely divided metals such as Nickel, Platinum or Palladium, to form alkanes. The reaction is termed as hydrogenation.

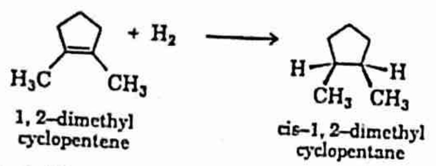
The temperature conditions employed vary with the nature of the catalyst. For example, hydrogenation in the presence of Raney Nickel is carried out at 200-250°C while, in the presence of palladium or platinum, it is carried out at room temperature.



The metal catalysts are often absorbed on support materials such as activated charcoal.

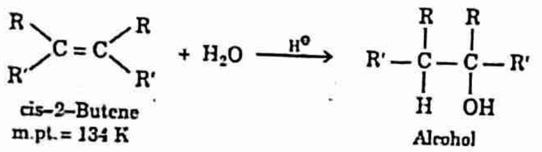
- **Mechanism of hydrogenation :** Hydrogenation of alkenes is a **heterogenous** reaction since the reactants undergo a chemical change at an interface, *i.e.*, on the surface of a solid catalyst. First, the catalyst adsorbs hydrogen on its surface. After this, complex formation occurs between the catalyst and alkene, by the overlap of vacant d–orbitals of the metal with the π electrons of the alkene. This is followed by a stepwise transfer of the H-atoms to the alkene.

The alkane so formed then diffuses away from the surface of the metal catalyst. Since both the H-atoms add on to the alkene from the same side of the molecule, therefore, hydrogenation is a syn addition process. For example, addition of hydrogen to 1,2-dimethyl cyclopentene gives rise to a cis-isomer upon catalytic hydrogenation.



(II) **Electrophilic Addition Reactions**

1. **Addition of water-formation of alcohols :** Alkenes add on a molecule of water in the presence of dilute acids to give alcohols.



For example,

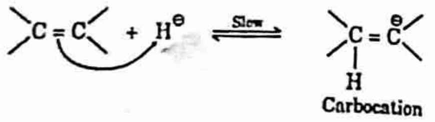
$$\underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O \xrightarrow{H^\oplus} \underset{\text{Ethyl alcohol}}{CH_3 - CH_2 - OH}$$

$$\underset{\text{Propylene}}{CH_3 - CH = CH_2} + H_2O \xrightarrow{H^\oplus} \underset{\text{Isopropyl alcohol}}{CH_3 - \underset{OH}{\underset{|}{CH}} - CH_3}$$

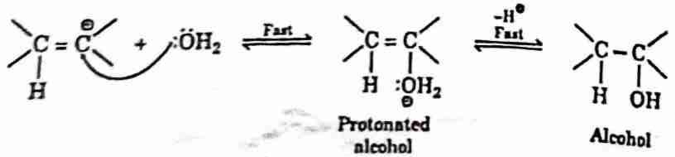
It may be noted that addition occurs in accordance with Markownikoff's Rule, which states that negative part of the reagent goes to the C–atom with less number of hydrogen atoms.

- **Mechanism :** The reaction involves electrophilic addition mechanism and occurs as follows :

Step 1 :



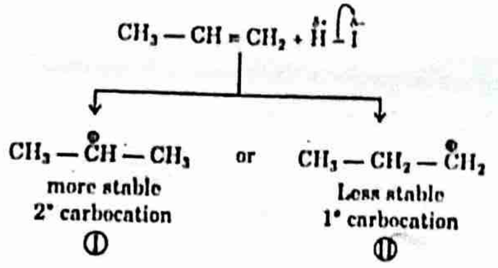
Step 2 :



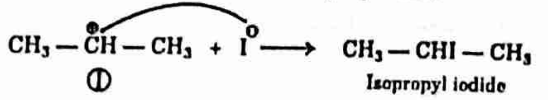
- **Markownikoff's Rule : Addition to Unsymmetrical alkenes :** Markownikoff's rule states that during addition to unsymmetrical alkenes, the negative part of the reagent goes to the C–atom with less number of hydrogens. For example, consider the addition of HI to propylene which gives two isomeric products n–propyl iodide and isoprophyl iodide of which the latter is formed in predominant amounts.

$$\underset{\text{Propylene}}{CH_3 - CH = CH_2} + HI \longrightarrow \underset{\substack{\text{Isopropyl iodide}\\ \text{(major)}}}{CH_3 - CHI - CH_3} + \underset{\substack{\text{n–Propyl iodide}\\ \text{(Minor)}}}{CH_3CH_2CH_2I}$$

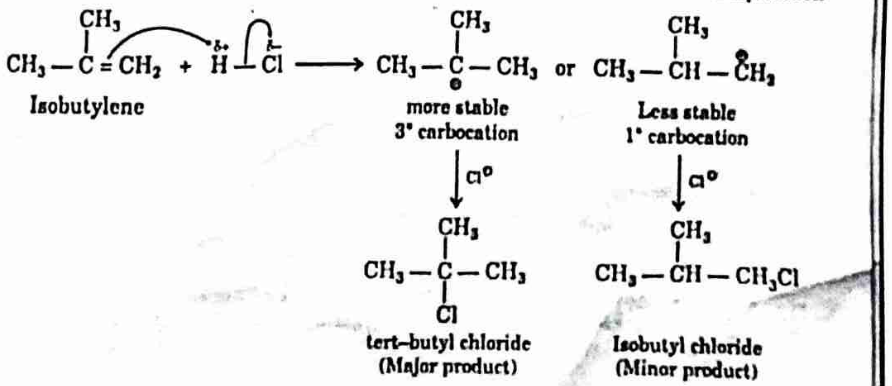
- **Theoretical Justification of Markownikoff's Rule :** The rule can be justified in terms of the ionic mechanism discussed before. The mechanism suggests the intermediate formation of a carbocation when alkene adds on a proton. Now consider the two possible carbocations that may be formed when propylene adds on a proton.



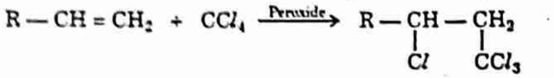
As seen out of the two possible carbocations, (I) being more stable is formed in preference to carbocation (II). Further reaction of this preferred carbocation with iodide ion gives isopropyl iodide as the major product.



Thus, Markownikoff's addition is governed by the relative stabilites of carbocations. Thus, a modern version of the rule has been put forward which states that : Addition to the ethylenic double bond involves the formation of the more stable carbocation. Similarly, addition of HCl to isobutylene gives tertbutyl chloride as the main product.

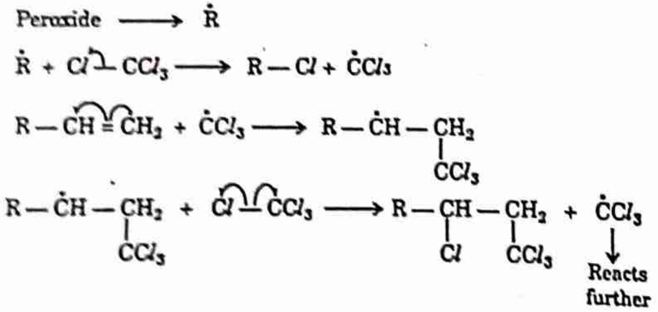


1. **Addition of Free Radicals :** It has already been discussed that peroxide effect i.e. Anti-Markownikoff's addition of HBr to alkenes in the presence of peroxides, occurs by a free radical mechanism.
Another example involving the free radical mechanism is addition of CCl_4 across the double bond. This addition also occurs in the presence of a peroxide.



$$R-CH=CH_2 + CCl_4 \xrightarrow{\text{Peroxide}} R-\underset{Cl}{CH}-\underset{CCl_3}{CH_2}$$

Mechanism :



$$\text{Peroxide} \longrightarrow \dot{R}$$

$$\dot{R} + Cl-CCl_3 \longrightarrow R-Cl + \dot{C}Cl_3$$

$$R-CH=CH_2 + \dot{C}Cl_3 \longrightarrow R-\dot{C}H-\underset{CCl_3}{CH_2}$$

$$R-\dot{C}H-\underset{CCl_3}{CH_2} + Cl-CCl_3 \longrightarrow R-\underset{Cl}{CH}-\underset{CCl_3}{CH_2} + \underset{\substack{\downarrow \\ \text{Reacts} \\ \text{further}}}{\dot{C}Cl_3}$$

8. **Hydroboration – Oxidation of Alkenes :** Alkenes react with diborane $(BH_3)_2$ to give alkyl boranes (a process known as hydroboration).
The alkyl boranes upon oxidation with an alkaline solution of hydrogen peroxide give rise to alcohols. The overall result of the reaction is addition of water to alkenes as per Anti-Markownikoff's addition to give alcohols.
Hydroboration occurs in three steps to first give a monoalkyl borane, then a dialkyl borane and finally a trialkyl borane. For example, consider the addition of diborane to ethylene

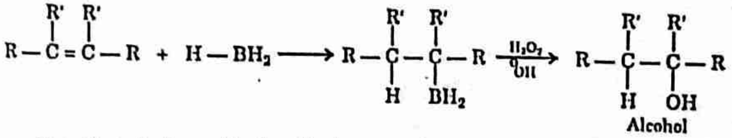
$$\underset{\text{Ethylene}}{CH_2=CH_2} + \underset{\text{Diborane}}{(BH_3)_2} \longrightarrow \underset{\text{Ethyl borane}}{CH_3CH_2BH_2} \xrightarrow{CH_2=CH_2}$$

$$\underset{\text{Diethylborane}}{(CH_3CH_2)_2BH} \xrightarrow{CH_2=CH_2} \underset{\text{Triethyl borane}}{(CH_3CH_2)_3B}$$

The borane so formed upon oxidation gives rise to alcohols.

$$(CH_3CH_2)_3B + 3H_2O_2 \xrightarrow{^{\ominus}OH} \underset{\text{Ethyl alcohol}}{3\,CH_3CH_2OH} + \underset{\text{Boric acid}}{H_3BO_3}$$

In general, the reaction may be represented as follows :



$$R-\overset{R'}{C}=\overset{R'}{C}-R + H-BH_2 \longrightarrow R-\underset{H}{\overset{R'}{C}}-\underset{BH_2}{\overset{R'}{C}}-R \xrightarrow[^{\ominus}OH]{H_2O_2} \underset{\text{Alcohol}}{R-\underset{H}{\overset{R'}{C}}-\underset{OH}{\overset{R'}{C}}-R}$$

Note that during oxidation the boron part gets replaced by – OH group to give alcohol as per Anti-Markownikoff's addition.
For example,
Consider hydroboration – oxidation of propylene which gives

$$\underset{\text{Propylene}}{CH_3-CH=CH_2} \xrightarrow{(BH_3)_2} \underset{n\text{–propyl borane}}{CH_3-CH_2CH_2BH_2} \xrightarrow{CH_3-CH=CH_2} \underset{\text{Di-}n\text{–propyl borane}}{(CH_3CH_2CH_2)_2BH}$$

$$\xrightarrow{CH_3-CH=CH_2} \underset{\substack{\text{Tri-n–propyl} \\ \text{Borane}}}{(CH_3CH_2CH_2)_3B} \xrightarrow[^{\ominus}OH]{H_2O_2} \underset{\substack{\text{n–propyl alcohol} \\ \text{(Anti-Markownikoff Addition Product)}}}{CH_3CH_2CH_2OH}$$

$$\text{or simply } \underset{\text{propylene}}{CH_3-CH=CH_2} \xrightarrow[(ii)\,H_2O_2/^{\ominus}OH]{(i)\,(BH_3)_2} CH_3CH_2CH_2OH$$

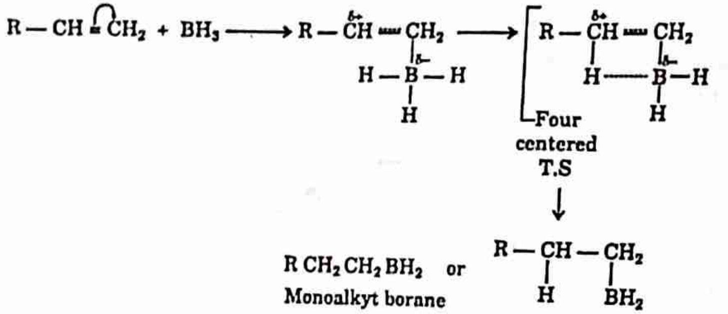
- **Mechanism of hydroboration oxidation :**

Step 1. Hydroboration : Diborane behaves like a dimer of borane $(BH_3)_2$. In borane BH_3, the boron atom is electrophilic, i.e., electron-deficient as it has six electrons in its valence shell. The π-electrons of the alkene attack the electrophilic borane with the boron atom getting attached to the less substituted doubly bonded C–atom. This leads to the development of partial negative charge on the boron atom. The attachment of born to the **less substituted C–atom** is favoured because of two reasons :

(i) The less substituted C–atom is sterically less crowded and can be easily approached by the boron atom.

(ii) The attachment of boron to the less substituted c–atom leads to the development of the partial positive charge on the more substituted C-atom, thus leading to greater stability of the transition state. This is followed by the transfer of hydrogen from the B – H bond of the borane along with its electrons to the c–atom carrying partial positive charge. The product so formed is a monoalkyl borane.

The step may be shown as follows :

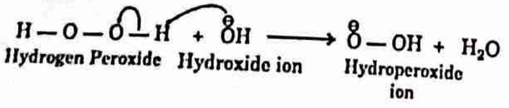


$$R-CH=CH_2 + BH_3 \longrightarrow R-\overset{\delta+}{C}H\cdots \underset{\underset{H}{|}}{\overset{|\delta-}{H-B-H}} \longrightarrow [\ldots] \longrightarrow R\,CH_2CH_2BH_2$$

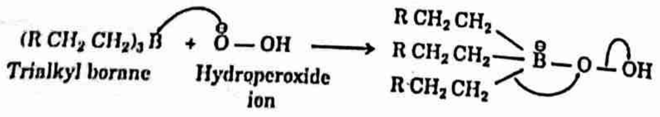
The steps may be repeated by the transfer of H of B–H bond of $R\,CH_2\,CH_2\,BH_2$ to another molecule of an alkene to give a dialkyl borane having the formula $(R\,CH_2\,CH_2)_2\,BH$. Similarly, another transfer of H from B – H bond of dialkyl borane to another molecule of alkene may give a trialkyl borane with the formula $(R\,CH_2\,CH_2)_3\,B$.

It may be noted here that unlike other ordinary electrophilic addition reactions, hydro boration does not involve the intermediate formation of a carbocation. This is evidenced by the fact that hydroboration oxidation never leads to rearranged products.

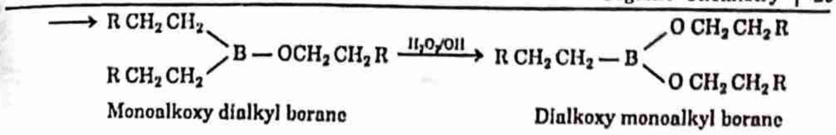
Step 2. : Oxidation of Alkylboranes : Oxidation involves nucleophilic attack of the hydroperoxide ion $(\overset{\ominus}{O}OH)$ on the electrophilic Boron atom of a trialkyl borane as shown below :



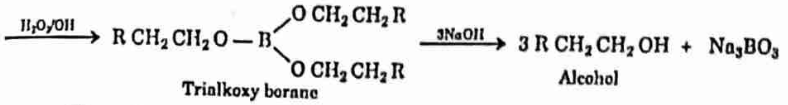
$$H-O-O-H + \overset{\ominus}{O}H \longrightarrow \overset{\ominus}{O}-OH + H_2O$$



$$(R\,CH_2\,CH_2)_3\,B + \overset{\ominus}{O}-OH \longrightarrow (R\,CH_2\,CH_2)_3\overset{\ominus}{B}-O-OH$$

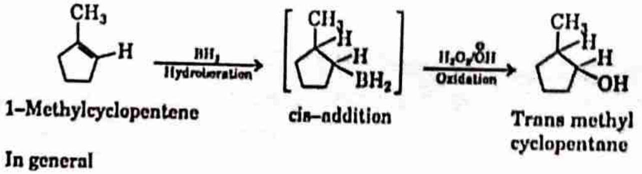


$$\longrightarrow (R\,CH_2\,CH_2)_2B-OCH_2\,CH_2\,R \xrightarrow{H_2O_2/OH} R\,CH_2\,CH_2-B(O\,CH_2\,CH_2\,R)_2$$

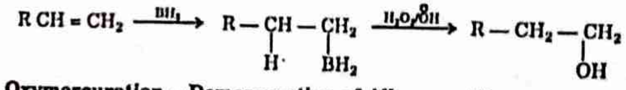


$$\xrightarrow{H_2O_2/OH} R\,CH_2\,CH_2\,O-B(O\,CH_2\,CH_2\,R)_2 \xrightarrow{3NaOH} 3\,R\,CH_2\,CH_2\,OH + Na_3BO_3$$

The net result is addition of water to an alkene as per Anti-Markownikoff's rule : During oxidation, the B-atom is replaced by an –OH group. **The above reaction is an example of a regioselective reaction as the hydroxyl group always appears at the less substituted c–atom.** For example,

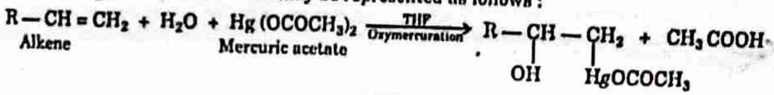


In general

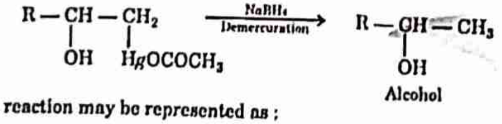


$$R\,CH=CH_2 \xrightarrow{BH_3} R-\underset{\underset{H}{|}}{C}H-\underset{\underset{BH_2}{|}}{C}H_2 \xrightarrow{H_2O_2/\overset{\ominus}{O}H} R-CH_2-\underset{\underset{OH}{|}}{C}H_2$$

9. **Oxymercuration – Demercuration of Alkenes :** Alkenes react with mercuric acetate in aqueous THF (tetrahydrofuran) solution to give hydroxy mercurial compounds. This is known as **oxymercuration.** This is followed by the reduction of the mercurial compound with $NaBH_4$ (sod. boro-hydride) reduction of the mercurial compound with $NaBH_4$ when the mercuri-acetate group gets replaced by hydrogen to give alcohols. This step is known as **demercuration.** In general, the reaction may be represented as follows :

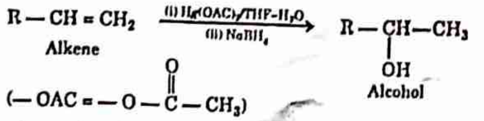


$$R-CH=CH_2 + H_2O + Hg(OCOCH_3)_2 \xrightarrow[Oxymercuration]{THF} R-\underset{\underset{OH}{|}}{C}H-\underset{\underset{HgOCOCH_3}{|}}{C}H_2 + CH_3COOH$$



$$R-\underset{\underset{OH}{|}}{C}H-\underset{\underset{HgOCOCH_3}{|}}{C}H_2 \xrightarrow[Demercuration]{NaBH_4} R-\underset{\underset{OH}{|}}{C}H-CH_3$$

Overall the reaction may be represented as :



$$R-CH=CH_2 \xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OAC)_2/THF-H_2O} R-\underset{\underset{OH}{|}}{C}H-CH_3$$

$$(-OAC = -O-\overset{\overset{O}{\|}}{C}-CH_3)$$

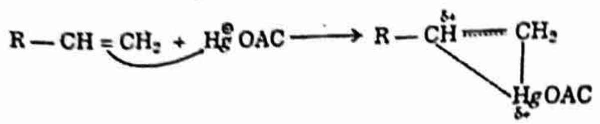
As seen above, the reaction is **highly regioselective and gives alcohols in accordance with Markownikoff's Rule**

300

- **Mechanism of Oxymercuration - Demercuration**

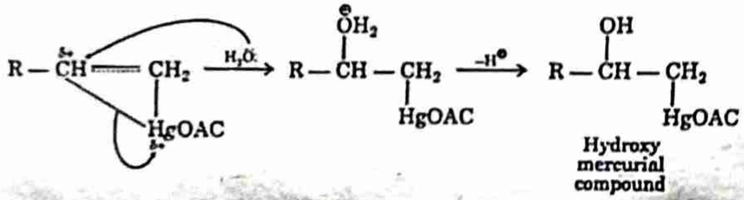
Step 1. : Oxymercuration

(a) The first step involves electrophilic attack by mercury species upon the dou bond to form mercury bridged carbocation.

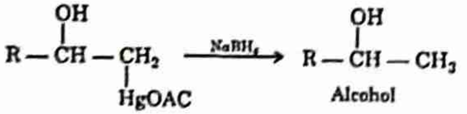


It is to be noted that the Hg species will attack the less-mercury bridged carbocation substituted doub bonded c–atom to the alkene.

(b) The mercury bridged carbocation then undergoes nucleophilic attack by wate to form hydroxy mercurial compound

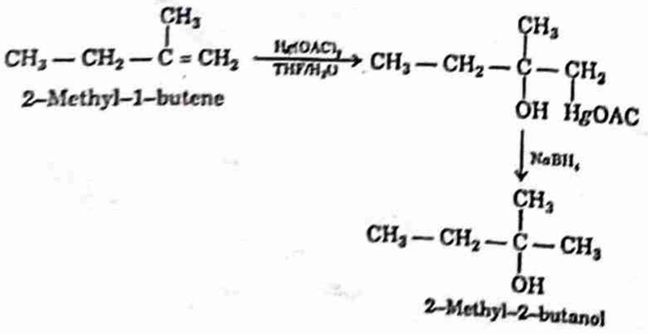


Step 2. Demercuration : The hydroxy mercurial compound upon reduction wit NaBH$_4$ undergoes demercuration to give alcohol as the final product.



From the mechanism, it is seen that as the Hg species gets attached to the less substituted doubly bonded C-atom of the alkene, the –OH group comes to the more substituted doubly bonded c–atom. Thus, giving rise to an alcohol in accordance with Markownikoff's rule.

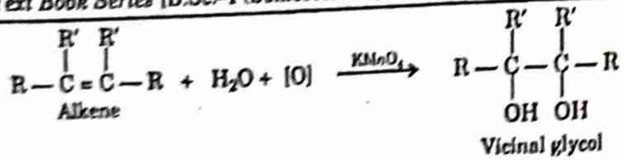
For example,



12. **Oxidation Reactions :** Certain oxidation reactions involve simple addition to the double bond, while others result in the cleavage of the double bond. Both types are being discussed below :

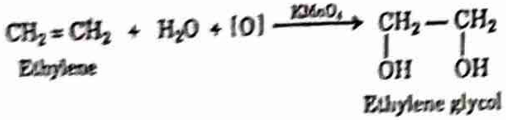
1. **Oxidation with cold dilute aqueous solution of potassium permanganate (KMnO$_4$).**

When treated with cold dilute aqueous KMnO$_4$ solution, alkenes undergo **cis-hydroxylation** (*i.e.* a hydroxy groups is added to each of the doubly bonded c-atoms from the same side of the double bond) to give **Vicinal glycols.**

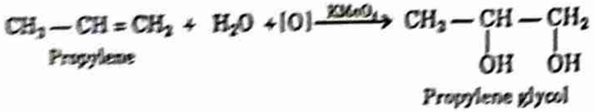


$$\underset{\text{Alkene}}{R-\overset{R'}{\underset{}{C}}=\overset{R'}{C}-R} + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{Vicinal glycol}}{R-\overset{R'}{\underset{OH}{C}}-\overset{R'}{\underset{OH}{C}}-R}$$

For example

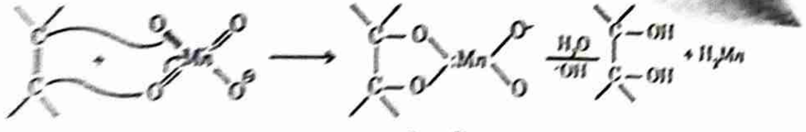


$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{Ethylene glycol}}{\underset{OH}{CH_2}-\underset{OH}{CH_2}}$$



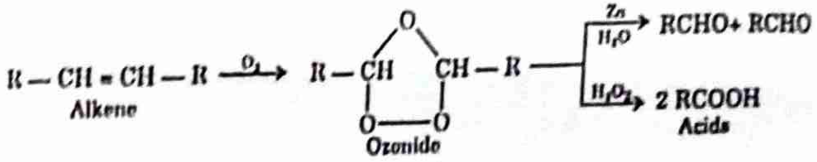
$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{Propylene glycol}}{CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}}$$

- **Baeyer's Test :** Since during the above oxidation, the pink colour of $KMnO_4$ is discharged, therefore, this may be used as a diagnostic test for the identification of a carbon-carbon double bond in a molecule. This test is called as the Baeyer's Test.
- **Mechanism :** Mechanism involves the formation of a cyclic manganate ester which upon hydrolysis gives rise to a glycol.

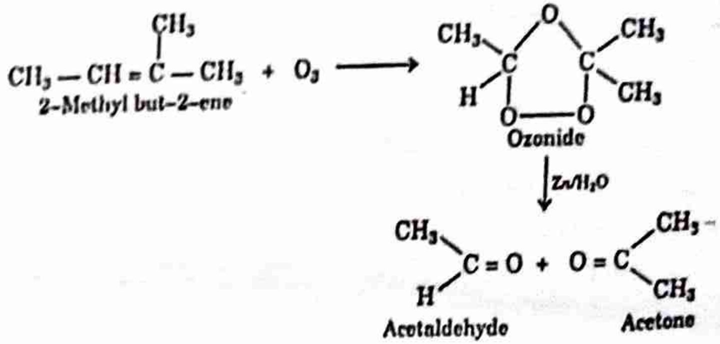


A cyclic manganate ester

5. **Ozonolysis :** It is an important reaction of alkenes which results in the cleavage of carbon carbon double bond of an alkene.
The reaction involves addition of ozone across the double bond of an alkene to form an ozonide. This ozonide upon decomposition with zinc dust and water gives rise to aldehydes or ketones, depending upon the structure of alkene. However, ozonide when treated with hydrogen peroxide (H_2O_2) gives rise to acids i.e.



For example,



QUESTIONS FOR PRACTICE

1. Name the following olefins according to IUPAC system
   (a) $CH_2 = CH_2$
   (b) $CH_3 CH = CH_2$
   (c) $CH_3 CH_2 CH = CHCH_2CH_3$
   (d) $CH_3 (CH_2)_3 C = CH_2$
   (e) $(CH_3)_2 C = C(CH_3)_2$
   (f) $(CH_3)_3 CCH = CHC (CH_3)_3$ (K
2. (a) Give the products and explain the mechanism involved in the following
   (i) Propene $\xrightarrow[\text{room temperature}]{Cl_2}$
   (ii) Propene $\xrightarrow[500°C]{Cl_2}$
   (b) Complete the following reactions :
   (i) But-2-ene + $CH_2N_2 \xrightarrow{h\nu}$
   (ii) Propene + $B_2H_6 \xrightarrow{H_2O_2/\overset{\ominus}{O}H}$
   (iii) $C_6H_5CH = CH_2 \xrightarrow[\text{Zn dust}]{O_3}$
   (iv) $CH_3 - CH = CH_2 \xrightarrow[\text{Peroxide}]{HBr}$ (M
3. Explain briefly the following
   (a) Regio selectivity alcohol dehydration
   (b) Relative stability of alkenes on the basis of hyperconjugation. (K
   (c) Substitution at allylic and vinylic positions of alkenes.
4. Write short notes on the following :
   (a) Saytzeff rule (K
   (b) Hofmann elimination
   (c) Industrial applications of ethylene and propene.
   (d) Peroxide effect
5. (a) Convert the following
   (i) Propene into Propan–1–ol
   (ii) Ethene into methanal

   (b) Explain the following in brief :
   (i) Why dipole moment of trans–But–2–ene is zero?
   (ii) Why is the boiling point of neopentane lower than *n*–pentane? (K.U.K. 2005)
6. Discuss the mechanism of the following :
   (i) Dehydration of alcohols
   (ii) Formation of halohydrin
   (iii) Free radical polymerisation of alkenes
   (iv) Dimerisation of isobutylene.
7. Explain briefly the mechanism of dehydrohalogenation of alkyl halides. Explain the orientation and ease of formation of alkenes. (K.U.K. 2002)
8. (a) Describe the preparation of alkene by dehydration of alcohol, giving E_2, mechanism
   (b) What happens when isobutylene reacts with
   (i) Chlorine water (ii) HBr
   (c) Explain free-radical polymerization with a suitable example. (M.D.U. 2003)
9. (a) Explain the mechanism of Markownikoff's addition to alkene with suitable examples.
   (b) Discuss the mechanism and relative reactivities of dehydration of alcohols. (K.U.K. 2003)
10. (a) What is anti Markownikoff's rule? Give its mechanism.
    (b) An alkene on ozonolysis gave two molecules of propanone. Identify the given structure and write equations involved.
    (c) What happens when propene is treated with :
    (i) Cold (1%) aqueous alk. solution of $KMnO_4$?
    (ii) Chlorine at high temperature 773K?
    (iii) Peroxide as initiator of Zeigler–Natta catalyst? (M.D.U. 2004)
11. Discuss the substitution of allylic and vinylic positions of alkenes by taking suitable examples. (K.U.K. 2004)
12. (a) Discuss the following mechanism : (M.D.U. 2007)
    (i) Addition of Br_2 to ethene
    (ii) Addition of Diborane to propene
    (b) What happens when
    (i) 1, 2-Dibromo propane is heated with zinc.
    (ii) Ethene reacts with cold alk. $KMnO_4$ soln.
    (c) Convert the following : (K.U.K. 2006)
    (i) Ethene into epoxyethane
    (ii) Propene into 1-Bromopropane
    (iii) Ethene into 1,2-Dibromoethane (K.U.K. 2011)
13. Write brief notes on (M.D.U. 2007)
    (i) Addition of carbene to alkene
    (ii) Dehalogenation of dihalides
14. (a) Give the cyclohalonium mechanism of addition of bromine to ethene
    (b) Complete the equations.
    (i) $CH_3 - CH = CH_2 + Cl_2 \xrightarrow{773\,K}$ (K.U.K. 2007)
    (ii) 1, 4-Dibromobutane + Zn $\longrightarrow$
    (c) Explain the alternation effect with reference to melting point of *n*–alkanes.

2

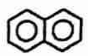
Arenes & Aromaticity

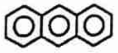
Introduction :

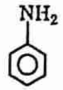
In the earlier times, the term aromatic was used for those compounds obtained from natural sources which had a characteristic smell. (Greek aroma = fragrant smell). The properties of these compounds were quite different from those of aliphatic compounds; instead they were found to closely resemble those of benzene. Later, a large number of compounds were identified which did not possess any characteristic odour but their properties resembled to those of benzene. Thus, the term aromatic is now applied to **those compounds which resemble benzene in their chemical properties.**

The characteristic properties of aromatic compounds which distinguish them from aliphatic compounds are termed as **aromatic properties**; like, aromatic compounds undergo substitution rather than addition reactions which are characteristic of unsaturated aliphatic compounds. Also, aromatic compounds are resistant to the action of oxidising agents and are thermally stable.

- **Classification :** Aromatic compounds are broadly classified into two categories :
  (a) Benzenoid aromatics
  (b) Non-benzenoid aromatics
  (a) **Benzenoid aromatics :** Those aromatic compounds which contain at least one benzene ring. For example, naphthalene, anthracene, anilines phenol are all benzenoid aromatics.


Naphthalene


Anthracene


Aniline


Phenol

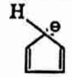
  (b) **Non-Benzenoid aromatics :** Those compounds which do not contain a benzene ring but still exhibit aromatic behaviour. For example, pyrrole, furan, thiophene, cyclopropenyl cation, cyclopentadienyl anion are all non-benzenoid aromatics.


Pyrrole

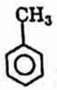

Furan


Thiophene

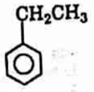

Cyclopropenyl cation

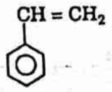

Cyclopentadienyl anion

- **Arenes :** In general, all aromatic hydrocarbons are known as arenes. The parent aromatic hydrocarbon is benzene. Arenes include all the alkyl, alkenyl or alkynyl substituted benzene compounds. The term also includes condensed aromatic hydrocarbons containing two, three or more benzene rings linked together, like, naphthalene, anthrace, biphenyl etc.


Toluene


p-Xylene


Ethyl benzene

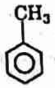

Styrene
(Vinyl benzene)

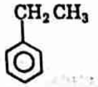
Nomenclature of Benzene Derivatives :

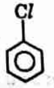
The word root for nomenclature of all benzene derivatives is **benzene.**

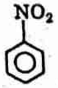
(a) **Nomenclature of monosubstituted Benzenes**

(i) The mono substituted benzenes are named by prefixing the name of the substituent before the word root. For example,

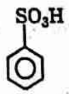

Methyl benzene


Ethyl benzene


Chloro benzene

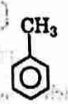

Nitro benzene

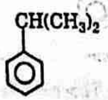
(ii) In some case the name of the substituent is written after the word root. For example,

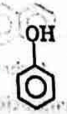

Benzene sulphonic acid


Benzene diazonium chloride

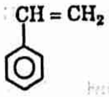
(iii) Many monosubstituted derivatives are known by their special names. For example,

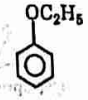

Toluene


Cumene

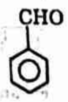

Phenol


Aniline


Styrene


Phenetole

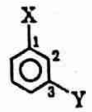

Anisole

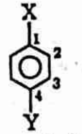

Benzaldehyde

(b) Nomenclature of monosubstituted benzene derivatives

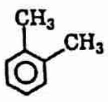
(i) Three isomeric forms are possible for disubstituted benzenes which are known as **ortho** (1, 2); **meta** (1, 3); **para** (1, 4) depending upon the relative position of the substituents.
Note that the use of **ortho, meta** and **para** is exclusively reserved for disubstituted benzenes and cannot be used for cyclohexanes or other ring systems.

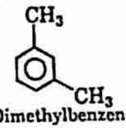

ortho (o–)
(1,2)


meta (m–)
(1,3)

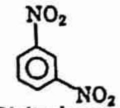

para (p–)
(1,4)

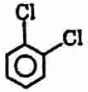
(ii) When two similar substituents are attached to the benzene ring, the prefix di is used before the name of the substituent and their relative positions are specified either by numbering or by the symbols 0, – *m*-orp–,
For exmaple,


1–2–Dimethylbenzene
(or o–Xylene)


1–3–Dimethylbenzene
(or *m*–xylene)

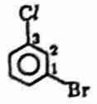

1,4–dimethyl
benzene
(or *p*–Xylene)

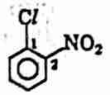

1,3–Dinitro benzene
or
m–Dinitro benzene


1,2–Dichloro benzene
or
o–Dichloro benzene

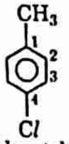
(iii) When the two substituents attached to benzene ring are different, then the names of the substituents are arranged alphabetically and the numbering is done in such a manner that the substituent which comes first in alphabetical order gets the lowest number,

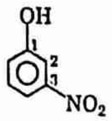
For example,

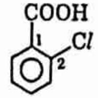

1–Bromo–3– chloro benzene
or
m–Bromo chloro benzene


1–Chloro–2–nitro benzene
or
o–chloro nitro benzene

(iv) If one of the groups imparts a special name to the compound, then the name of the other group is prefixed to the special name.
For example,

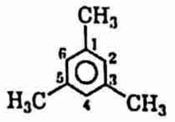

4–Chloro toluene
or
p–chloro toluene

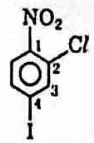

3–Nitrophenol
or
m–Nitrophenol

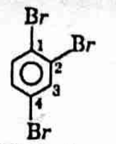

2–Chlorobenzoic acid
or
o–Chlorobenzoic acid

(c) Nomenclature of tri-and higher poly-substituted benzene derivatives :

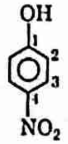
(i) The position of the substituents is indicated by membering which is done as per the lowest set of locants rule. For example,

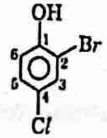

1, 3, 5– Tri methyl benzene
(or Mesitylene)

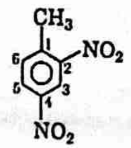

2–Chloro–4–iodo
nitro benzene


1, 2, 4–Tribromobenzene
& not
1, 3, 5–tribromobenzene

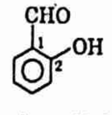
(ii) If one of the substituents imparts a special name to the compound, then the numbering of the ring starts from that carbon.
For example,

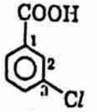

4–Nitrophenol
or
p–Nitrophenol


2–Bromo–4–Chlorophenol

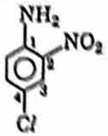

2, 4–Dinitrotoluene

(iii) When different functional groups are attached to the benzene ring, then the numbering with the principal functional group.
For example,


o–hydroxy benzaldehyde
(also known as
salicylaldehyde)

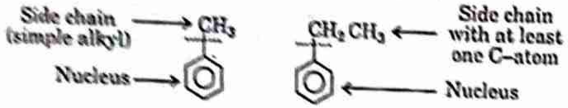

3–Chloro benzoic acid
or
m–Chloro benzoic acid


2–Bromo–4–hydroxy benzene sulphonic acid

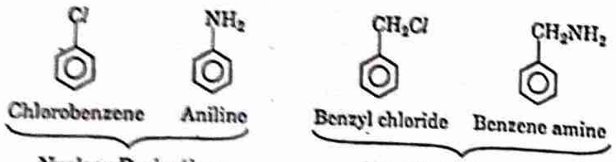

4–Chloro–2–nitro aniline

Aromatic Nucleus, the Side Chain and the Aryl Group

- **Aromatic Nucleus :** The aromatic nucleus refers to the aromatic ring of six carbon atoms in benzene and its derivatives.
- **Side Chain :** Any alkyl group or any other substituent with at least one C-atom linked to the aromatic nucleus is known as side chain.



- Note that functional groups like $-NO_2$, $-CHO$, $-COOH$, $-NH_2$, $-Cl$, $>C=O$ etc. directly attached to benzene ring do not constitute a side chain.
- Compounds in which the functional group is directly attached to the benzene ring are called **nuclear derivatives** and the compounds in which the functional group is present in a side chain are called **side chain derivatives.** For example,



Chlorobenzene Aniline Benzyl chloride Benzene amine

Nuclear Derivatives Side Chain Derivatives

Aromaticity

- Certain characteristic properties distinguish benzene and some other compounds from aliphatic compounds. Such characteristic properties define **aromaticity** or **aromatic character.** These are listed as follows :
  (a) Even though their molecular formulae suggest a high degree of unsaturation, yet they **resist addition reactions** characteristic of aliphatic unsaturated compounds. Instead aromatic compounds **undergo electrophilic substitution reactions.**

(b) They are **unusually stable compounds** as evident from their **low heats of combustion and hydrogenation.**

(c) They are **cyclic compounds** containing five, six or seven membered rings.

(d) **The rings present in their molecules are** generally flat or so.

Initially, aromaticity was thought to be only associated with those compounds which contain a benzene ring in their structure (**called benzenoids**). Later on many hetero cyclic compounds and many other cyclic compounds which do not contain only benzene ring are also found to be aromatic (called **non-benzenoids**).

- **Huckel's Rule**

Eric Huckel gave the most satisfactory explanation of aromaticity. This is known as the $(4n + 2)\,\pi$ rule.

According to this rule, for a compound to be aromatic, it must fulfil the following requirements :

(a) It must have a planar ring structure.

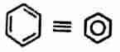
(b) It must have a cyclic delocalised π electron clouds above and below the plane of the entire ring.

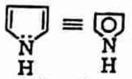
(c) The π-electron cloud must contain a total of $(4n + 2)\,\pi$ electrons where $n = 0, 1, 2, 3$ ..... etc.)

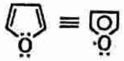
Thus, as discussed above for a compound to aromatic, it is not necessary for it to contain a benzene ring. The essential requirement for aromaticity is the presence of a flat ring (benzenoid or not) and a cyclic delocalised π electron clouds lying above and below the plane of the ring with a total of $(4n + 2)\,\pi$ electrons.

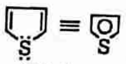
Some examples of aromatic systems :

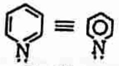
(a) **Mono cyclic systems**


Benzene


Pyrrole

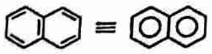

Furan

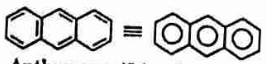

Thiophene


Pyridine

All the above aromatic compounds contain a total of 6π electrons. The heterocyclic compounds are examples of non-benzenoid aromatics. In case of pyrrole, furan and thiophene, the heteroatom donates two electrons to the π-electron could while in pyridine the heteroatom, i.e., N-atom donates as single electron to the π-cloud.

(b) **Polycyclic Systems :** Though the Huckel's rule was essentially developed for monocyclic systems, the rule is also applicable to some polycyclic systems. For example,

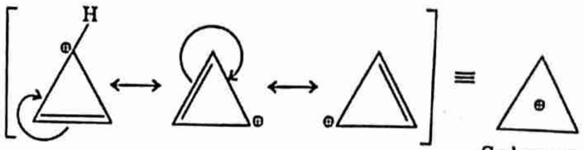

Naphthalene (10 π electrons)


Anthracene (14 π electrons)

(c) **Aromatic Ions :** There are certain ions which possess stabilities characteristic of aromatic compounds.

A few of them are discussed below :

(i) **Cyclo propenyl cation :** It satisfies Huckel's rule as it has 2π-electrons $(4n + 2)\,\pi$ with $n = 0$.

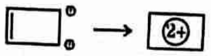


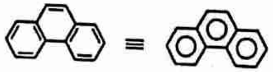
Cyclopropenyl cation

It is to be noted that cyclopropene which also contains 2π electrons, is not aromatic since the 2π-electrons are not delocalised over all the three C-atoms.

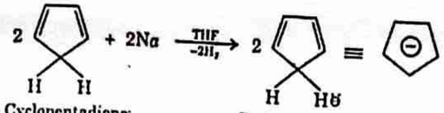

Cyclopropene

(ii) **Cyclobutadienyl dication :** They are also non-benzenoid aromatic compounds. They are represented as follows :




Phenanthrene
14 π electrons

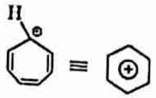
(iii) **Cyclopentadienyl anion :** Cyclopentadienyl cation contains 6π electrons and is aromatic. The ion is formed by the reaction of 1, 3 – cyclopentadiene with sodium metal.



Cyclopentadiene (Non aromatic)

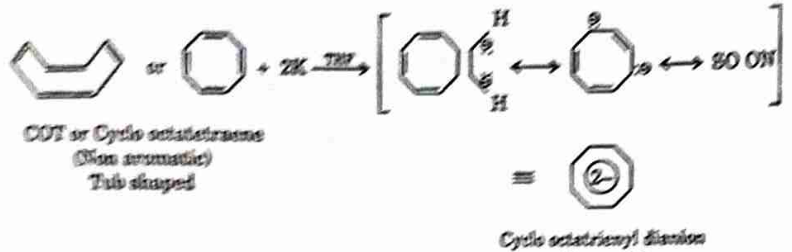
Cyclopentadienyl anion (aromatic)

(iv) **Cycloheptatriemyl cation (or Tropylium ion) :** Tropylium ion has 6π-electrons delocalised over seven C-atoms and is shown below. Here the carbon carrying positive charge does not contribute any electron to the π-cloud.



Cycloheptatrienyl cation or Tropylium ion

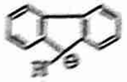
(v) **Cyclooctatrienyl dianion :** The dianion is derived by the reaction of cyclooctatetraene which is a tub-shaped molecule, with potassium metal in THF. The dianion is aromatic and has 10π electrons.



Cyclo octatrienyl dianion
(Aromatic)

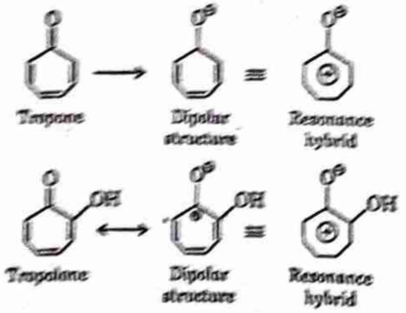
(vi) **Cyclo nonatetraenyl anion :** The anion is aromatic with 10 π-electrons

(vii) **Fluorene anion :** The fluorene anion has 14π-electrons and is aromatic.



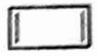
Fluorene anion

(viii) **Tropone and Tropolone :** Their dipolar structures have 6π electrons and are aromatic.



- **ANNULENES :** Annulenes are completely conjugated monocyclic compounds containing even number of C-atoms in their molecules. Their general formula is
  $(CH = CH)_n$
  They are generally named by writing the ring size in bracket followed by the word **'annulene'. For example, benzene may be referred to as [6] annulene and so on.**

Benzene
[6] Annulene



Cyclobutadiene
[4] Annulene

Cyclooctatetraene
[8] Annulene

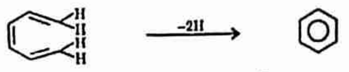
A number of large ring annulenes have also been synthesised. For example,


[10] Annulene


[12] Annulene.

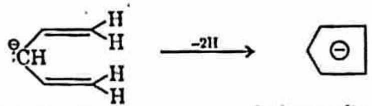

[18] Annulene

(i) **Aromatic Systems : The cyclic systems whose π-electron energy is less than that of the corresponding open chain systems, are said to be aromatic.** The presence of delocalised π electron cloud leads to the stabilisation of aromatic compounds. For example,



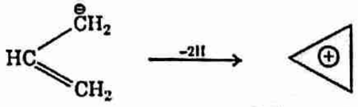
1, 2, 5–Hexatriene
Acyclic
6π–electrons

Benzene cyclic
Cyclic 6π electron cloud
has greater delocalisation
energy or lesser π–electron energy
∴ Aromatic



Pentadienyl anion
6π–electrons

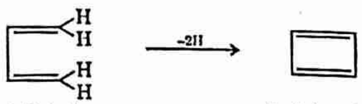
Cyclopentadienyl anion
cyclic 6π–electron cloud
has lesser π–electron energy.
∴ Aromatic



Allyl cation
2π–electrons

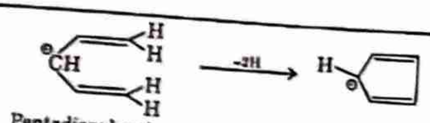
Cyclopropenyl cation
cyclic 2π–electron cloud
has lesser π–electron energy.
∴ Aromatic

(ii) **Anti-Aromatic Systems : The cyclic systems whose π-electron energy is greater than that of the corresponding open chain systems, are said to be anti-aromatic.** In other words, the formation of delocalised cyclic π-electron cloud leads to the destabilisation of anit-aromatic compounds. For example,



1, 3–Butadiene
4π–electrons

Cyclo butadiene
cyclic 4π electron cloud
has lesser delocalisation energy
or greater π–electron energy
∴ Anti–Aromatic



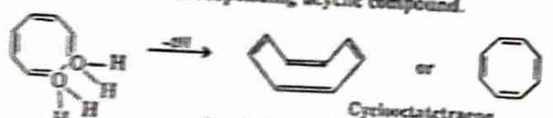
Pentadienyl cation
4π–electrons

Cyclopentadienyl cation
cyclic 4π–electron cloud
has greater π–electron energy.
∴ Anti–Aromatic

Allyl anion
4π–electrons

Cyclopropenyl anions
cyclic 4π–electron cloud
has greater π–electron energy.
∴ Anti–Aromatic

(iii) **Non-Aromatic Systems :** The cyclic systems whose π-electron energy is comparable to that of the corresponding open chain systems, are said to be non-aromatic. In other words, the non-aromatic compound is almost as stable as its corresponding acyclic compound.



1, 3, 5, 7– Octatetraene
8π electrons

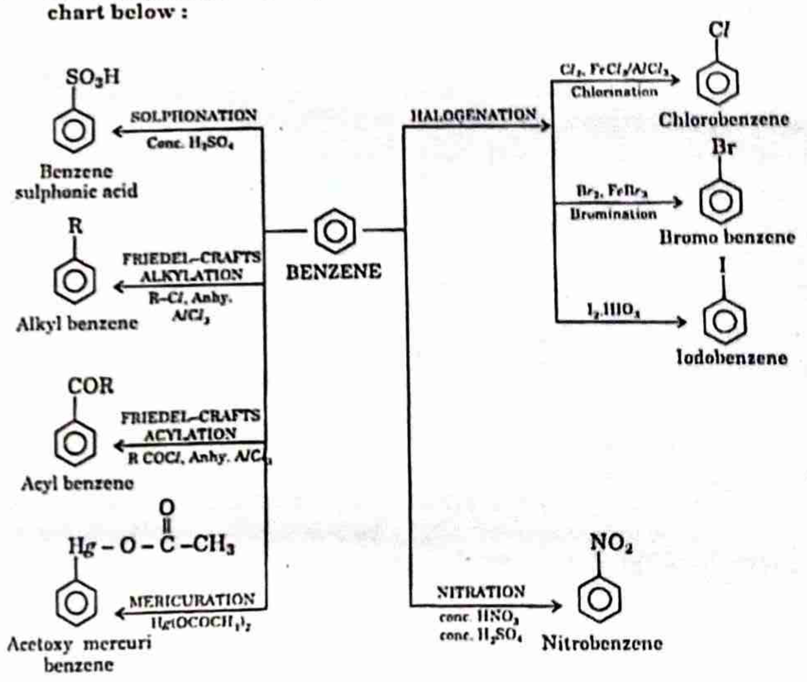
Cyclooctatetraene
8π–electrons, Non–AROMATIC tub shaped molecule,
not planar no delocalisation of electrons has also
same delocalisation or π–electron energy

Heptatrienyl anion
8π–electrons

Cycloheptatrienyl anion
8π–electrons, NON–AROMATIC
Non–Planar molecule hence no delocalisation
of π electrons has same π–electrons energy

Aromatic Electrophilic Substitution

- **Electrophilic Substitution reactions are characteristic reactions of aromatic substrates.**
  Reason : The presence of a cyclic delocalised π-electron cloud above and below the plane of the ring, attracts electrophilic (electron deficient) reagents. Further, due to delocalisation or resonance stabilisation, they undergo substitution rather than addition.
- **Some important electrophilic substitution reactions are shown in the chart below :**

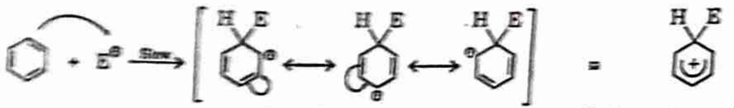


- General mechanism of aromatic electrophilic substitution reactions

Step 1 : Generation of electrophile

$$E-Z \xrightarrow{Fast} E^{\oplus} + Z^{\ominus}$$

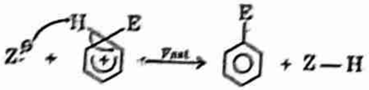
Step 2 : Attack of electrophile on the benzene ring leading to the formation of a resonance stabilised carbocation.



Carbocation or wheland intermediate or Arenium ion

The formation of carbocation constitutes the rate-determining step of the mechanism. The resonance stabilised carbocation so formed is also termed as the **arenium ion** or **σ-complex** or **Wheland Intermediate.** It is to be noted that it is **non-aromatic** in nature as it has 4π electrons which are delocalised over five sp^2-hybridised C-atom. The C-atom carrying the electrophile becomes sp^3 hybridised and no longer participates in the formation of π-electron cloud.

Step 3 : Removal of a proton by the base from the carbocation to form the substitution product :



Product

In this step, the aromaticity of the benzene ring is restored.

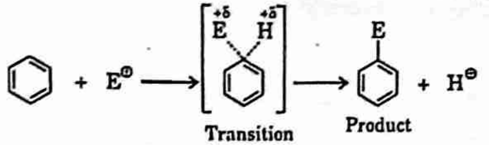
(i) **Evidences in favour of mechanism :**

From the isotopic tracer technique studies, it is found that the rate of substitution in the substrates labelled with deuterium is same as that of the substrates containing ordinary hydrogen or

$$\left.\begin{array}{l} C_6H_6 \xrightarrow[\text{Substitution}]{\text{Electrophilic}} C_6H_5E \\ C_6D_6 \xrightarrow[\text{Substitution}]{\text{Electrophilic}} C_6D_5E \end{array}\right] \text{Both occur at the same rate}$$

protium. This can happen only if the carbon hydrogen cleavage is not involved in the rate determining step as suggested by the mechanism. As a carbon-deuterium bond is broken more slowly than a carbon-protium bond, the absence of isotope effect in aromatic substitution can be justified only if the rate determining step of the reaction does not involve any cleavage of C—H bond.

(ii) The absence of isotope effect also rules out the possibility of a single step concerted mechanism. Since then the C—H bond cleavage would have been a part of the single rate determining step and then **isotopic effect** would have been observed.



Transition state

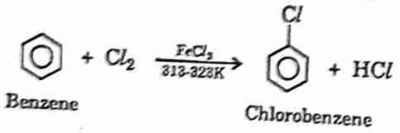
Product

Single step concerted mechanism would exhibit a large isotopic effect

But this is not found to be so in actual practice, as aromatic electrophilic substitution occurs by a stepwise mechanism in which the formation of carbocation is the rate determining step.

(T.S. for formation of σ-complex has higher E_{act} than the T.S. for π-complex)

- **Mechanisms of some common aromatic electrophilic substitution reactions.**
  1. **Halogenation :** Bromine or chlorine reacts with benzene at low temperature (313-323 K) in the presence of strong *Lewis* acids such as ferric halides or aluminium halides, to form bromo-or chloro-benzene.



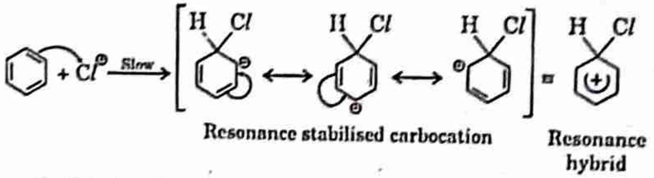
Reaction with fluorine occurs vigorously and is difficult to handle. While reaction with iodine (I_2) does not proceed, as the equilibrium is unfavourable and the reverse reaction proceeds much faster than aromatic substitution.

- **Mechanism :** The lewis acid catalyst forms a complex with halogen molecule, by virtue of which one halogen atom becomes strongly positively polarised. This positively polarised halogen atom then attacks the π-electron cloud of benzene ring to form a resonance stabilised carbocation, which then eliminates a proton to form the substitution product. This is shown as below :

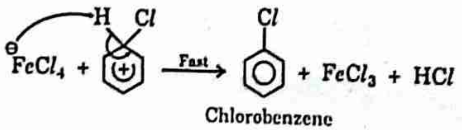
Step 1 : Generation of Electrophile

$$Cl-Cl + FeCl_3 \rightleftharpoons \overset{\delta+}{Cl}\cdots\cdots Cl\cdots\cdots \overset{\delta-}{FeCl_3} \longrightarrow \underset{\text{Chloronium ion}}{\overset{\oplus}{Cl}} + \overset{\ominus}{FeCl_4}$$

Step 2 : Formation of Carbocation

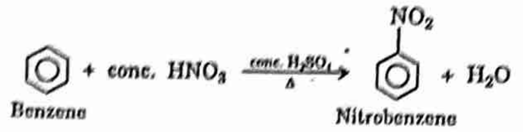


Step 3 : Elimination of a proton from the carbocation to form the substitution product

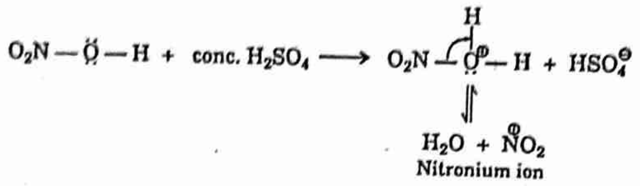


Halogenation may also be brought about with hypohalous acid in the presence of strong protonic acids or by the use of interhalogen compounds. The respective mechanisms are shown below :

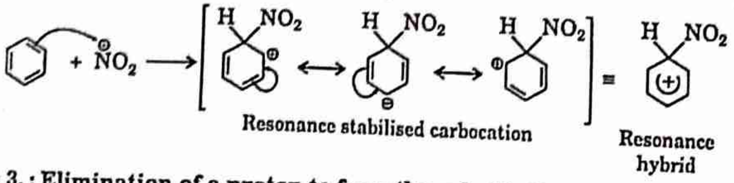
2. **Nitration :** Nitration is carried out by heating benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



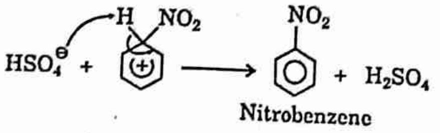
Mechanism :
Step 1. : Generation of electrophile



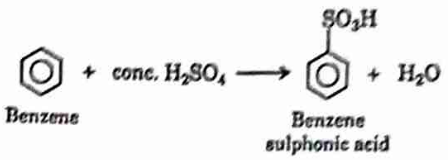
Step 2. : Formation of carbocation



Step 3. : Elimination of a proton to form the substitution product



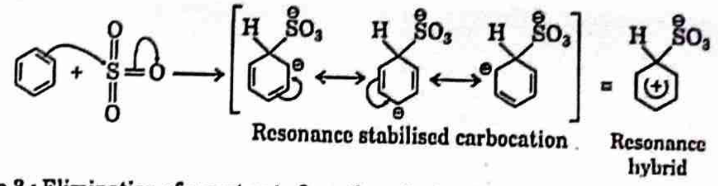
3. **Sulphonation :** Sulphonation is carried out by treating benzene with concentrated sulphuric acid or oleum ($H_2SO_4 + SO_3$).



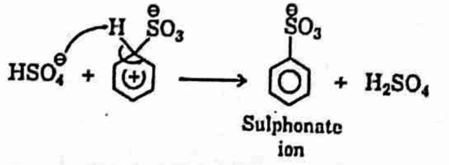
Mechanism :
Step 1 : Generation of electrophile

$$2\,H_2SO_4 \rightleftharpoons \underset{\text{Electrophile}}{SO_3} + H_3\overset{\oplus}{O} + HSO_4^{\ominus}$$

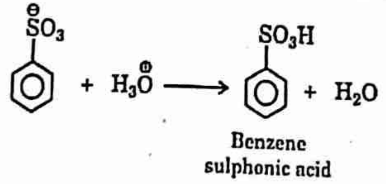
Step 2 : Formation of carbocation



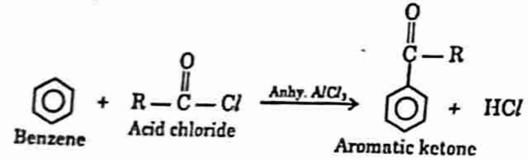
Step 3 : Elimination of a proton to form the substitution product



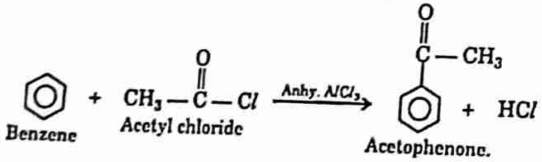
Step 4 : Reaction between sulphonate ion and hydronium ion to form sulphonic acid



5. **Friedel Crafts Acylation :** The reaction is similar to that of alkylation, except that acid chloride is used in place of alkyl halide. The reaction gives aromatic ketones as product.

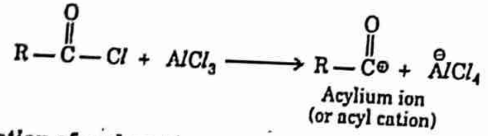


For example,



Mechanism :

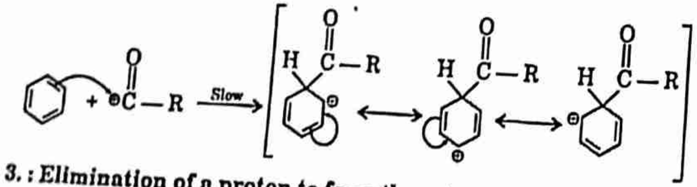
Step 1. : Generation of electrophile



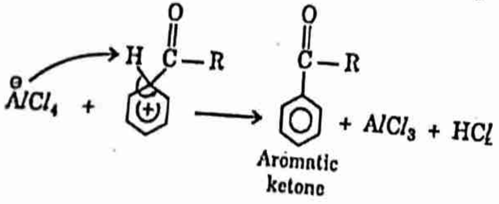
$$R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}{}^{\oplus} + \overset{\ominus}{AlCl_4}$$

Acylium ion
(or acyl cation)

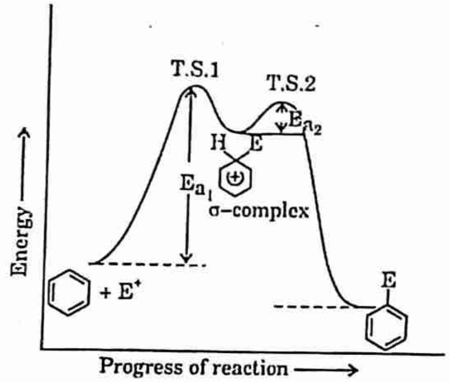
Step 2. : Formation of carbocation



Step 3. : Elimination of a proton to form the substitution product



- **Energy Profile**
  Diagram for Aromatic Electrophilic Substitution



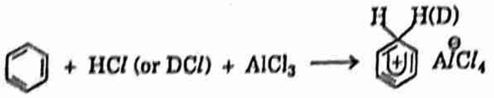
The energy changes as expected from the mechanism discussed before are shown above :

(i) Since the formation of the carbocation (also known as the arenium ion) is the rate determining step, hence the first step is shown to have a high energy transition state (T.S.I.) with a high energy of activation (E_{a_1}). This step is highly endothermic and takes place at a slow rate. This is obvious as the benzene ring loses its aromaticity as the electrophilic begins to attach itself to the ring. In T.S.I., the bond between the ring carbon and electrophilic is only partially formed.

(ii) The second step leading to the substitution product from the arenium ion is a fast step with a T.S.II with a smaller energy of activation E_{a_2}. Note that in T.S. II, the bond between the ring carbon and hydrogen is only partially broken.

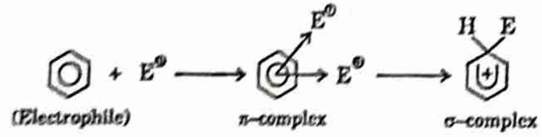
- **Role of σ π Complexes in Aromatic Electrophilic Substitution :** As discussed in the mechanism before, the electrophile attacks the benzene ring to form a **resonance stabilised carbocation,** which is also known as the **arenium ion** or

wheland intermediate or also known as the **σ-complex.** The name is derived on **the fact that the electrophilic is actually bonded to the ring carbon by means of a σ-bond.** The ionic character of this σ-complex is evidenced by the fact that benzene when treated with HCl in the presence of anhydrous $AlCl_3$ forms a coloured complex whose solution is conducting, thus reflecting its ionic character. This σ-complex then eliminates a proton to form a substitution product. The formation of a substitution product is proved as when DCl is used in place of HCl, the benzene hydrogens are successively replaced by deuterium.



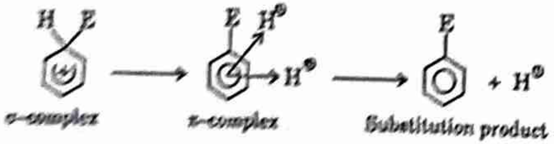
Arenium ion
or
σ–complex
(coloured & conducts electricity)

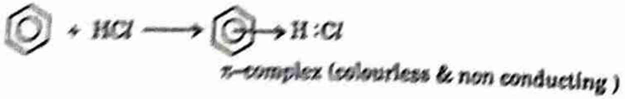
But this σ complex is not formed directly. Before the bond formation between the electrophile and the ring carbon atom, the electrophile forms a loose association with the π electron cloud of the benzene ring. This is known as the **π-complex.** Note that in π-complex, **there is no actual bond formation, but the electrophic is merely held close to the π-electron cloud of the aromatic ring.** This π-complex then changes into a π-complex.



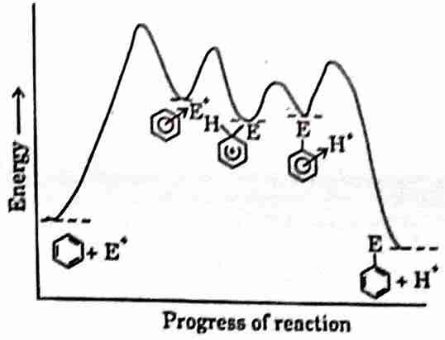
The non-ionic character of π-complex is evidenced by the fact the benzene when treated with HCl in absence of AlC_3, forms 1 : 1 complex whose solution is colourless and non-conducting in nature.

Similarly, the elimination of a proton from the π-complex also takes place via a π-complex. In the latter π-complex, the departing proton is held loosely to the π-electron cloud of the ring. This π-complex then loses the proton completely to form the final substitution product.



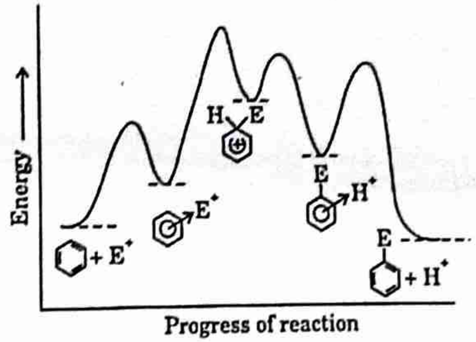


In most of the reactions, formation of σ-complex is rate determining. However, in some aromatic substitutions, even the formation of π-complex could be rate determining. The respective energy profile diagrams for both the situations are shown below :



(a) Energy profile diagram of electrophilic aromatic substitution in which formation of π complex is rate-determining.

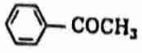
(T.S. for formation of π-complex has higher E_{act} than the T.S. for σ-complex)

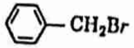


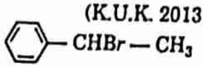
(b) Energy profile diagram of electrophilic aromatic substitution in which formation of σ-complex is rate determining.

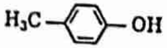
QUESTIONS FOR PRACTICE

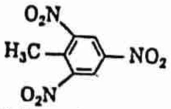
1. Give appropriate names to the following compounds : (K.U.K. 2013)

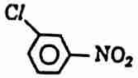
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

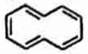
2. Which of the following exhibit aromaticity and non-aromaticity.
(i) Cyclooctatetraene
(ii) Cyclopentadienyl anion
(iii) Tropylium ion
(Hint : (i) Non-aromatic, (ii) and (iii) are aromatic in nature.)

State Huckel's rule and illustrate it with the help of heterocyclic compounds and aromatic ions. (K.U.K. 2012) (M.D.U. 2007)

Discuss mechanism of electrophilic substitution in the benzene ring with reference to the following reaction, giving the energy profile diagrams (K.U.K. 2013)
(i) Halogenation
(ii) Nitration
(iii) Sulphonation
(iv) Friedel Crafts Reactions

(a) Synthesise *m*-nitrobenzoic acid from benzene
(b) Give one method of formation of Toluene cyclohexane from benzene (K.U.K. 2005)

Though benzene is unsaturated hydrocarbon yet it fails to give Baeyer's test, explain. (M.D.U. 2012) (K.U.K. 2007)

(a) Cycloheptatrienly cation is more stable than cycloheptatriene. (K.U.K. 2009)
(b)  contain 10π-electrons, yet it is non-aromatic and gives typical addition reactions of alkenes. (K.U.K. 209)

8. Assign appropriate reasons for the following : (K.U.K. 2012)
(i) Methyl group, without having lone pair of electrons, is ortho and para directing in nature.
(ii) Halogens are ortho and para directing though they are deactivating in nature.
(iii) Nitration of toluene takes place more easily as compared to benzene or toluene. (M.D.U. 2012)
(iv) In the case of ortho and para disubstitution, the para isomer generally dominates.
(v) Alkoxy group acts as activating and ortho and para directing even though oxygen is more electronegative than carbon.
(vi) Amino group in aniline is ortho-para directing but aniline hydrogen chloride is meta directing.
(vii) Nitration of benzene takes place more readily than that of nitrobenzene. (M.D.U. 2012, K.U.K. 2012)
(viii) *o*, *p*-directing effect of $-CH_3$ in toluene during electrophilic substitution. (K.U.K. 2013)

9. Discuss the mechanism of nitration of benzene and mention rate determining step of the reaction. (K.U.K. 2012)

10. (a) Arrange the following compounds in order of increasing tendency to undergo electrophilic aromatic substitution :
(i) Nitrobenzene, (ii) Benzene, (iii) Phenol and (iv) Toluene
(b) Pick out the substituents which are (i) Ring activating, (ii) Ring deactivating — Br, $-NH_2$, $-CH_2$, $-NO_2$. (K.U.K. 2006)

11. Outline the synthesis of the following compounds starting from benzene :
(a) *p*-Nitrotoluene
(b) 1,3,5-trinitrobenzene
(c) 3, 5-Dinitrobenzoic acid
(d) *m*-Bromobenzoic acid
(e) *p*-Bromonitrobenzene
(f) *p*-Chloronitrobenzene

12. Convert benzene into toluene. (K.U.K. 2013)

13. Write the mechanism of Friedel-Craft alkylation of benzene and discuss its limitations. (M.D.U. 2007, K.U.K. 2009)

14. (a) Give the mechanism of Fridel-Craft acylation. (M.D.U. 2005 April, K.U.K. 2006, 2007)
(b) Why does side chain halogenation in alkyl benzene take place preferentially at position alpha to the ring.

3

Dienes & Alkynes

A. DIENES

Introduction

Dienes are unsaturated hydrocarbons containing two carbon-carbon double bonds per molecule. They are also referred to as **alkadienes.**

They have the general formula C_nH_{2n-2} and are isomeric with alkynes. But their properties are entirely different from one another.

Classification of Dienes

Depending upon the relative positions of the two carbon-carbon double bonds, they are classified as follows :

(a) **Isolated Dienes :** The dienes in which the double bonds are separated by more than one single bonds are isolated dienes. They are also called as non-conjugated dienes. For example,

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H=\overset{6}{C}H_2$$

1, 5–Hexadiene

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H=\overset{8}{C}H_2$$

1, 7-Octadiene

(b) **Cummulated Dienes :** The dienes containing double bonds between successive carbon atoms are cummulated dienes. They are also referred to as **allenes** or **cummulenes.**

For example,

$$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H_2 \qquad \overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}=\overset{1}{C}H_2$$

1, 2–Propadiene (or Allene)

1, 2–Butadiene (or Methylallene)

(c) **Conjugated Dienes :** Dienes containing alternate system of single and double bonds are conjugated dienes.

For example,

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2 \qquad \overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$$

1, 3-Butadiene

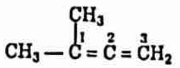
1, 3-Pentadiene

Nomenclature

- The simplest cummulated diene is allene, $CH_2 = C = CH_2$. All other cummulated dienes are termed as alkyl derivatives of allene.

  For example,

  $CH_3-\overset{1}{C}H=\overset{2}{C}=\overset{3}{C}H_2$ Methyl allene

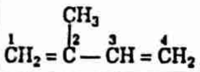
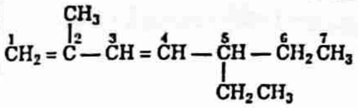
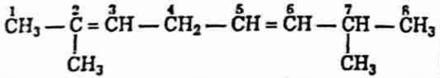
  

  $CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\overset{1}{C}}=\overset{2}{C}=\overset{3}{C}H_2$ 1, 1 – Dimethyl allene

  $CH_3-\overset{3}{C}H=\overset{2}{C}=\overset{1}{C}H-CH_2CH_3$ 1 – Ethyl – 3 – methyl allene

- According to **IUPAC Nomenclature,** all types of dienes are named as **alkadienes.** The longest carbon chain containing the two double bonds is selected as the parent chain and is then suitably numbered so that the position of the double bonds gets the lowest possible number. The position of the double bonds and substituents of any are in dictated before the name of the diene.

  For example,

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2$	1, 3 – Butadiene
 $\overset{1}{C}H_2=\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H_2$	2 – Methyl – 1, 3 – butadiene
$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$	1, 2 – Butadiene
 $\overset{1}{C}H_2=\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H-\underset{\underset{\displaystyle CH_2CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_2\overset{7}{C}H_3$	5 – Ethyl – 2 – methyl – 1, 3 – heptadione
 $\overset{1}{C}H_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}H_2-\overset{5}{C}H=\overset{6}{C}H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{7}{C}H}-\overset{8}{C}H_3$	2, 7 – Dimethyl – 2, 5 – octadiene

Relative Stabilities of Dienes

The conjugated dienes are found to be more stable than the non-conjugated dienes. This is clear from the comparison of their heats of hydrogenation. For a diene, its heat of hydrogenation is expected to be the sum of the heats of hydrogenation of the individual double bonds. Lower the heat of hydrogenation, greater is the stability of the compound. For conjugated dienes, the observed value of heat of hydrogenation is found to be less than the expected value. For example, consider 1, 3 – and 1, 4 – pentadienes, which are isomeric dienes.

$CH_3 - CH = CH - CH = CH_2$
1, 3 – Pentadiene
(A conjugated diene)

$CH_2 = CH - CH_2 - CH = CH_2$
1, 4 – Pentadiene
(A non-conjugated diene)

The observed heat of hydrogenation of 1, 4 – Pentadiene, a non-conjugated diene is 254.4 KJ/mole which is close to the expected value of 251.1 KJ/mole. But the observed heat of hydrogenation of 1, 3–Pentadiene, a conjugated diene is found to be 16.7 KJ/mole less than the expected value.

Since, a conjugated diene evolves lesser energy; this means it contains lesser energy and hence is more stable than the non-conjugated dienes. The greater stability of conjugated dienes is attributed to resonance, which is explained in detail in the next article.

Structure of 1, 3 – Butadiene

The extra stability of conjugated dienes can be explained in terms of their structure. Consider 1,3 – Butadiene, which exists as a resonance hybrid of the following contributing structures :

$$\underset{(A)}{CH_2 = CH - CH = CH_2} \longleftrightarrow \underset{(B)}{\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2} \longleftrightarrow \underset{(C)}{\overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2}$$

Out of the above three structures, structure (A) is the most stable as it does not involve separation of charges and makes the most important contribution to the resonance hybrid. Butadiene exists as a resonance hybrid of the above structures.

- **Orbital Picture :**

  All the four c-atoms of butadiene are sp^2-hybridised. Each c-atom uses its three sp^2-hybrid orbitals in the formation of three sigma σ-bonds. Now each C-atom is left with an unhybridised p-orbitals for the formation of pi π-bonds. These p-orbitals may undergo sideways overlapping as shown in the figure below :

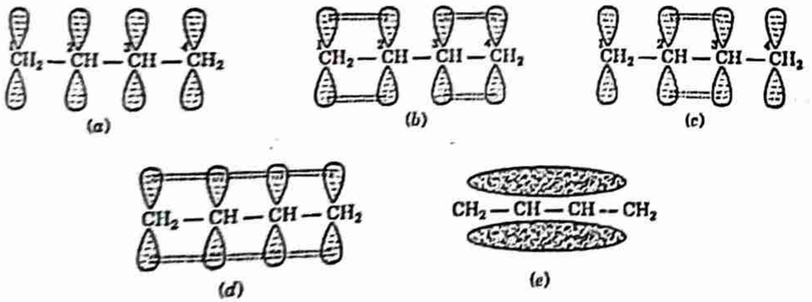


Fig (a) shows the four unhybridised p-orbitals. Fig. (b) shows the overlap of p-orbitals of C-1 with C-2 & C-3 with that of C-4. Fig. (c) shows the overlap of p-orbitals of C-2 with C-3 Fig. (d) shows that C-1 overlaps with C-2, C-2 with C-3, C-3 with C-4.

Or in other words, it may be said that the π molecular orbitals is spread over all the four c-atoms. Such a molecular orbital which is spread over the nuclei of more than two atoms is known as **delocalised molecular orbital** and the electrons present in them are termed as **delocalised electrons** and the phenomenon is referred to as **delocalisation.**

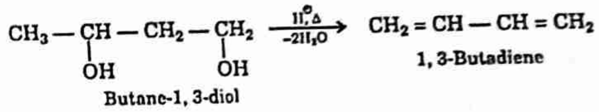
Thus, delocalisation is responsible for the extra stability of conjugated dienes like 1, 3-Butadiene where the delocalised electrons are attracted by four nuclei and not two nuclei. Also, as a result of delocalisation the carbon-carbon bond lengths in 1, 3 – Butadiene neither corresponds to a pure C–C single bond length nor to a pure C = C double bond length, but it lies in between the two.

Methods of Preparation of Dienes

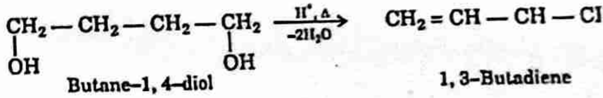
Following are listed some important methods of preparation of a conjugated diene like 1, 3-Butadiene :

1. **By dehydration of diols :**

   1, 3-Butadiene may be prepared by the acid catalysed dehydration of butane – 1, 3 – diol or butane – 1, 4 – diol as shown below :



$$\underset{\text{Butane-1, 3-diol}}{CH_3 - \underset{OH}{CH} - CH_2 - \underset{OH}{CH_2}} \xrightarrow[-2H_2O]{H^{\oplus}, \Delta} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2}$$

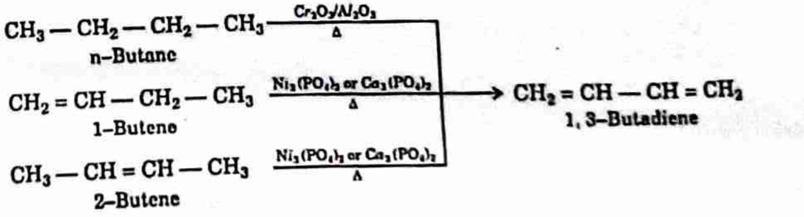


$$\underset{\text{Butane-1, 4-diol}}{\underset{OH}{CH_2} - CH_2 - CH_2 - \underset{OH}{CH_2}} \xrightarrow[-2H_2O]{H^{+}, \Delta} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH - CH_2}$$

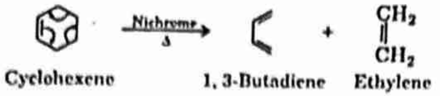
2. **By dehydrohalogenation of dihalogen derivatives Dehydrohalogenation of 1, 3 - Dichlorobutane with alocholic KOH gives 1, 3 – Butadiene**

$$\underset{\text{1, 3 – Dichlorobutane}}{CH_3 - CHCl - CH_2 - CH_2Cl} \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{1, 3 – Butadiene}}{CH_2 = CH - CH = CH_2}$$

3. **By catalytic dehydrogenation of alkanes/alkenes : 1, 3 – Butadiene may be prepared by the dehydrogenation of n–butane, 1–Butene or 2–Butene over heated catalyst.**



4. **By pyrolysis of cycloalkenes (Retro Diels-Alder Reaction) :** Vapours of cyclohexene when passed over heated nichrome catalyst (an alloy of nickel, iron and chromium) gives 1, 3-Butadiene. The reaction is the reverse of Diels Alder reaction and is referred to as retro Diels Alder reaction.



5. **By dimerisation of acetylene :** Dimerisation of acetylene in the presence of Nieucoland catalyst ($NH_4Cl - CuCl$) gives Vinylacetylene which upon partial reduction gives 1, 3-Butadiene.

$$\underset{\text{Acetylene}}{2CH \equiv CH} \xrightarrow{NH_4Cl - CuCl} \underset{\text{Vinylacetylene}}{CH_2 = CH - C \equiv CH} \xrightarrow[\text{Partial Reduction}]{H_2, Pt, BaSO_4} \underset{\text{1, 3 - Butadiene}}{CH_2 = CH - CH = CH_2}$$

Chemical Reactions of Dienes

- The chemical reactions of non-conjugated dienes are similar to those of simple alkenes except that the reagent is consumed in an amount twice to that required for one double bond.
- But the properties of conjugated dienes are modified because of the interaction between the two double bonds.

Some important reactions of dienes are discussed as follows :

1. Electrophilic Addition Reactions

(a) **Addition of halogens**

- **With two moles of halogen, dienes react to give tetrahalogen derivatives.** For example,

$$\underset{\text{1, 3 - Butadiene}}{CH_2 = CH - CH = CH_2} + 2Br_2 \longrightarrow \underset{\text{1, 2, 3, 4 - Tetrabromo butane}}{BrCH_2 - CHBr - CHBr - CH_2Br}$$

- **With one mole of halogen,** the addition in case of **non-conjugated dienes** may occur across either of the two double bonds as the two double bonds act independent of each other. For example,

$$\underset{\text{1, 4 - Pentadiene}}{CH_2 = CH - CH_2 - CH = CH_2} + Br_2 \longrightarrow \underset{\text{4, 5 - Dibromo - 1 - pentene}}{CH_2 = CH - CH_2 - CHBr - CH_2Br}$$

But in case of **conjugated dienes,** two different products are formed. For example,

$$\underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2} + Br_2 \longrightarrow \begin{cases} \underset{\substack{\text{3, 4-Dibromo-1-Butene} \\ \text{(1,2-Addition product)}}}{Br\,CH_2 - CHBr - CH = CH_2} \\ \underset{\substack{\text{1, 4-Dibromo-2-Butene} \\ \text{(1,4-Addition product)}}}{Br\,CH_2 - CH = CH - CH_2Br} \end{cases}$$

The first product which is the expected 3, 4-Dibromo-1-butene is formed as a result of 1, 2 – addition across a double bond (i.e. addition on adjacent c-atoms). The second product which is unexpected 1, 4 – Dibromo-2-butene is a result of 1, 4-addition or conjugate addition (i.e., addition to terminal c-atoms of a conjugate system).

- **Mechanism of addition**

Step 1. : Formation of allylic carbocation

The non-polar bromine molecule gets polarised upon approaching the diene and the positively polarised Bromine atom then adds to a doubly bonds C-atom to form a carbocation

$$\underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2} + \underset{\substack{\text{Polarised} \\ \text{bromine} \\ \text{molecule}}}{\overset{\delta+}{Br} - \overset{\delta-}{Br}} \xrightarrow{-Br^{\ominus}} \underset{\substack{\text{Allylic carbocation} \\ \text{(Resonance} \\ \text{stabilised)}}}{CH_2 = CH - \overset{\oplus}{CH} - CH_2Br}$$

$$\text{\& not } \underset{\substack{\text{1° Carbocation} \\ \text{(less stable)}}}{CH_2 = CH - CHBr - \overset{\oplus}{CH_2}}$$

Two carbocations are possible as seen above. But it is the allylic carbocation which is formed as it is more stable than the other 1° carbocation. **The allylic carbocation so formed is a resonance hybrid of the following two structures :**

$$CH_2 = CH - \overset{\oplus}{CH} - CH_2Br \longleftrightarrow \overset{\oplus}{CH_2} - CH = CH - CH_2Br$$

$$\underset{\text{Resonance hybrid}}{\overset{4\,\delta+}{CH_2} \overset{3}{=\!=} CH \overset{2\delta+}{=\!=} CH - \overset{1}{CH_2}Br}$$

The resonance hybrid has its positive charo delocalised over carbon atoms c-2 and C-4.

Step 2 : Attack of Bromide ion

The allylic carbocation so formed may be attacked by the bromide ion either at C-2 or C-4. Attack at C-2 gives the 1, 2-addition product, *i.e.*, 3-4-Dibromo 1-butane (the expected product). While attack at C-4 gives the 1, 4 – addition product, i.e., 1, 4 – Dibromo – 2 butene (the unexpected product).

$$\underset{\text{Allylic carbocation}}{\overset{4\,\delta+}{CH_2} \overset{3}{=\!=} CH \overset{2\delta+}{=\!=} CH - \overset{1}{CH_2}Br}$$

$$\downarrow Br^{\ominus}$$

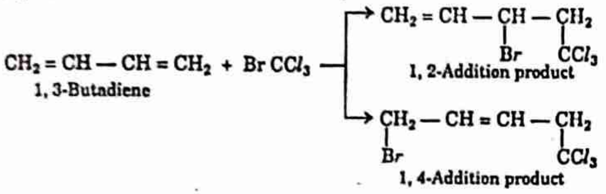
$$\underset{\substack{\text{3, 4-dibromo-1-Butene} \\ \text{1, 2-Addition product} \\ \text{(Formed by addition} \\ \text{on adjacent C-atoms)}}}{CH_2 = CH - CHBr - CH_2Br} \qquad \underset{\substack{\text{1, 4-Dibromo-2-butene} \\ \text{1, 4-addition product} \\ \text{(formed by addition} \\ \text{on terminal C-atoms)}}}{BrCH_2 - CH = CH - CH_2Br}$$

controlled.

2. Addition of Free Radicals

Like alkenes, **conjugated dienes also undergo free radical addition reactions but at a much faster rate again leading to the formation of 1, 2–as well as 1, 4–addition products.**

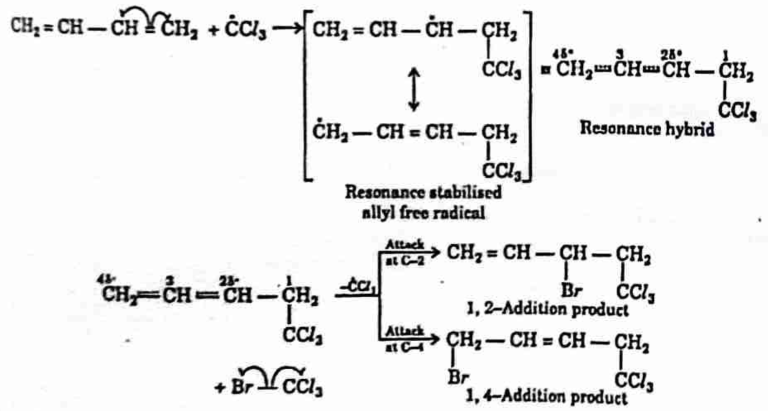
For example,



- **Mechanism :** The free radical mechanism occurs in the presence of peroxides.

$$\text{Peroxide} \xrightarrow{\Delta} \dot{R}\ \text{(Radical)}$$

$$\dot{R} + Br - CCl_3 \longrightarrow R - Br + \dot{C}Cl_3$$



As seen from the mechanism, the allyl free radical so formed is a resonance hybrid of two contributing structures. This resonance hybrid has its odd electron distributed between C–2 and C–4. Subsequent attack of the bromine radical on C–2 gives rise to 1, 2–adduct and attack on C–4 gives rise to the 1, 4 – adduct. The newly formed $\dot{C}\,CCl_3$ radical reacts further to continue the chain process.

- **Though the conjugated dienes are more stable than alkenes, yet free radical addition reactions of dienes proceed at a much faster rate as compared to alkenes.**

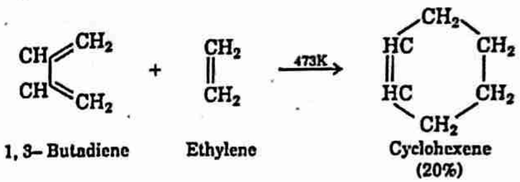
  Reason : This is because the allylic free radical so formed in case of conjugated dienes is very stable, hence, the energy of activation, *i.e.,* E_{act} for its formation is very less as compared to the E_{act} for the formation of the intermediate free radical in case of alkenes. Thus, the allyl free radical is more readily formed and the reaction occurs at a much faster rate in case of conjugated dienes.

3. Diels-Alder Reaction : (4 + 2) Cyclo addition Reaction

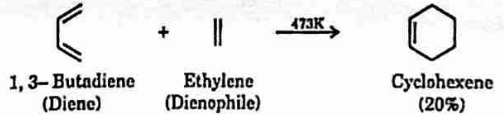
Diels Alder Reaction is an important reaction of conjugated dienes. **It involves an addition reaction between a conjugated diene (a 4π-electron system) and a compound containing a double bond called a dienophile (a 2π-electron system) to form a six-membered cyclic compound.**

As the reaction involves the addition of 4π-electron system to a 2π-electron system to form cyclic products, the reaction is also referred to as **[4 + 2] cyclo addition reaction.**

A typical example is the reaction between 1, 3-Butadiene and ethylene to form cyclohexene.

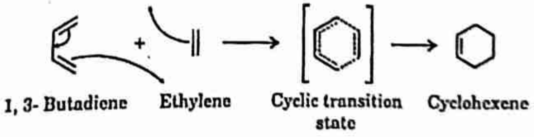


Or simply,



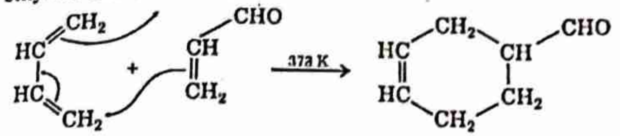
The reaction occurs slowly and gives poor yield.

- **Mechanism :** The reaction occurs by a single step concerted mechanism involving a cyclic transition state when two new σ-bonds are formed at the cost of two π bonds as shown below :



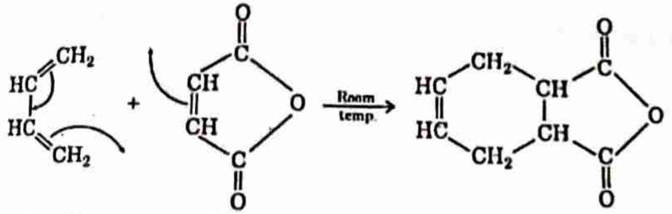
Factors which favour the reaction :

- (a) **Presence of electron-withdrawing groups in the dienophile :** For example, the reaction between 1, 3-Butadiene and acrolein (which contains an electron withdrawing carbonyl group) occurs under comparatively milder conditions along with a quantitative yield of the adduct as compared to the reaction between ethylene and butadiene.



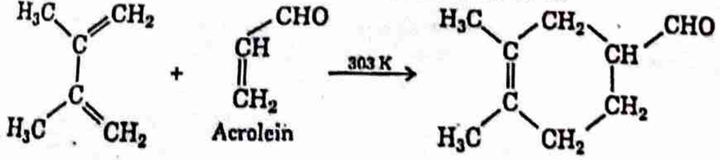
1, 3–Butadiene   Acrolein (dienophile)   1, 2, 3, 6–Tetrahydro benzaldehyde

Another example is that of the reaction between that of butadiene and maleic anhydride (which contains two carbonyl groups) which takes place at room temperature with increased yields of the adduct.



1, 3–Butadiene   Maleic anhydride   cis–1, 2, 3, 6–tetrahydro phthalic anhydride.

(b) **Presence of electron-releasing groups in the diene : 2, 3-Dimethyl – 1, 3 – butadiene which contains two electrons releasing methyl groups is about five times more reactive than 1, 3 – butadiene towards Diels Alder Reaction. Its reaction with acrolein occurs at 303 K, as compared to the reaction between 1, 3 – Butadiene and acrolein which occurs at 373 K.**



2, 3–Dimethyl–1, 3–butadiene   Acrolein   1, 2, 3, 6–Tetrahydro –4, 5–dimethyl benzaldehyde

B. ALKYNES

Introduction

Alkynes are open-chain unsaturated hydrocarbons having the general formula C_nH_{2n-2} contain a carbon-carbon triple bond (C ≡ C) in their structure.

Types of Alkynes

(a) **Terminal alkynes :** Alkynes containing the triple bond at the end of the carbon chain are terminal alkynes.

(b) **Internal alkynes :** Alkynes containing the triple bond somewhere in the middle of the carbon chain are internal or non-terminal alkynes. 1–pentyne is an example of a terminal alkyne and 2–pentyne is an example of an internal alkyne.

$HC \equiv C-CH_2CH_2CH_3$	$H_3C-C \equiv C-CH_2CH_3$
1 – Pentyne	2 – Pentyne
(Terminal alkyne)	(Internal alkyne)

Nomenclature of Alkynes

There are two systems of nomenclature :

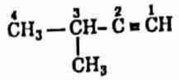
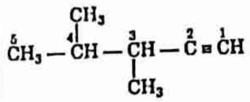
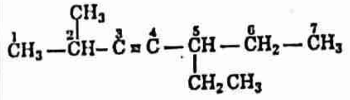
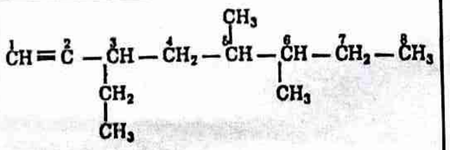
(a) **Common System : In this system of nomenclature, they are termed as derivatives of acetylene. Although some of them have special names as well.**

Formula	**Common Name**	**Trivial Name**
$HC \equiv CH$	Acetylene	
$CH_3-C \equiv CH$	Methyl acetylene	Allylene
$CH_3CH_2-C \equiv CH$	Ethyl acetylene	α-Crotonylene
$CH_3-C \equiv C-CH_3$	Dimethyl acetylene	β-Crotonylene
$CH_3-C \equiv C-CH_2CH_3$	Ethyl methyl acetylene	

(b) **IUPAC system of nomenclature :.** According to this system, the name of the alkyne are derived by replacing the suffix 'ane' of the corresponding alkane by 'yne'

$$\text{Alkane} \xrightarrow[+yne]{-ane} \text{Alkyne}$$

The carbon chain is then numbered in such a way that the position of the double bond gets the lowest possible number. The position of the substituents are indicated accordingly. In case both the double and triple bonds are present, both are treated at par in getting the lowest number combination, the lowest number is then given to the double bond and the name of the compound ends with the word-yne. Such compounds are termed as alkenynes. Some examples are listed below :

Formula	IUPAC Name
$CH \equiv CH$	Ethyne
$CH_3-C\equiv CH$	Propyne
$CH_3CH_2-C\equiv CH$	But-1-yne
$CH_3-C\equiv C-CH_3$	But-2-yne
$CH_3-CH_2CH_2-C\equiv CH$	Pent-1-yne
$CH_3CH_2-C\equiv C-CH_3$	Pent-2-yne
 $\overset{4}{C}H_3-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H$	3–Methyl but–1–yne
 $\overset{5}{C}H_3-\overset{\displaystyle CH_3}{\overset{4}{C}H}-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H$	3, 4 – Dimethyl pent-1-yne
 $\overset{1}{C}H_3-\overset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}\equiv\overset{4}{C}-\underset{\displaystyle CH_2CH_3}{\overset{5}{C}H}-\overset{6}{C}H_2-\overset{7}{C}H_3$	5-Ethyl-2-methyl hept-3-yne
 $\overset{1}{C}H\equiv\overset{2}{C}-\underset{\displaystyle \underset{\displaystyle CH_3}{CH_2}}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{\displaystyle CH_3}{\overset{5}{C}H}-\underset{\displaystyle CH_3}{\overset{6}{C}H}-\overset{7}{C}H_2-\overset{8}{C}H_3$	3-Ethyl –5,6 – dimethyl oct – 1 – yne
$\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_2\overset{6}{C}H_3$	Hex-3-en-1-yne
$\overset{6}{C}H\equiv\overset{5}{C}-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$	Hex-1-en-5-yne (and not hex-5-ene-1-yne)

Structure of Alkynes

Let us consider the structure of acetylene.

Both the C-atoms of acetylene are *sp*-hybridised. Each C-atom uses its two hybrid orbitals in the formation of one C–C σ bond and one C – H σ-bond. As the overlap of the *sp*-hybrid orbitals takes place along the internuclear axis, all the four atoms of acetylene lie along a straight line. Hence, acetylene is a linear molecule with H – C – C bond angle being 180°.


$H\overset{s-sp}{—}C\overset{sp-sp}{—}C\overset{sp-s}{—}H$

Fig. 4.1 The skeleton of acetylene molecule showing only σ-bonds.

After the formation of σ-bonds, each C–atom is now left with two unhybridised *p*-orbitals which are mutually perpendicular to each other as well as perpendicular to the *sp*-hybrid orbitals. The unhybridised *p*-orbitals of one C–atom undergo sideways overlapping with the *p*-orbitals of the similar type of the other C–atom to form two π-bonds in planes at right angle to each other,

30

i.e., if the electron cloud of one π-bond lies above and below the line joining the carbon nuclei, then the electron cloud of the other π-bond lies in front and at back of the line. The electron clouds of the two π-bonds merge to give rise to a cylindrical π-electron cloud symmetrical about the inter-nuclear axis. This is shown in the figure below.

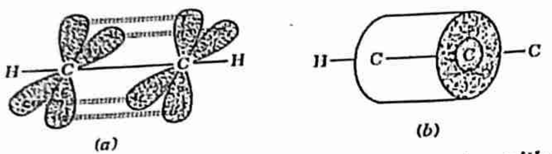


Fig. 4.2 (a) Sideways overlapping of the p-orbitals of one carbon with similar orbitals of other carbon

(b) Cylindrically symmetrical p electron cloud of acetylene.

Thus a C ≡ C bond consists of one strong σ and two weak π bonds and has a bond strength of 828 KJ/mole greater than that of C = C bond strength (682 KJ/mole), which in turn is greater than the C – C single bond strength (368 KJ/mole).

Further, due to the smaller effective size of the sp-hybrid orbitals and the formation of two π-bonds by additional sideways overlapping, the carbon-carbon and carbon-hydrogen bond lengths are shorter as compared to the corresponding bond lengths in ethylene and ethane as given below :

Formula	Carbon-carbon bond lengths	Carbon-hydrogen bond length
Acetylene $H-C\equiv C-H$	1.20Å (C≡C)	1.06 Å
Ethylene $H_2C=CH_2$	1.34 Å (C = C)	1.09 Å
Ethane H_3C-CH_3	1.54 Å (C – C)	1.10 Å

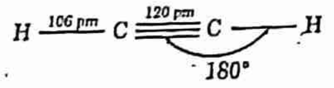


Fig. : Bond angles and bond lengths in acetylene.

Methods of Preparation of Alkynes

The various methods of preparation may be studied under the following headings :

(I) General Methods of Preparation :

(a) By dehydrohalogenation of dihalides :

The dihalides required for the purpose may be geminal, i.e., 1, 1–dihalides or vicinal, i.e., 1, 2–dihalides.

The reaction occurs in two steps. The first step dehydrohalogenation requires the use of alcoholic potash and results in the formation of a haloalkene. The second step dehydrohalogenation requires the use of a stronger base like sodium amide and results in the formation of an alkyne.

The general reactions are :

$$\underset{\text{Vicinal or 1, 2 - dihalide}}{R-CHX-CHX-R'} \xrightarrow[-KX,-H_2O]{alc.\ KOH} \underset{\text{Halo alkene}}{R-CH=CX-R'} \xrightarrow[-NaX,-NH_3O]{NaNH_2} \underset{\text{Alkyno}}{R-C\equiv C-R'}$$

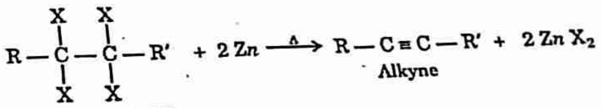
$$\underset{\text{Geminal or 1, 1 - dihalide}}{R-CH_2-CX_2-R'} \xrightarrow[-KXm-H_2O]{alc\ KOH} \underset{\text{Halo alkene}}{R-CH=CX-R'} \xrightarrow[-NH_3]{NaNH_2} \underset{\text{Alkyne}}{R-C\equiv C-R'}$$

For example,

$$\underset{\text{1, 2 - Dibromoethane}}{CH_2Br-CH_2Br} \xrightarrow[-KBr,-H_2O]{alc.\ KOH} \underset{\text{Bromoethene}}{CHBr=CH_2} \xrightarrow[-NaBr,-NH_3]{NaNH_2} \underset{\text{Acetylene}}{CH\equiv CH}$$

$$\underset{\text{1, 1 - Dibromoethane}}{CH_3-CHBr_2} \xrightarrow[-KBr,-H_2O]{alc.\ KOH} \underset{\text{Bromoethene}}{CH_2=CHBr} \xrightarrow[-NaBr,-NH_3]{NaNH_2} \underset{\text{Acetylene}}{CH\equiv CH}$$

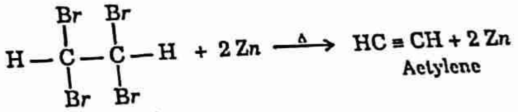
(b) By dehalogenation of tetrahalides : 1, 1, 2, 2 – Tetrahalides when heated with zinc dust, undergo dehalogenation to form alkynes. General reaction is :



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-R' + 2Zn \xrightarrow{\Delta} \underset{\text{Alkyne}}{R-C\equiv C-R'} + 2ZnX_2$$

1, 1, 2, 2-Tetrahalide

For example,



$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H + 2Zn \xrightarrow{\Delta} \underset{\text{Aetylene}}{HC\equiv CH} + 2Zn$$

1, 1, 2, 2,–Tetrabromo ethane

(II) Special Methods of Preparation of Acetylene :

(a) By controlled oxidation of methane at high temperature

$$\underset{\text{Methane}}{6CH_4 + O_2} \xrightarrow{1770K} \underset{\text{Acetylene}}{2CH\equiv CH} + 10H_2 + 2CO$$

(b) By action of water on calcium carbide

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + Ca(OH)_2$$

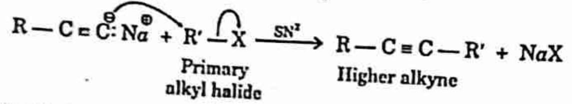
(c) By dehalogenation of haloform upon heating with silver powder

$$\underset{\text{Iodoform}}{CH\boxed{I_3 + 6Ag + I_3}CH} \longrightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6Ag\,I$$

(III) Preparation of higher alkynes from lower alkynes :

Terminal alkynes when treated with sodium amide, are converted into their sodium salts which upon reaction with an alkyl halide are converted into higher alkynes. The general reaction may be represented as follows :

$$\underset{\text{Terminal alkyne}}{R-C\equiv C-H} + NaNH_2 \xrightarrow{\text{liq. NH}_3} \underset{\substack{\text{Sod. salt of}\\ \text{alkyne}}}{R-C\equiv \overset{\ominus}{C}\!:\overset{\oplus}{Na}} + NH_3$$



$$R-C\equiv \overset{\ominus}{C}\!:\overset{\oplus}{Na} + \underset{\substack{\text{Primary}\\ \text{alkyl halide}}}{R'-X} \xrightarrow{SN^2} \underset{\text{Higher alkyne}}{R-C\equiv C-R'} + NaX$$

The alkyl halide chosen is preferably a 1° one, since the use of 2° or 3° alkyl halides leads to undesirable side reactions.

Physical Properties of Alkynes

1. The first four members are gases, next eight members are liquids and the higher ones are solids at room temperature.
2. All alkynes are colourless and odourless except acetylene which has a garlic like smell due to the presence of phosphine and hydrogen sulphide as impurities.
3. Alkynes are insoluble in water and soluble in organic solvents like either, acetone, CCl_4 etc.
4. Boiling points and melting points show a regular increase with increase in molecular weight. But the **boiling points and melting points are higher than those of alkanes and alkenes.** This is because of the linear structure of alkynes which fits better in the crystal lattice than alkenes and alkynes.

Chemical Properties of Alkynes

Like alkenes, alkynes also undergo addition reactions due to the presence of two π-bonds in their molecules. They undergo electrophilic as well as nucleophilic addition reactions. Some important reactions of alkynes are being discussed as follows :

(I) Addition of Hydrogen (Reduction)

When heated with hydrogen in the presence of nickel, platinum or palladium catalyst, alkynes get reduced first to give alkenes and then finally alkanes.

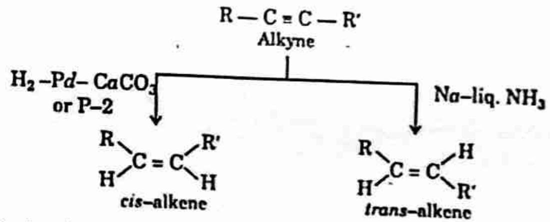
$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow[\text{Ni/Pt/Pd}]{H_2} \underset{\text{Alkene}}{R-CH=CH-R'} \xrightarrow[\text{Ni/Pt/Pd}]{H_2} \underset{\text{Alkane}}{R-CH_2-CH_2-R'}$$

For example

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

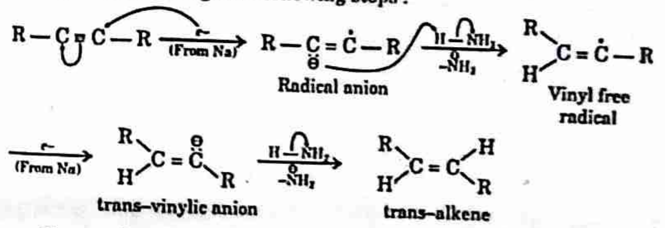
- **Partial Reduction of Alkynes :** It is possible to stop the reduction at the alkene stage by the use of some special catalysts like :
  - (i) **Lindlar's Catalyst** (which is Palladium supported over $CaCO_3$ and partially poisoned by quinoline or lead acetate).
  - (ii) **Nickel Boride Catalyst** (also known as P – 2)
  - (iii) **or with sodium or lithium in liquid ammonia.**
- **Stereoselective Nature of Reduction**

  Partial reduction of alkynes with Lindlar's catalyst or P- 2 results in the formation of *cis*-alkenes mainly as the addition of hydrogen take place from the same side of the alkyne (also known as syn-addition). While **partial reduction of alkyne with sodium or lithium in liquid ammonia results in** the formation of **trans-alkenes** as the addition of hydrogen occurs from opposite sides of the alkynes (also known as **anti-addition**). Thus, it follows that partial reduction of alkynes is stereo-selective in nature.



- **Mechanism of metal-ammonia reduction :**

  It proceeds through the following steps :



The mechanism starts with the donation of an electron from sodium or lithiummetal to the triply bonded C–atom to form a radical anion. This radical anion has both a negative charge as well as an unpaired electron. Abstraction of a proton from liq. ammonia by the radical anion results in the formation of a vinyl free radical. Further donation of an electron from metal then results in the formation a trans-vinylic anion (this is more stable as the bulky group are far apart as compared to the cis-vinylic anion of formed). Protonation of this trans-vinylic anion gives a trans-alkene as the product.

(II) Electrophilic Addition Reactions

Due to the presence of two π-bonds in their molecules, alkynes like alkenes also undergo electrophilic addition reactions, with the reagent being consumed in an amount twice per mole of alkyne.

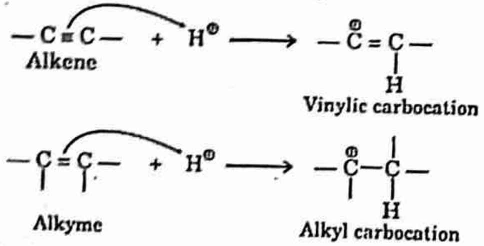
Alkynes which contain two π-bonds are expected to be more reactive than alkenes towards electrophilic addition but, in fact, alkynes are less reactive than alkenes towards electrophilic addition.

Reasons :

(i) As the triply bonded C-atoms in an alkyne are *sp*-hybridised as compared to alkenes where the doubly bonded C–atoms are sp^2–hybridised, therefore, due to greater *s*-character and smaller effective size of *sp*-orbitals, the π-electrons are held tightly and less easily available for attack by electrophiles as compared to alkenes.

(ii) Further the two π-bonds in an alkyne merge to form a single cylindrical π-electron cloud symmetrical about the internuclear axis. There is greater delocalisation of electron in this cylindrical π-electron cloud as compared to the situation when the two π-bonds had not merged together. Thus, due to greater delocalisation of π-electrons, they are less easily available for attack by electrophiles. Because of the same reason, alkynes are more stable than alkenes.

(iii) Another reason is the less stability of the intermediate ion formed by the attack of the electrophile on the π-electrons in case of alkynes as compared to alkenes. For example, consider the addition of a proton to an alkene as well as an alkyne.

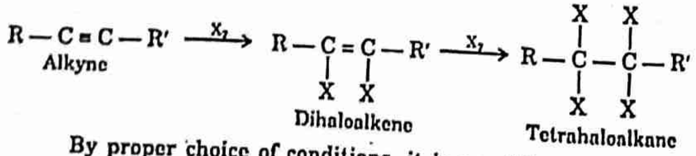


As a vinylic carbocation formed in case of alkynes, is less stable than the alkyl carbocation formed in case of alkenes. Therefore, a vinylic carbocation is less easily formed and hence, alkynes are less reactive than alkenes towards electrophilic addition reactions.

Some important electrophilic reactions of alkynes are discussed as follows :

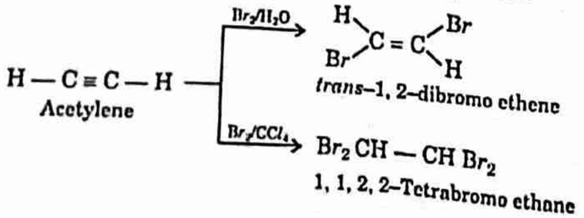
(a) **Addition of Halogens (X_2)**

Halogens (Cl_2 and Br_2) add on to alkynes to first form a dihaloalkene and finally tetrahaloalkanes.



$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow{X_2} \underset{\text{Dihaloalkene}}{R-\underset{X}{\underset{|}{C}}=\underset{X}{\underset{|}{C}}-R'} \xrightarrow{X_2} \underset{\text{Tetrahaloalkane}}{R-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-R'}$$

By proper choice of conditions, it is possible to obtain *di* or tetrahalo products. For example, acetylene on treatment with bromine-water gives 1, 2–dibromoethene as the product while treatment with bromine in CCl_4 gives 1, 1, 2, 2 – tetra bromoethane as the product.

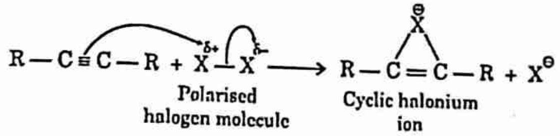


As the reddish brown colour of bromine get discharged during the reaction, therefore, this reaction may be used to detect the presence of unsaturation (both for double as well as triple bond) in a compound. But this test cannot distinguish between a double and a triple bond, it can just indicate their presence.

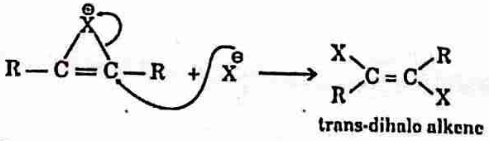
- **Mechanism of halogenation :**

The mechanism proceeds via the intermediate formation of a cyclic halonium ion.

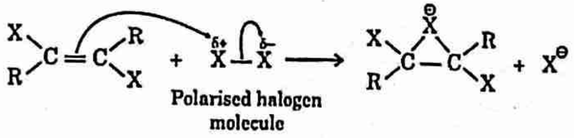
Step 1 :



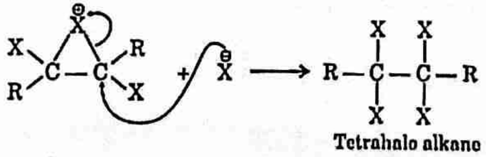
Step 2 :



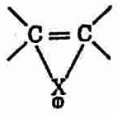
Step 3 :



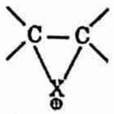
Step 4 :



As compared to alkenes, **alkynes are less reactive towards the addition of halogens.** This is due to the less stability of the cyclic halonium ion formed in case of alkynes (strained due to the presence of a double bond) as compared to alkenes.



Cyclic halonium ion formed in case of alkynes less stable



Cyclic halonium ion formed in case of alkenes more stable

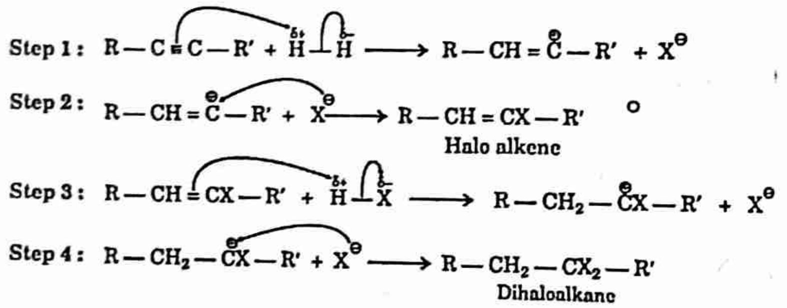
(b) Addition of hydrogen halides (HX) : The hydrogen halides (HCl, HBr or HI) add on to alkynes to first form a haloalkene and finally a dihalo alkane in accordance with Markownikoff's rule.

$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow{HX} \underset{\text{Haloalkene}}{R-CH=CX-R'} \xrightarrow{HX} \underset{\text{Dihalo alkane origeminal dihalide}}{R-CH_2-CX_2-R'}$$

For example,

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{HCl} \underset{\substack{\text{Vinyl chloride}\\ \text{or 1-chloro ethene}}}{CH_2=CHCl} \xrightarrow{HCl} \underset{\substack{\text{1, 1-Dichloro ethano or}\\ \text{Ethylidene dichloride}}}{CH_3-CHCl_2}$$

Mechanism : The reaction occurs through the following steps :



Step 1 : $R-C\equiv C-R' + \overset{\delta+}{H}-\overset{\delta-}{H} \longrightarrow R-CH=\overset{\oplus}{C}-R' + X^{\ominus}$

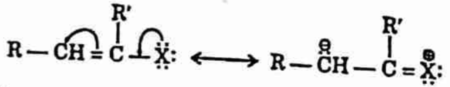
Step 2 : $R-CH=\overset{\oplus}{C}-R' + \overset{\ominus}{X} \longrightarrow \underset{\text{Halo alkene}}{R-CH=CX-R'}$

Step 3 : $R-CH=CX-R' + \overset{\delta+}{H}-\overset{\delta-}{X} \longrightarrow R-CH_2-\overset{\oplus}{C}X-R' + X^{\ominus}$

Step 4 : $R-CH_2-\overset{\oplus}{C}X-R' + X^{\ominus} \longrightarrow \underset{\text{Dihaloalkane}}{R-CH_2-CX_2-R'}$

It may be noted here that in the step (3) of mechanism, the carbocation formed could also be $R-\overset{\ominus}{C}H-CHX-R'$. But this is not formed. Instend, the carbocation formed is $R-CH_2-\overset{\ominus}{C}X-R'$.

Reason : This is because of the + R effect of halogen atom which causes a shift of π-electrons on the C–atom away from the halogen, which then accepts a proton so that the carbocation formed is $R-CH_2-\overset{\ominus}{C}X-R'$.



$$R-\overset{\ominus}{C}H=\overset{R'}{\overset{|}{C}}-\ddot{\underset{..}{X}}: \longleftrightarrow R-\overset{\ominus}{C}H-\overset{R'}{\overset{|}{C}}=\overset{\oplus}{\underset{..}{X}}:$$

- In the presence of peroxides, the addition of HBr occurs against the Markownikoff's rule.

For example,

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromo-1-propene}}{CH_3-CH=CHBr}$$

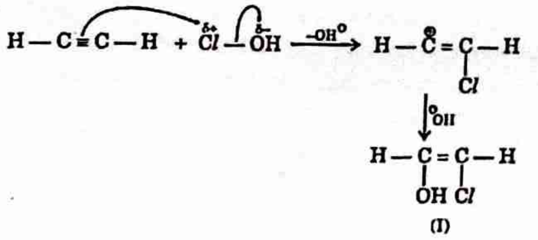
Anti-Markownikoff's addition occurs via a free radical mechanism as discussed for alkenes.

(c) Addition of hypohalous acids (HOX) : Alkynes add on two moles of hypohalous acids to first form a dihalodihydroxy compound, which then decomposes to form a dihalocarbonyl compound. For example,

$$\underset{\text{Acetylene}}{CH\equiv CH} + \underset{\substack{(\text{or } Cl_2+H_2O)\\ \text{Hypochlorous}\\ \text{acid}}}{Cl-OH} \xrightarrow{-HCl} CHCl=CHOH \xrightarrow[-HCl]{HOCl} \underset{\text{(Unstable)}}{CHCl_2-CH(OH)_2} \xrightarrow{-H_2O} \underset{\substack{\text{Dichloro}\\ \text{acetaldehyde}}}{CHCl_2-CHO}$$

- **Mechanism of addition :**

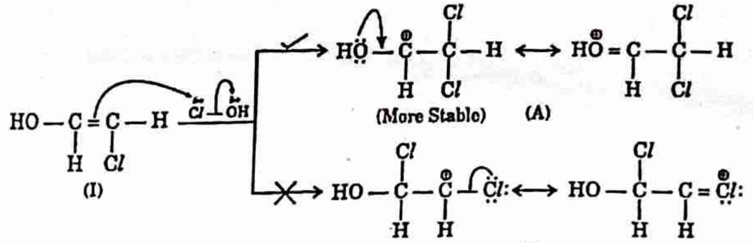
Step 1 :



$$H-C\equiv C-H + \overset{\delta+}{Cl}-\overset{\delta-}{OH} \xrightarrow{-OH^{\ominus}} H-\overset{\oplus}{C}=\underset{Cl}{\underset{|}{C}}-H \xrightarrow{\overset{\ominus}{O}H} \underset{(I)}{H-\underset{OH}{\underset{|}{C}}=\underset{Cl}{\underset{|}{C}}-H}$$

2-chloro ethen-1-ol

Step 2. : Addition of $\overset{\oplus}{Cl}$ again to intermedinte (I) can give rise to two types of carbocations :

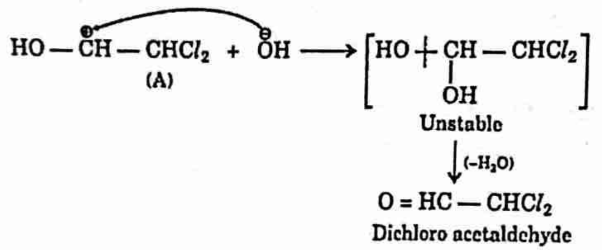


(More Stable) (A)

(Less Stable) (B)

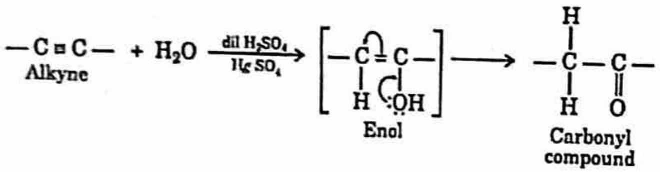
Both the carbocations (A) and (B) are resonance stabilised. But the carbocation (A) is better stabilised by resonance since in it resonance occurs through overlap between orbitals of same size, *i.e.*, 2*p*-orbital of C–atom and 2*p*–orbital to O-atom. While in (B) overlap occurs between orbitals of unequal size, *i.e.* 2*p*-orbital of C-atom and 3*p*-orbitals of Cl-atom. Thus, reaction proceeds via carbocation (A) and not (B)

Step 3. :



$$HO-\overset{\ominus}{C}H-CHCl_2 + \overset{\ominus}{O}H \longrightarrow [HO-CH(OH)-CHCl_2] \xrightarrow{(-H_2O)} O=HC-CHCl_2$$

(d) **Addition of water : Hydration Reaction :** In the presence of dilute sulphuric acid and mercuric sulphate catalyst, alkynes add on water in accordance with Markownikoff's rule to first form an **enol**, which then undergoes rearrangement to form the more stable carbonyl compound. The general reaction is :

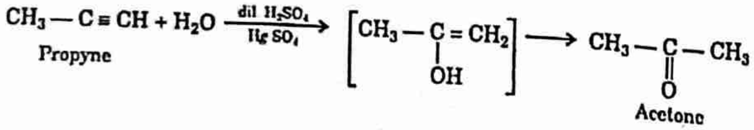


Hydration of different alkynes gives different products :

(i) Hydration of acetylene gives acetaldehyde

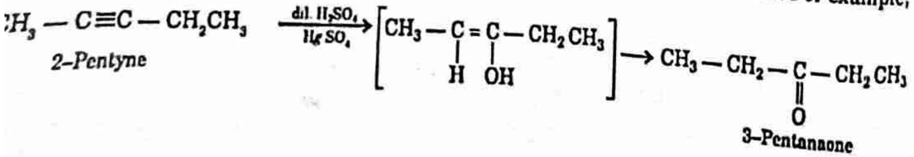
$$\underset{\text{Acetylene}}{H-C\equiv C-H} + H_2O \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\text{Vinyl alcohol}}{[CH_2=CH-OH]} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3-CHO}$$

(ii) Hydration of higher terminal alkynes gives methyl ketones. For example,



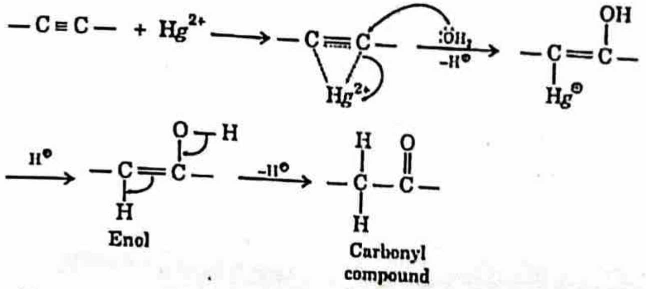
$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2O \xrightarrow[HgSO_4]{\text{dil } H_2SO_4} [CH_3-C(OH)=CH_2] \longrightarrow \underset{\text{Acetone}}{CH_3-CO-CH_3}$$

(iii) Hydration of higher interval alkynes gives other ketones. For example,



$$\underset{\text{2-Pentyne}}{H_3-C\equiv C-CH_2CH_3} \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} [CH_3-C(H)=C(OH)-CH_2CH_3] \longrightarrow \underset{\text{3-Pentanaone}}{CH_3-CH_2-CO-CH_2CH_3}$$

- **Mechanism :** The reaction involves formation of a complex of mercuric ions with the alkyne, which is then attacked by water to form a hydroxy-mercurical compound. The mercury is then replaced by a proton to give an enol which subsequently tautomerises to form a carbonyl compound.



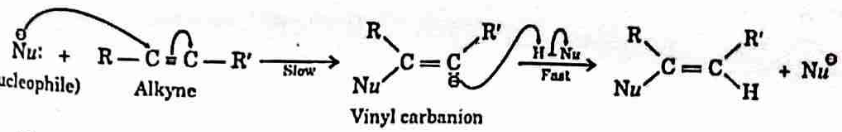
(e) **Addition of Acetic acid :** In the presence of mercuric salts, alkynes add on acetic acid to form addition products.
For example,

$$\underset{\text{Acetylene}}{CH\equiv CH} + CH_3COOH \xrightarrow{Hg^{2+}} \underset{\text{Vinyl acetate}}{CH_2=CH-OOC\,CH_3}$$

Nucleophilic Addition Reactions

Due to greater electronegativity of the *sp*-hybridised carbon, alkynes undergo nucleophilic addition reactions as well, apart from the electrophilic addition reaction.

The general mechanism of nucleophilic addition reactions of alkynes is depicted as follows :

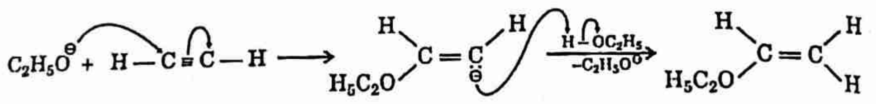


First, the nucleophile attacks the alkyne to form a vinyl carbanions which then takes up a proton to give the final product. Some important nucleophilic addition reactions are being discussed as follows :

(a) **Addition of alcohols :** Alkynes add on alcohols in the presence of base to give unsaturated ethers. (or substituted vinyl ethers)
For example,

$$\underset{\text{Acetylene}}{CH\equiv CH} + \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\text{Pot. ethoxide}]{C_2H_5O^{\ominus}K^{\oplus}} \underset{\text{Ethyl vinyl ether}}{CH_2=CH-OC_2H_5}$$

- **Mechanism :**

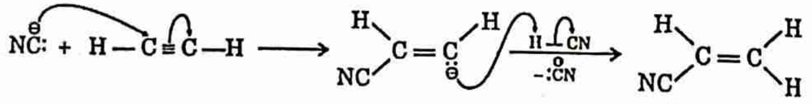


Ethyl vinyl ether

(b) **Addition of hydrogen cyanide :** Alkynes add on hydrogen cyanide in the presence of barium cyanide or cuprous chloride-catalysts to give vinyl cyanides.
For example,

$$\underset{\text{Acetylene}}{H-C\equiv C-H} + HCN \xrightarrow{Cu_2Cl_2} \underset{\text{Vinyl cyanide or Acrylonitrile}}{CH_2=CH-CN}$$

- **Mechanism :**

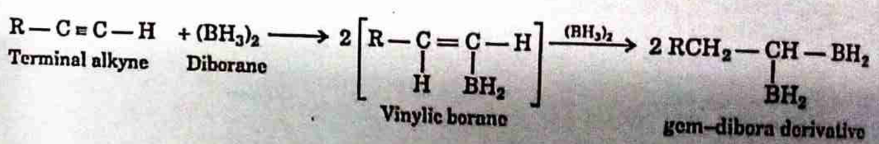


Vinyl cyanide

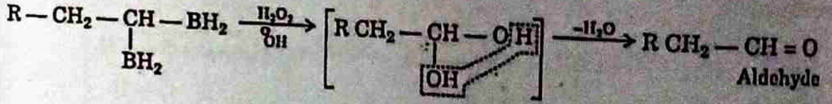
Oxidation Reactions

With different oxidising agents, alkynes give different products, as discussed below :

(a) **Hydroboration – Oxidation of alkynes**
Terminal alkynes react with diborane, to first form a **vinylic borane** and then a gem-dibora derivative which upon **oxidation** with alkaline hydrogen peroxide give aldehydes.

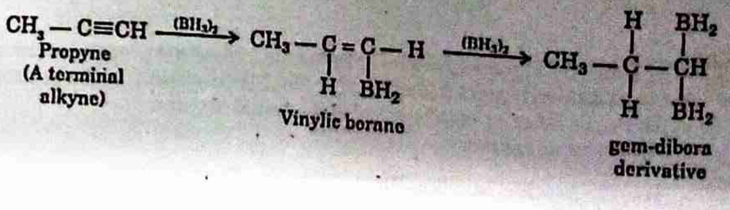


$$\underset{\text{Terminal alkyne}}{R-C\equiv C-H} + \underset{\text{Diborane}}{(BH_3)_2} \longrightarrow 2\underset{\text{Vinylic borane}}{\left[R-\underset{H}{C}=\underset{BH_2}{C}-H\right]} \xrightarrow{(BH_3)_2} \underset{\text{gem–dibora derivative}}{2\,RCH_2-CH-\underset{BH_2}{}BH_2}$$



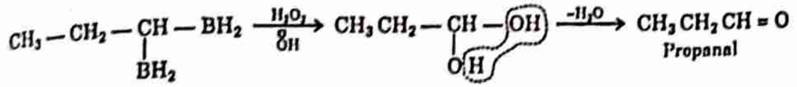
$$R-CH_2-\underset{BH_2}{CH}-BH_2 \xrightarrow[\overset{\ominus}{O}H]{H_2O_2} \left[R\,CH_2-\underset{OH}{CH}-OH\right] \xrightarrow{-H_2O} \underset{\text{Aldehyde}}{R\,CH_2-CH=O}$$

For example,



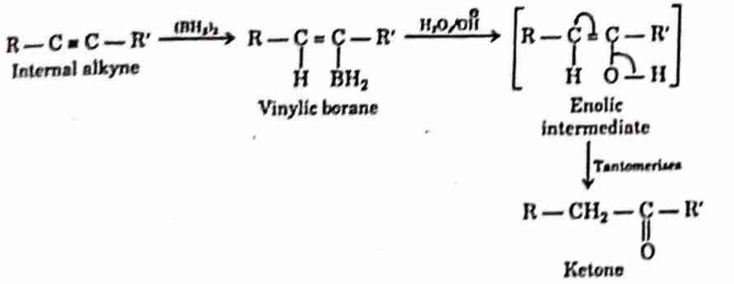
$$\underset{\text{Propyne (A terminal alkyne)}}{CH_3-C\equiv CH} \xrightarrow{(BH_3)_2} \underset{\text{Vinylic borane}}{CH_3-\underset{H}{C}=\underset{BH_2}{C}-H} \xrightarrow{(BH_3)_2} \underset{\text{gem-dibora derivative}}{CH_3-\overset{H}{\underset{H}{C}}-\overset{BH_2}{\underset{BH_2}{CH}}}$$

For example,

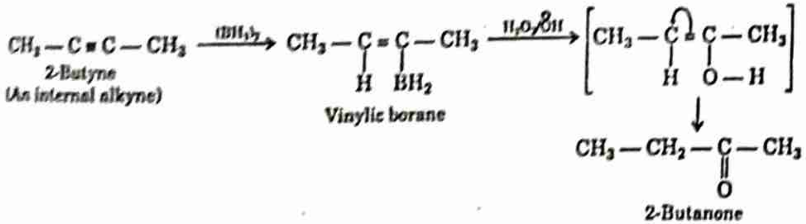


Note that the borane part gets attached to the less hindered triply bonded C-atom.

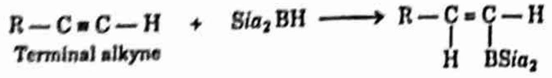
- In case of internal alkynes, hydroboration can be stopped at the vinylic stage by using a suitable amount of reagent. Oxidation with hydrogen peroxide, then results in the formation of ketones. :



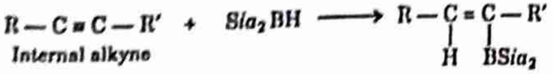
For example,



- With sterically hindered boranes, like *bis* (1, 2-dimethyl propyl) borane also known as disiamyl borane (abbreviated as *Sia*$_2$BH), the oxidation can be stopped at the vinylic stage for both terminal and internal alkynes.
This is shown as follows.

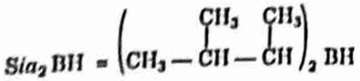


$$\underset{\text{Terminal alkyne}}{R-C\equiv C-H} + Sia_2BH \longrightarrow R-\underset{H}{\underset{|}{C}}=\underset{BSia_2}{\underset{|}{C}}-H$$



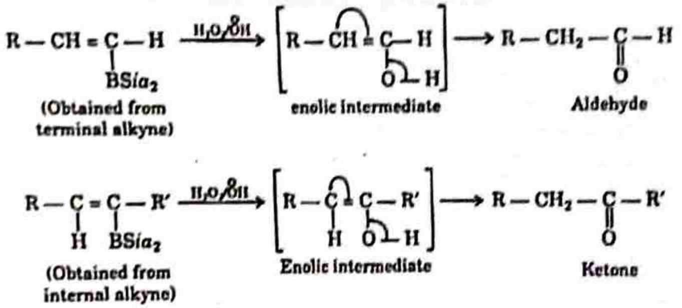
$$\underset{\text{Internal alkyne}}{R-C\equiv C-R'} + Sia_2BH \longrightarrow R-\underset{H}{\underset{|}{C}}=\underset{BSia_2}{\underset{|}{C}}-R'$$

where,



$$Sia_2BH = \left(CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}\right)_2 BH$$

Oxidation of these vinylic boranes with alkaline hydrogen peroxide then gives aldehydes/ketones via enolic intermediates. Here again, **terminal alkynes will give aldehydes and internal alkynes will give ketones.**



It may be noted here that hydroboration-oxidation results in Anti-Markownikoff's addition of – H and – OH.

QUESTIONS FOR PRACTICE

1. (a) Explain why 1, 3-butadine undergoes 1, 2 and 1, 4-addition.
   (b) What happens when 2-butyne is treated with :
      (i) Pd/$BaSO_4$ (Lindlar's catalyst)
      (ii) Sodium dissolved in liquid ammonia (M.D.U. 2003)
   (c) Give the mechanism of addition of Br_2 to 1, 3-butadiene.

2. (a) Write chemical equations for the following :
      (i) Propyne reacts with alkaline $KMnO_4$ at 298 K.
      (ii) 1, 3-Butadiene reacts with HBr at 313 K.
   (b) Explain why :
      (i) Alkynes undergo nucleophilic addition
      (ii) Conjugated dienes are more stable than isolated dienes.
   (c) Write chemical reactions for the following :
      (i) Acetylene reacts with ammonical cuprous chloride solution. (K.U.K. 2003)
3. Which one, out of 1, 4–and 1, 3 – pentadienes do you expect to be more stable and why? (M.D.U. 2012)
4. Convert 1, 3–Butadiene into cyclohexane. (K.U.K. 2012)
5. (a) Discuss the mechanism of :
      (i) Addition of Bromine to Buta-1, 3-diene.
      (ii) $CH_2 = CH—CH = CH_2 + HBr \xrightarrow[\text{(major product)}]{313\text{ K}}$ 1, 4-Adduct

   (K.U.K. 2007, 2012, 2013)

   (b) Though benzene is unsaturated hydrocarbon, yet it fails to give Baeyer's test. Explain.
   (c) Complete the equations :
      (i) $CH_3 — C \equiv C — CH_3 + H_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar}}$ (M.D.U. 2012), (K.U.K. 2007)
      (ii) $CH \equiv CH + 2Cl_2 \xrightarrow{CCl_4}$ (M.D.U. 2012), (K.U.K. 2007)
6. (a) Compare the reduction of alkynes with Lindlar's catalyst and with alkali metals in liquid ammonia.
   (b) How do you explain that alkynes undergo nucleophilic addition reaction but alkenes do not? (M.D.U. 2000)
7. Starting with acetylene, how would you synthesize the following compounds :
   (a) Acetaldehyde, (b) Acetone, (c) Benzene, (d) 1-Butyne, (e) 2-Butyne, (f) Chloropyrene, (g) 2-Butanone, (h) Vinyl bromide, (i) Vinylacetylene, (j) Vinylmethyl ether. (K.U.K. 2011)
8. (a) 1, 3-butadiene is more stable than 1, 4-pentadiene. Why?
   (b) Write short notes on :
      (i) Diel's Alder reaction.
9. (a) Give the mechanism for Birch reduction in 2-butyne.
   (b) Convert
      (i) Acetylene to Dichloroacetaldehyde
      (ii) Acetylene to Methylvinyl ether
   (c) How will you justify the extra stability of dienes?
   (d) Give the reaction of 1, 3-butadiene with maleic anhydride, also name the reaction. (H.P.U. 2003)

   (e) Differentiate between alkenes and alkynes based on spectral studies.
10. What are dienes? How do conjugated and cummulated dienes differ in their structures? (K.U.K. 1992)
11. Explain the following :
    (i) Mechanism of Diels-Alder reaction.
    (ii) Why Diels-Alder reaction is referred to the (4 + 2) cyclo-addition reaction. (M.D.U. 1999, 2006)

    (iii) Mechanism of free radical addition to conjugated dienes. (M.D.U. 2006)
12. Discuss the mechanism of 1, 2- and 1, 4-addition of 1, 3-butadiene.

4

Alkyl & Aryl Halides

I. ALKYL HALIDES

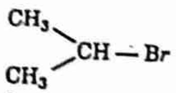
Introduction

Alkyl halides are the compounds obtained by the replacement of a hydrogen atom of an alkane by a halogen atom. Or, they may be simply regarded as monohalogen derivatives of alkanes. They may be represented by the general formula $C_nH_{2n+1}X$ or as $R-X$ (where R is an alkyl group).

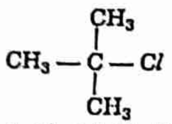
For example,

CH_3Cl

Methyl chloride
or
chloro methane



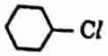
Isopropyl bromide
or
2-Bromo propane



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

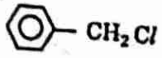
tert-butyl chloride
or
2-chloro-2-methyl
propane

Alkyl halides also include the molohalogen derivatives of cycloalkanes. For example,



Cyclohexyl chloride
or
chlorocyclo hexane

Alkyl halides also include the monohalogen side-chain derivatives of alkyl benzenes. For example,



Benzyl chloride
or
phenyl chloro methane

Classification of Alkyl Halides

Alkyl halides may be classified as primary, secondary or tertiary depending upon the nature of the carbon atom to which the halogen is attached :

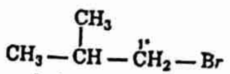
(i) **Primary alkyl halides :** When the halogen atom is attached to a 1° carbon atom. For example,

$CH_3\overset{1^\circ}{C}H_2-Cl$

Ethyl chloride

$CH_3-CH_2-\overset{1^\circ}{C}H_2-Br$

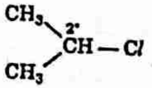
n–Propyl bromide



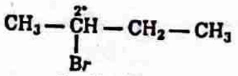
$$CH_3-\overset{CH_3}{CH}-\overset{1^\circ}{C}H_2-Br$$

Isobutyl bromide
or
1–Bromo–2–methyl
propane

(ii) **Secondary (Sec) alkyl halides :** When the halogen atom is attached to a 2° carbon atom. For example,



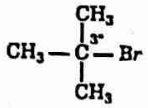
Isopropyl chloride
or
2-chloropropane



$$CH_3-\underset{Br}{\overset{2^\circ}{C}H}-CH_2-CH_3$$

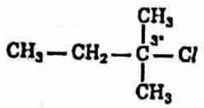
Sec-Butyl bromide
or
2-Bromo butane

(iii) **Tertiary (tert.–) alkyl halides :** When the halogen atom is attached to a 3° carbon atom. For example,



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{3^\circ}{C}}}-Br$$

tert-Butyl bromide
or
2-Bromo-2-methyl
propane



$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{3^\circ}{C}}}-Cl$$

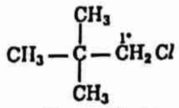
tert-Pentyl chloride
or
2-Chloro-2-methylbutane

- It may be noted that fluoroalkanes or fluoroderivatives of alkanes differ widely from the chloro-bromo-iodo-derivatives and are treated separately. Hence, in this chapter, we shall limit our discussion to alkyl chlorides, bromides and iodides only.

Nomenclature of Alkyl Halides

There are two systems of nomenclature :

(i) **Common System :** Under this system, the individual alkyl halides are called as halides of the particular alkyl group present in the molecule. For example, CH_3Cl is called as methyl chloride.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{1^\circ}{C}H_2Cl$$

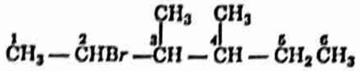
neo–Pentyl chloride
or
1-Chloro–2, 2–dimethyl propane

(ii) **IUPAC System :** Under this system, the alkyl halides are named, as per the following rules :

(a) The longest straight chain of C–atoms including the carbon carrying the halogen atom is chosen as the parent alkane.

(b) The carbon chain is then number in such a manner that the C-atom carrying the halogen atom gets the samllest number.

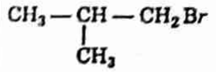
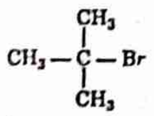
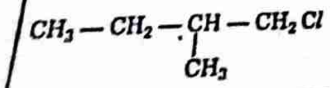
(c) The names and positions of the sides chains and the halogen are prefixed before the name of the parent alkane. For example,

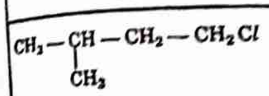
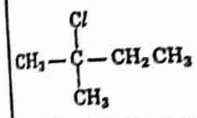
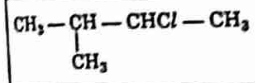
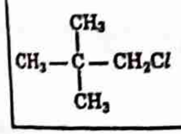


$$\overset{1}{C}H_3-\overset{2}{C}HBr-\overset{3}{\underset{}{C}}H(CH_3)-\overset{4}{C}H(CH_3)-\overset{5}{C}H_2\overset{6}{C}H_3$$

2-Bromo-3, 4-dimethyl hexane

The IUPAC and common names of some alkyl halides are listed in the table below :

Formula	Common Name	IUPAC Name
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-I	Ethyl iodide	Iodoethane
$CH_3-CH_2-CH_2-Br$	*n*-Propyl bromide	1-bromopropane
$CH_3-CHBr-CH_3$	Isopropyl bromide	2-Bromopropane
$CH_3-CH_2-CH_2-CH_2Br$	*n*-Butyl bromide	1-Bromobutane
$CH_3-CH_2-CHBr-CH_3$	*sec*-Butyl bromide	2-Bromobutane
 $CH_3-CH(CH_3)-CH_2Br$	isobutyl bromide	1-Bromo-2-methyl propane
 $CH_3-C(CH_3)_2-Br$	tert-butyl bromide	2-Bromo-2-methyl propane
$CH_3-CH_2-CH_2-CH_2-CH_2Cl$	*n*-Pentyl chloride	1-Chloropentane
$CH_3-CH_2-CH_2-CHCl-CH_3$		2-Chloropentane
$CH_3-CH_2-CHCl-CH_2-CH_3$		3-Chloropentane
 $CH_3-CH_2-CH(CH_3)-CH_2Cl$		1-Chloro-2-methyl butane

Formula	Common Name	IUPAC Name
 $CH_3-CH(CH_3)-CH_2-CH_2Cl$		1-Chloro-3-methyl butane
 $CH_3-CCl(CH_3)-CH_2CH_3$		2-Chloro-2-methyl butane
 $CH_3-CH(CH_3)-CHCl-CH_3$		2-Chloro-3-methyl butane
 $CH_3-C(CH_3)_2-CH_2Cl$	Neopentyl chloride	1-chloro-2, 2-dimethyl propane

Methods of Preparation of Alkyl Halides

(1) **By halogenation of Alkanes :** Alkyl halides may be prepared by the direct halogenation of alkanes in the presence of light.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloro methane}}{CH_3Cl} + HCl$$

- However, direct halogen does not give pure mono halogen derivative, rather a mixture of polyhalogen derivatives is obtained even if alkane and halogen are taken in equimolar amounts.
  For example in chlorination of methane, chloromethane initially formed reacts further to give *di* – , *tri* – and tetra – chloromethane.

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\substack{\text{Dichloromethane}\\ \text{Or}\\ \text{Methylene chloride}}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\substack{\text{Thrichloro methane}\\ \text{or}\\ \text{chloroform}}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

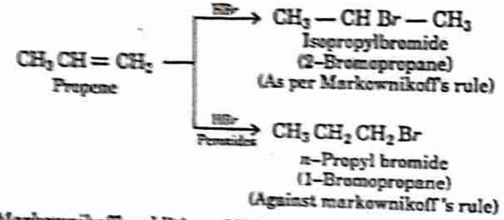
- In case of mono halogenation, a mixture of isomeric monosubstituted products is obtained. For example, chlorination of propane gives both *n*-propyl chloride and isopropyl chloride.

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[HCl]{Cl_2/hv} \underset{n\text{-Propyl chloride}}{CH_3-CH_2-CH_2-Cl} + \underset{\text{Isopropyl chloride}}{CH_3-CHCl-CH_3}$$

(2) **By addition of hydrogen halides to alkenes :** Alkenes add on hydrogen halides (or halogen acids) to give alkyl halides. For example,

$$\underset{\text{Ethene}}{CH_2=CH_2 + HCl} \longrightarrow \underset{\text{Ethyl chloride}}{CH_3CH_2Cl}$$

The addition occurs in accordance with Markownikoff's rule. But if carried out in the presence of peroxides, the addition occurs against Markownikoff's rule. For example,



This Anti-Markownikoff's addition of HBr to alkenes which occurs in the presence of peroxides is referred to as the **Anti-Markownikoff Effect or Peroxide Effect or Kharasch Effect.** Note that this effect is observable only for HBr.

(3) **From Alcohols :** Alkyl halides can be prepared from alcohols by 3 ways :

(a) By reaction of alcohols with hydrogen halides

$$R-OH + H-X \longrightarrow R-X + H_2O$$

- The order of reactivity of various hydrogen halides (or halogen acids) towards alcohols is :

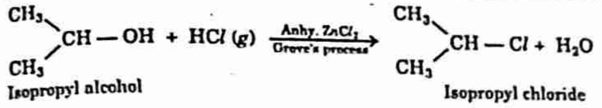
$$HI > HBr > HCl$$

The above order is the same as the order of nucleophilicity of various halide ions, *i.e.*,

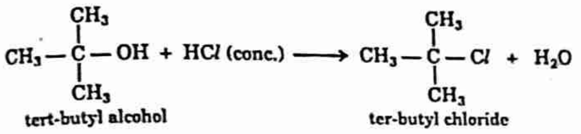
$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus}$$

- The order of reactivity of various alcohols towards halogen acids is : 3° > 2° > 1°. The above order of reactivity is evident from the fact that reaction of 1° and 2° alcohols with HCl required the use of a catalyst such as anhydrous is $ZnCl_2$ (reactions of ROH with HX in the presence of anhy. $ZnCl_2$ is referred to as **Grove's Process**). While reaction of 3° alcohols with HCl occurs in the absence of anhy. $ZnCl_2$. For example, consider the preparation of **Alkyl Chlorides.**

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + HCl(g) \xrightarrow[\text{Groove's Process}]{\text{Anhy } ZnCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl + H_2O}$$



$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CH-OH} + HCl(g) \xrightarrow[\text{Grove's process}]{\text{Anhy. } ZnCl_2} \underset{\text{Isopropyl chloride}}{(CH_3)_2CH-Cl} + H_2O$$



$$\underset{\text{tert-butyl alcohol}}{(CH_3)_3C-OH} + HCl\text{ (conc.)} \longrightarrow \underset{\text{ter-butyl chloride}}{(CH_3)_3C-Cl} + H_2O$$

- **Alkyl bromides :** are prepared by heating alcohol with excess of boiling HBr (48%) or by the reaction of alcohol with sodium bromide and concentrated sulphuric acid.

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + HBr\ (48\%) \longrightarrow \underset{\text{Ethyl bromide}}{CH_3CH_2-Br} + H_2O$$

$$CH_3CH_2OH + NaBr + H_2SO_4 \xrightarrow{\Delta} CH_3CH_2Br + H_2O + NaHSO_4$$

In the above reaction, HBr is produced insitu by the reaction of NaBr and conc. H_2SO_4 as follows :

$$NaBr + H_2SO_4 \longrightarrow HBr + NaHSO_4$$

- **Alkyl iodides** are prepared by heating alcohol with the excess of boiling HI (57%) or by the reaction of alcohol with potassium iodide and phosphoric acid.

$$\underset{\text{Methyl alcohol}}{CH_3-OH} + HI(57\%) \longrightarrow \underset{\text{Mithyl iodide}}{CH_3-I} + H_2O$$

$$CH_3OH + KI + H_3PO_4 \longrightarrow \underset{\text{Methyl iodide}}{CH_3-I} + H_2O + KH_2PO_4$$

Again, in the above reaction, HI is produced in situ by the reaction of KI and H_3PO_4 as follows :

$$KI + H_3PO_4 \longrightarrow HI + KH_2PO_4$$

(b) **By reaction of alcohols with phosphorous halides (PX_3 or PX_5)**

$$\underset{\text{Alcohol (Or } P+X_2)}{3\,ROH + PX_3} \longrightarrow \underset{\text{Alkyl halide}}{3\,R-X} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

$$\underset{\text{Alcohol}}{ROH} + PX_5 \longrightarrow \underset{\text{Alkyl halide}}{R-X} + POX_3 + HX$$

- **Alkyl Chloride** are produced by the reaction of alcohols with PCl_3 or PCl_5. For examples

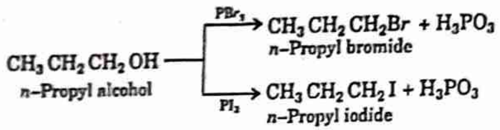
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + PCl_3 \longrightarrow \underset{\text{Ethyl chloride}}{3\,CH_3CH_2Cl} + H_3PO_3$$

$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} + PCl_5 \longrightarrow \underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} + HCl + POCl_3$$

- **Alkyl bromides and Alkyl iodides** are generally prepared by the reaction of alcohols with PBr_3 or PI_3, which are not very stable compounds and are generally prepared in situ by the reaction of red phosphorous on bromine or iodine

$$2P + 3Br_2 \rightarrow 2PBr_3$$

$$\text{or } 2P + 3I_2 \longrightarrow 2PI_3$$



$$CH_3CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2Br + H_3PO_3$$

$$CH_3CH_2CH_2OH \xrightarrow{PI_3} CH_3CH_2CH_2I + H_3PO_3$$

n–Propyl alcohol; n–Propyl bromide; n–Propyl iodide

(c) By reaction of alcohols with thionyl chloride ($SOCl_2$): Alkyl chlorides can be prepared by reflexing alcohols with thionyl chloride ($SOCl_2$) in the presence of pyridine

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Alkyl chloride}}{RCl} + SO_2\uparrow + HCl\uparrow$$

For example,

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

This method is the most preferred one for the preparation of alkyl chlorides, because the by products so formed *i.e.*, SO_2 and HCl, being gaseous escape the reaction mixture, leaving behind the product, *i.e.*, alkyl chloride in almost pure state.

(4) From silver salts of carboxylic acids Hundsdiecker Reaction) : Alkyl chlorides or bromides can also be prepared by reflexing silver salts of carboxylic acids with chloride or bromine in the presence of CCl_4. The reaction is referred to as **Hundsdiecker Reaction.**

$$RCOOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} RBr + CO_2 + AgBr$$

$$\text{e.g., } \underset{\text{Silver acetate}}{CH_3COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + CO_2 + AgBr$$

- However, with iodine, esters are obtained instead of alkyl iodides. This reaction is known as **Birnbaum – Simomini Reaction**.

$$2RCOOAg + I_2 \xrightarrow[\text{Reflux}]{CCl_4} RCOOR + 2AgI + CO_2$$

(5) By halide exchange (Finkelstein Reaction) : Alkyl iodides can be easily prepared from the corresponding alkyl chlorides or bromides by treating them with a solution of sodium iodide in acetone. The iodide ion, being a very good nucleophile, displaces the other halogen from alkyl halide to give alkyl iodides.

$$\underset{\text{Alkyl bromides}}{R-Br} + NaI \xrightarrow{\text{Acetone}} \underset{\text{Alkyl iodide}}{R-I} + NaBr$$

Similarly, alkyl fluorides can be prepared from the corresponding alkyl chlorides or bromides with inorganic fluorides.

$$2RCl + HgF_2 \xrightarrow{0°C} 2RF + HgCl_2$$

Physical Properties of Alkyl Halides

(1) Physical state colour and odour

- Lower alkyl halides like CH_3Cl, CH_3Br, CH_3I are colourless gases, while higher members with high molecular weights are solids.
- CH_3I and majority of members are colourless, pleasant smelling liquids.
- Alkyl iodides turn brown upon standing due to decomposition by light.

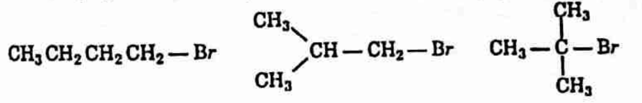
(2) Solubility : Though alkyl halides are polar molecules, yet they are insoluble in H_2O.
Reason : Since alkyl halides cannot form hydrogen bonds with water, hence they are water – insoluble. However, they are soluble in organic solvents.

(3) Boiling Points

- Alkyl halides have considerably higher b.pts. than the corresponding hydrocarbons.
  Reason : This is because alkyl halides have higher molecular masses and are also polar in nature.
- For a given alkyl group, the boiling points of various halides follow the order :

$$RCl < RBr < RI$$

  Reason : This can be explained on the basis of increased in the mol. mass of the halide leading to greater inter-molecular forces of attraction.
- For a given halogen, the b.pts. of alkyl halides increase with the increase in the size of the alkyl group.
  Reason : This again can be attributed to the increase in molecular mass leading to greater inter molecular forces of attraction.
- Amongst isomeric alkyl halides, the boiling points decrease with branching. For example, consider the b.pts. of various isomers of C_4H_9Br.



Bpt. K 374.6 K 364.7 K 346 K

Reason : With branching, the surface area and hence the Vander Waal's forces of attraction decrease and so does the bpt.

(4) Density

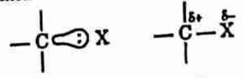
- Alkyl chlorides are lighter than water while bromides and iodides are heavier.
- For a particular alkyl group, the densities of the halides follow the order :

$$RCl < RBr < RI$$

I. Chemical Properties of Alkyl halides

Due to the presence of a polar carbon-halogen bond, alkyl halides are quite reactive and undergo a variety of reactions like nucleophilic substitutions elimination, reduction etc. Some important reactions are being discussed as follows :

(1) Nucleophilic Substitution Reactions : Due to high electronegativity of halogen atom as compared to carbon the C – X band is polar with the halogen atom (X) acquiring a small negative charge and the carbon atom acquiring a small positive charge.



Polorised C–X bond

The positively polarised C-atom is susceptible to attack by nucleophilic reagents. Thus in the presence of strong nucliophiles like $\overset{\ominus}{O}H$, $\overset{\ominus}{C}N$ etc. the halide ion (a weak nucleophile) is readily displaced. Thus, **alkyl halides undergo a variety of nucleophilic substitution reactions.**

$$Nu:^{\ominus} + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow \underset{\text{Substitution product}}{R-Nu} + X:^{\ominus}$$

The reaction involves the heterolytic cleavage of C–X bond, with the halogen atom departing with the pair of electrons (acts a leaving group) and the electrons brought by the nucleophile are used in the form of a new band of C-atom with the nucleophile.

- **Order of Reactivity among the various alkyl halides :** The reactivity depends upon the strength of carbon-halogen band stronger the C – X band, lesser will be the reactivity.

Thus the reactivity of various alkyl halides increased in the order :

$$R-F < R-Cl < R-Br < R-I$$

Due to small size of fluorine atom, the C – F bond has the smallest bond length, and therefore, the C – F bond has the maximum strength and thus, alkyl fluorides are the least reactive. As the size of the halogen atom increases on moving from F → Cl → Br → I, the corresponding carbon – halogen bond length increases and hence reactivity increases and this explains the above reactivity order of alkyl halides. The order of reactivity may also be explained on the basis of ease of elimination of the leaving groups which follows the order :

$$I^{\ominus} < Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

Better the leaving group, more will be the rate of nucleophilic substitution reaction. Hence alkyl iodides have the maximum reactivity and alkyl fluorides have the least. Some important nucleophilic substitution reactions of alkyl halides are listed as follows :

(a) **Substitution by hydroxyl group-formation of alcohols :** Alkyl halides when treated with aqueous NaOH or KOH solution or with moist silver oxide (AgOH) or Ag_2O/H_2O, give rise to alcohols.

$$R-X + \overset{\oplus}{K}\overset{\ominus}{O}H_{(aq.)} \longrightarrow \underset{\text{Alcohol}}{R-OH} + KX$$

$$R-X + \overset{\oplus}{Ag}\overset{\ominus}{O}H \longrightarrow \underset{\text{Alcohol}}{R-OH} + AgX$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2-Br} + \overset{\oplus\ominus}{KOH}\,(aq.) \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + KBr$$

(b) **Substitution of alkoxy group – Formation of ethers Alkyl halides upon reaction with sodium or potassium alkoxides, give rise to ethers. The reaction is referred to as Williamson's synthesis.**

$$R-X + \underset{\text{Sod. alkoxide}}{\overset{\oplus}{Na}\overset{\ominus}{O}R'} \longrightarrow \underset{\text{Ether}}{R-OR'} + NaX$$

eg. $$\underset{\text{Methyl bromide}}{CH_3-Br} + \underset{\text{Sod. ethoxide}}{\overset{\oplus}{Na}\overset{\ominus}{O}C_2H_5} \longrightarrow \underset{\text{Ethyl methyl ehter}}{CH_3-O-C_2H_5} + NaBr$$

Ethers are also formed by reaction of alkyl halides with dry silver oxide.

$$2CH_3-Br + \underset{(dry)}{Ag_2O} \longrightarrow \underset{\text{Dimethyl ether}}{CH_3-O-CH_3} + 2AgBr$$

(c) **Substitution by cyano group**
– Formation of nitrites or cyanides
Alkyl halides upon reaction with alcoholic solution of potassium cyanide, give rise to cyanides or nitrites.

$$R-X + \overset{\oplus}{K}\overset{\ominus}{C}N\,(alc.) \longrightarrow \underset{\substack{\text{Alkyl cyanide}\\ \text{or alkane nitrite}}}{R-CN} + KX$$

eg. $$CH\,CH_2-Br + \overset{\oplus}{K}\overset{\ominus}{C}N \longrightarrow \underset{\substack{\text{Ethyl cyanide}\\ \text{or}\\ \text{propane nitrile}}}{CH_3CH_2-CN} + KBr$$

Alkyl cyanides can be further converted into amides, acids or amines by the following methods : For example,

$$\underset{\substack{\text{Ethyl cyanide}\\ \text{or}\\ \text{Propane nitrile}}}{CH_3CH_2-CN} \xrightarrow[\text{Partial hydrolysis}]{\text{Alkaline } H_2O_2} \underset{\text{Propanamide}}{CH_3CH_2CONH_2}$$

$$CH_3CH_2-CN \xrightarrow[\text{Complete hydrolysis}]{\text{dil. acid or alkali}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

$$CH_3CH_2-CN \xrightarrow[\substack{\text{(Mendius reduction)}\\ \text{or}\\ H_2/Ni \text{ or } LiAlH_4}]{Na/C_2H_5OH} \underset{\text{Propanamine}}{CH_3CH_2CH_2NH_2}$$

(d) **Substitution by Isocyanide group**
– Formation of isocyanides or isonitrites
Alkyl halides upon reaction with silver cyanide at high temperature give rise to isocyanides.

$$R-X + Ag-CN \longrightarrow \underset{\text{Isocyanide}}{R-N{\equiv}C} + AgX$$

$$CH_3-I + Ag-CN \longrightarrow \underset{\text{Methyl isocyamide}}{CH_3-N{\equiv}C} + AgI$$

• Note : With alcoholic NaCN or KCN, cyanides are formed while with Ag CN, isocyanides are formed.

Mechanism & Stereochemistry of Nucleophilic Substitution Reactions

Alkyl halides undergo nucleophilic substitution reaction by either of the two possible mechanisms.

(i) Bimolecular nucleophilic substitution ($S_N{}^2$)

(ii) Unimolecular nucleophilic substitution ($S_N{}^1$).

Both these mechanisms are being discussed as follows :

(a) **Bimolecular Nucleophilic substitution ($S_N{}^2$)**

Consider the hydrolysis of methyl bromide to methyl alcohol.

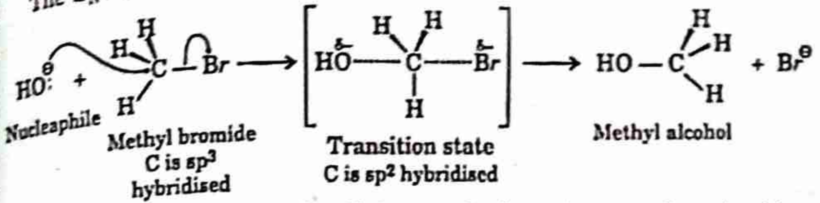
$$\overset{\ominus}{HO} + CH_3 - Br \longrightarrow HO - CH_3 + \overset{\ominus}{Br}$$

- The reaction occurs by a **concerted mechanism** *i.e.* occurs in a **single step** involving the attack of $\overset{\ominus}{OH}$ ion and simultaneous loss of $\overset{\ominus}{Br}$ ion. The single step mechanism is evidenced by the fact that the rate of reaction is found to depend both on the concentration of alkyl halide and hydroxide ion.

$$\text{Rate} \propto [CH_3 Br]\,[\bar{O}H]$$

Thus the reaction follows **second order kinetics**.

- **The S_N^2 mechanism may be shown as follows :**



- **It may be noted that the hydroxide ion attacks the carbon atom from the side opposite to that of Bromine in order to avoid repulsion by the negatively polarised bromine. This is known as the back side attack and results in inversion of configuration.** (stereochemical evidence discussed later).
- **In the transition state the bond between carbon and hydroxide ion is partically formed and the bond between carbon and bromine is partially broken. As the electrons on hydroxide ion begin to be shared by carbon, the negative charge on hydroxide ion decreases and acquires a partial negative charge. In a similar manner, bromine has partially begun to remove the electrons but not completely bromine also begins to develop a partial negative charge but not a full negative charge.**

The energy profile diagram for a $S_N{}^2$ reaction is shown below.

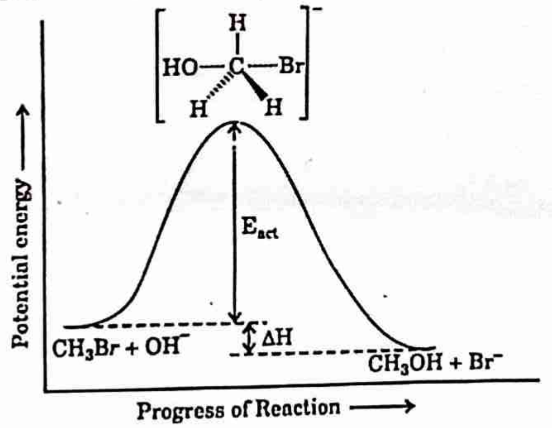
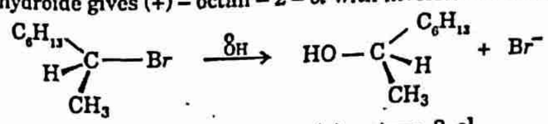


Fig. 4.1 Potential energy diagram for S_N2 reaction.

- **Stereochemistry of $S_N{}^2$ Reactions :** Due to the backside attack of the nucleophile, inversion of configuration occurs i.e. we get a product with configuration opposite to that of the reactant. This inversion of configuration is also referred to as 'Walden Inversion'. This is supported by the fact that hydrolysis of (–)–2-Bromoctane with sodium hydroide gives (+)–octan–2–*ol* with inversion of configuration.

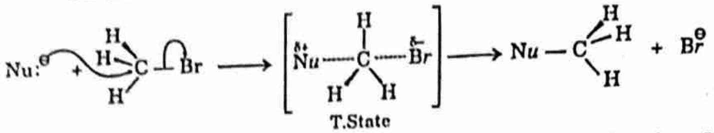


(–)–2–Bromo octane
[x] = –34.6°

(+)– octane–2–ol
[x] = +9.9°

- **Factors affecting $S_N{}^2$ Reactions**

(a) **Nature of alkyl group in alkyl halide (Steric Effect)**
As seen from the mechanism, the tetrahedral C-atom carrying the halogen in the alkyl halide, becomes pentavalent in the T.S. For example again consider the attack of a nucleophile on methyl bromide



In this case, the C-atom in the transition state is attached to three H-atoms along with halogen and nucleophile, *i.e.* C-atom is pentavalent. As the H-atom's are successively replaced by alkyl groups and also further as the size of the alkyl groups increases, crowding around the central C-atom increases giving rise to strong non-bonded interactions. As a result, energy of the T.S. increases and consequently, the energy of activation for its formation also increases and hence the rate of reaction decreases. Thus the order of reactivity of alkyl halides (having the same halogen) towards $S_N{}^2$ reactions follows the order :
Methyl halide > primary halide > Secondary halide > Tertiary halide.

(b) **Nature of halogen in alkyl halide :** The reactivity of alkyl halides towards S_N2 reaction also depends upon the nature of the leaving group i.e. the halide ion ($X^{\ominus}$). Weaker the base, the more is the ability of $X^{\ominus}$ to accommodate the negative charge, and thus better will be the leaving group. The more easily the $X^{\ominus}$ ion is eliminated, more will be the rate of reaction.
The basic strength of halide ions increase in the order :

$$I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$$

The case of elimination of halide ion would thus follow the reverse order :

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

Hence the order of reactivity of various alkyl halides will be the same as the leaving group ability *i.e.,*

$$R-I > R-Br > R-Cl > R-F$$

(c) **Nature of attacking nucleophile**
Stronger the nucleophile, faster will be the rate of S_N2 reaction. A few common nucleophiles arranged in decreasing order of their strength are given as under:

$$\overset{\ominus}{C}N > \overset{\ominus}{I} > CH_3CH_2\overset{\ominus}{O} > \overset{\ominus}{O}H > C_6H_5\overset{\ominus}{O} > \overset{\ominus}{Cl} > R_3\ddot{N} > CH_3CO\overset{\ominus}{O} > H_2O > F^{\ominus}$$

(d) **Nature of solvent medium :** In S_N2 reactions, the transition state is less polar than the reactants as the negative charged is dispersed over different atoms.

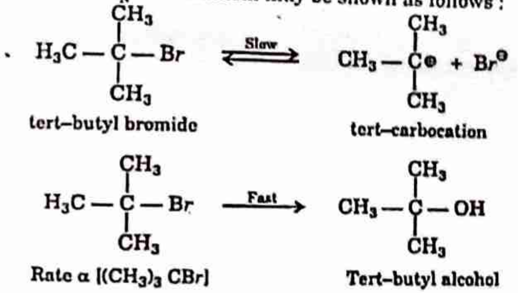
$$\underset{\text{Mole polar reactants}}{Nu\overset{\ominus}{:} + \overset{+\delta}{R}-\overset{-\delta}{X}} \longrightarrow \underset{\substack{\text{Transition state}\\ \text{(Less polar)}}}{\left[\overset{\delta-}{Nu}\text{----}R\text{----}\overset{\delta-}{X}\right]} \longrightarrow Nu-R+X^{\ominus}$$

Thus increase in polarity of the solvent will lower the energy of the polar reactants more than the less polar transition state. Overall, the energy of activation for the reaction will increase leading to a decrease in the rate of reaction.

(b) **Unimolecular Nucleophilic Substitution ($S_N{}^1$)**
Consider the hydrolysis of tert-butyl bromide to tert-butyl alcohol.

$$\underset{\text{tert– butyl bromide}}{(CH_3)_3C-Br} + \overset{\ominus}{O}H \longrightarrow \underset{\text{tert–butyl alcohol}}{(CH_3)_3C-OH} + Br^{\ominus}$$

- The reaction occurs by a two - step mechanism. The first step involves slow and reversible dissociation of alkyl halide to alkyl carbocation and the halide ion. The second step fast involves nucleophilic attack by the hydroxide ion on the alkyl carbocation to yield an alcohol.
- The reaction follows **first-order kinetics** and the rate of reaction is found to depend on the concentration of alkyl halide. This indicates that the first step involving the dissociation of alkyl halide is the slow, rate-determining process and that the attack of nucleophile occurs in a fast step.
- Thus, the S_N1 mechanism may be shown as follows :



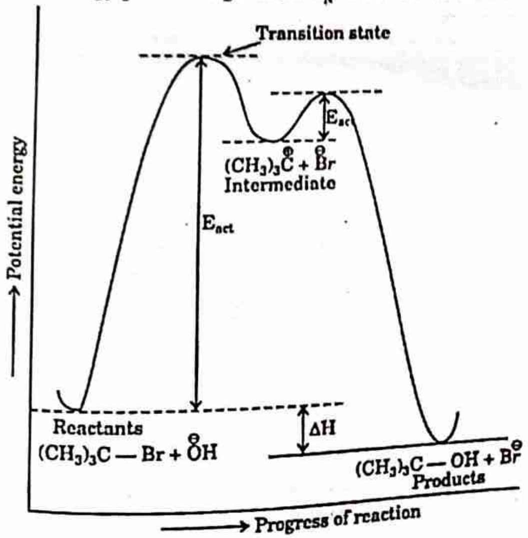
$$\underset{\text{tert–butyl bromide}}{H_3C-C(CH_3)_2-Br} \overset{\text{Slow}}{\rightleftharpoons} \underset{\text{tert–carbocation}}{CH_3-\overset{\oplus}{C}(CH_3)_2} + Br^{\ominus}$$

$$H_3C-C(CH_3)_2-Br \xrightarrow{\text{Fast}} \underset{\text{Tert–butyl alcohol}}{CH_3-C(CH_3)_2-OH}$$

Rate α [(CH₃)₃ CBr]

It may be noted that the energy required to break the C–Br bond is provided by the solvation of the ions thus produced.

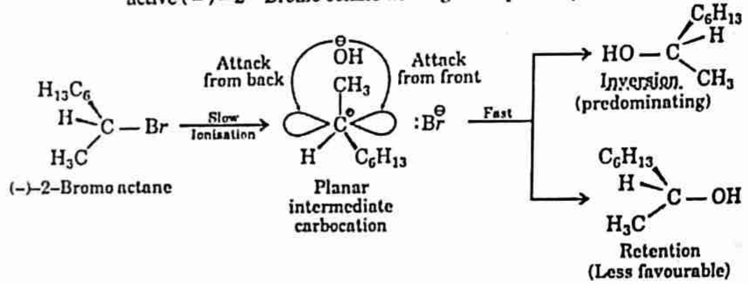
- The energy profile diagram for S_N1 reaction is shown as follows :



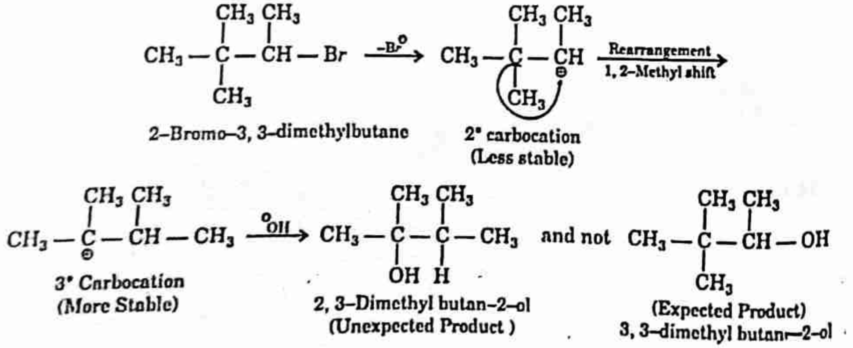
From the energy profile diagram it may be seen that the energy of activation E_{act} for the first step is much more than that of the second step $E_{act'}$. This suggests that the formation of carbocation is the rate determining step of the reaction.

- **Stereo Chemistry of SN¹ reactions :** The undermediate carbocation so formed is a planar species which can be attacked by the nucleophile from either face, the product thus obtained is a race mic mixture. Attack from the front side (i.e. the same side as the halogen) gives a product with the same configuration as the parent alkyl halide. While attack from the back side/side opposite to that of the halogen) gives a product with the inverted configuration. The back side attack however, is some what preferred over the front side attack. This means that the product consists of a mixture of enantiomers but the enantiomer with the inverted configuration predominates leading to partial vacumisation.

The stereochemical course of S_N1 reaction is evidenced by the hydrolysis of optically active (–)–2–Bromo octane which gives a partially vacumised product.



- **Rearrangements in S_N1 Reactions :** S_N1 reactions often give rise to unexpected rearranged products. This is because the intermediate carbocation so formed may rearrange to form more stable carbocation whereas possible. For example, the hydrolysis of 2-Bromo- 3, 3-dimethyl butane gives the unexpected product 2, 3-dimethyl butan-2-ol instead of the expected 3, 3-Dimethyl butan-2-ol.



The unexpected product arises due to the rearrangement of the initially formed 2° carbocation to the more stable 3° carbocation.

- **Factor affecting S_N1 Reactions**

  (a) **Nature of alkyl halide (Electronic Factor) :** Since formation of the carbocation intermediate is the rate determining step of the reaction. Therefore, the relative reactivities of alkyl halides follow the same order as the relative stabilities of carbocation. As stable the carbocation, greater will be its ease of formation and faster will be the rate of the reaction. Thus, parallel to the order of relative stabilities of carbocations, the order of relative reactivities of alkyl halides towards S_N1 reaction is found to be :

  Tertiary alkyl halides > secondary alkyl halides > Primary alkyl halides > Methyl halides

  (b) **Nature of halogen in alkyl halides :** As the rate determining step in S_N1 reactions involves the ionisation of alkyl halide to form the carbocation, thus, better the leaving group, faster will be the formation of carbocation and more will be the rate of reaction. The ease of elimination of various halide ions follows the order :

  $$I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$$

  Hence the order of reactivity of various alkyl halides will be the same as the leaving group ability, i.e. $R-I > R-Br > R-Cl > R-F$.

  It may be noted here that the nature of halogen influences both the S_N1 and S_N2 reactions in a similar manner.

  (c) **Nature of attacking nucleophile :** Since the nucleophile is not involved in the rate determining step of S_N1 reaction, therefore, its nature does not influence much the rate of reaction. However, weak nucleophiles tend to prefer to S_N1 mechanism, since it is easier for them to attack the carbocation rather than to push the halogen away from the alkyl and halide, as is the requirement of S_N2 mechanism. Thus, in general, strong nucleophiles like $\overset{\ominus}{O}H$ & $\overset{\ominus}{O}R$ ions favour S_N2 mechanism while weak nucleophiles like alcohol, water favour S_N1 mechanism, (but their nature does not influence the rate of S_N1 reactions).

  (d) **Nature of solvent medium :** Increase in polarity of the solvent facilitates the formation of carbocation. This is because in S_N1 reaction, the transition state for the rate determining step (*i.e.* the Transition the transition state for the rate determining step (*i.e.* the Transition state which leads to the carbocation or T.S. of step 1 of mechanism) is more polar than the reactants.

  $$R - X \longrightarrow \underset{\text{T.S. more polar than reactants}}{\left[\overset{\delta+}{R}\cdots\cdots\overset{\delta-}{X}\right]} \longrightarrow R^{\oplus} + X^{\ominus}$$

  Thus, a polar transition state is strongly stabilised by a polar solvent due to dipole-dipole interactions. This lowers the energy of activation of the rate determining step, thereby, increasing the rate of reaction.

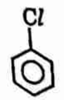
Comparison of S_N1 & S_N2

S.No.	S_N2 Reaction	S_N1 Reaction
1.	Involves a single step mechanism.	Involves a two step mechanism.
2.	No intermediate is involved.	Reactions involves formation of carbocation intermediate.
3.	Reaction follows second order kinetics.	Reaction follows first order kinetics.
4.	Due to the exclusive back side attack by the nucleophile, we get a product with inverted configuration.	The flat carbocation may be attacked by the nucleophile form both the front and back sides, although the back side attack predominates. Thus we get a product with partial vacumisation.
5.	Order of reactivity of alkyl halides is : Methyl > 1° > 2° > 3° halides.	Order of reactivity of alkyl halides is : 3° > 2° > 1° > Methyl halides
6.	Rearranged products are not obtained.	Rearranged product are obtained.
7.	Reaction is favoured by strong nucleophiles.	Reaction is favoured by mild nucleophiles.
8.	Reaction rate is controlled by steric factors.	Reaction rate is controlled by electronic factors.
9.	Reaction is favoured by solvents of low polarity.	Reaction is favoured by solvents of high polarity.
10.	Favoured by high concentration of nucleophiles.	Favoured by low concentration of nucleophiles.

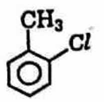
II. ARYL HALIDES

Introduction

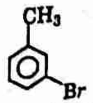
Aryl halides are aromatic compounds in which the halogen atom is directly attached to the aromatic ring. For example, chlorobenzene, o–chlorotoluene, m-bromo toluene etc are some examples of aryl halides.



Chloro benzene



o–Chloro toluene

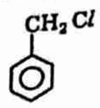


m–Bromo toluene

p–dichloro benzene

They are represented by the general formula Ar–X, where Ar represents an aryl group.

It must be noted that aryl halides do not include those aromatic halogen compounds in which halogen is present in the side chain. For example, benzyl chloride is not an aryl halides. Rather such compounds are referred to as **aralkyl halides** (i.e. aryl susbstituted alkyl halides).

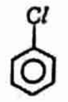


Benzyl chloride
(an aralkyl halide)

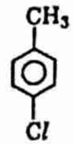
Aralkyl halides are entirely different from aryl halides in their properties and are studied as a different class altogehter.

Nomenclature

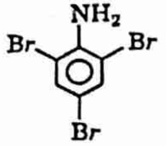
Aryl halides are named by prefixing the name of the halogen to the name of the parent aromatic compound. If more than one halogen atoms are present on the ring, the name of the halogen is then preceded by the prefixes



Chloro benzene



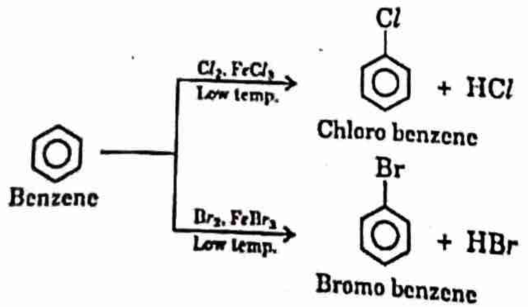
p–Chlorotoluene



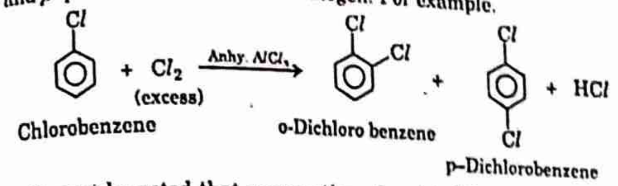
2, 4, 6, Tribromo aniline

Methods of Preparation

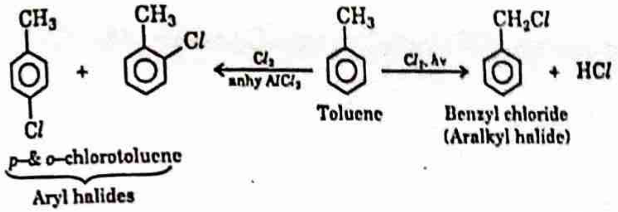
1. **By Nuclear Halogenation :** Aryl chlorides and bromides can be prepared by direct halogenation of the aromatic ring. The reaction is carried out by treating benzene or any other substituted benzene with chlorine or bromine **at low temperature and in the absence of sunlight and in the presence of Lewis acids catalysts** such as ferric halides or aluminium halides. The function of the catalyst is to act as **a halogen carrier.** The reaction may also be carried out with some iron fillings and halogen which reacts to give the corresponding Lewis acid ferric halide. For example, ferric chloride can be generated in situ by the reaction between iron and chlorine.



If excess of halogen is used, then the second halogen gets introduced in the ring at *o*– and *p*–positions w.r.t. the first halogen. For example,



- It must be noted that preparation of aryl halides must be carried out in the absence of sunlight and in the presence of Lewis acid catalyst. For if halogenation is carried out **in the presence of sunlight and in the absence of Lewis acid catalysts alkyl benzenes give rise to aralkyl halides,** i.e. halogenation then occurs in the side chain and not in the aromatic ring. For example, consider halogenation of toluene under the two opposing conditions.



- Aryl iodides cannot be prepared by direct halogenation as HI produced during the reaction makes it reversible. Thus the process requires the use of an oxidising agent such as HNO_3, HIO_3 etc. in order to shift the process in the forward reaction by removing HI.

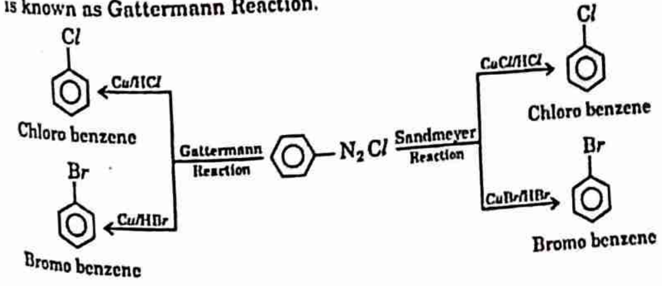
$$C_6H_6 + I_2 \xrightleftharpoons{AlCl_3} C_6H_5-I + HI$$

$$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

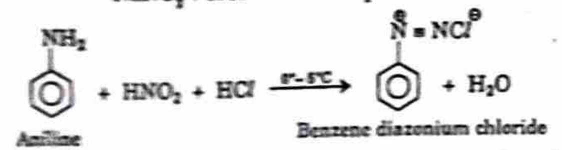
- Aryl fluoride cannot be prepared by the above method since the reaction is very violent.

2. **By decomposition of diazonium salts:** Aryl chlorides and bromides may be prepared from **Sandmeyer's or Gattermann** Reaction.
   Sand meyer's Reaction involves the reaction of diazonium salt with cuprous chloride dissolved in HCl or cuprous bromide in HBr.
   If copper powder is used in place of CuCl or CuBr, with HCl or HBr, then the reaction is known as Gattermann Reaction.

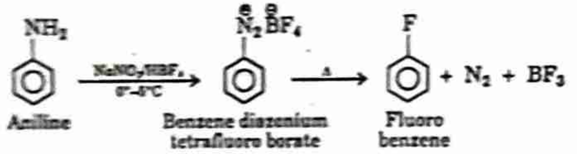


Diazonium salts required for the purpose are generated by the reaction of aromatic amines with nitrous acid. Nitrous acid is generated insitu by the reaction of sodium nitrite and HCl.

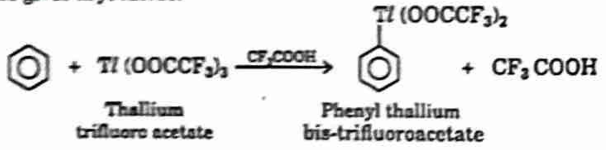
$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

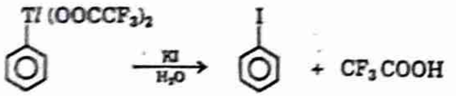


Aryl fluorides are prepared by decomposing diazanium tetrafluoroborates by heating. The reaction is referred to as Balz-Schiemann Reaction.

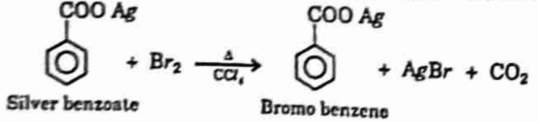


3. **From Organothallium Compounds:** Arenes when treated with thallium tri fluoro acetate in trifluoro acetic acid, undergo aromatic electrophile substitution to form aryl thalloum bis-trifluoroacetate. The latter compound upon reaction with potassium iodide gives aryl idoide.





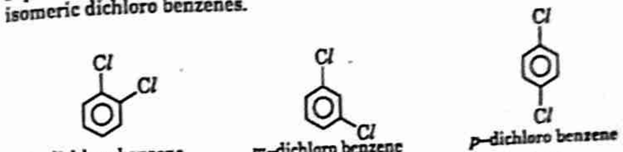
4. **By Hundsdiecker Reaction :** Aryl bromides may be prepared from silver salts of aromatic acids upon treatment with bromine in carbon tetrachloride.



Physical Properties

1. **Physical state, colour and odour :** Aryl halides are colourless oily liquids and higher members are crystalline solids having odour characteristic of aromatic compounds.
2. **Solubility :** Aryl halides are insoluble in water but soluble in common organic solvents such as alcohol, ether, etc. In a particular solvent, the solubility of the para-compound is less as compared to the ortho isomer. This fact can be employed for the separation of ortho- and para - isomers.

3. **Melting and Boiling Points**
   (a) For a particular aryl group, the melting and boiling points increase as the size of the halogen atom increase. *i.e.* m.pts. and b.pts. increase in the following order fluoro < chloro < bromo < iodo.
   (b) For a particular halogen, the m.pts and b.pts. increase as the size of the aryl group increases.
   (c) The boiling points of isomeric dihalides do not differ widely, thus making their separation by distillation very difficult. For example, consider the b.pts. of isomeric dichloro benzenes.



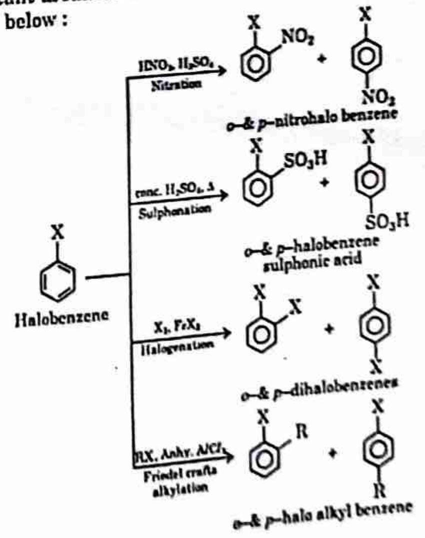
	o–dichloro benzene	m–dichloro benzene	p–dichloro benzene
B.pt.(K)	453	446	448
M.pt.(K)	256	249	325

   (d) While as seen from above, the melting points of isomeric dihalides differ widely of the three isomers, the para-isomer has the higher melting point. This is because, the para-isomers being symmetrical are closely packed in the crystal lattice. Due to efficient packing, the para-isomers have large melting points.

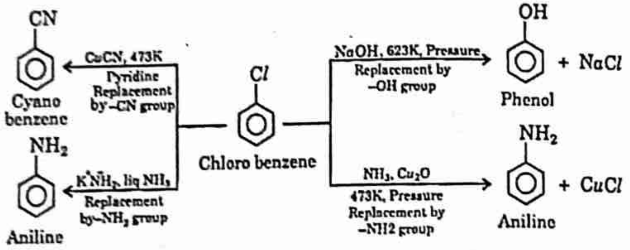
Chemical Properties

In general, aryl halides are quite less reactive under ordinary conditions. Some important reactions which aryl halides undergo are given as follows :

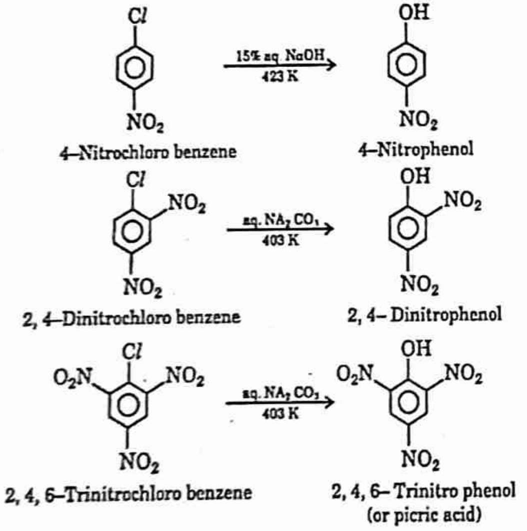
1. **Aromatic Electrophilic Substitution :** The presence of halogen atom deactivates the benzene ring towards aromatic electrophilic substitution. The deactivating effect of halogens is attributed to their strong – I effect. At the same time, halogens are ortho–, para-directing. The directing influence is attributed to their + R effect. Some important aromatic electrophilic substitution reactions of halo benzenes are summarised below :



2. **Aromatic Nucleophilic Substitution :** Aryl halides undergo nucleophilic substitution but only under drastic conditions employing the use of high temperature and pressure and strong nucleophiles. Some important nucleophilic substitution reactions are given as follows :



- **Effect of substituents on Aromatic Nucleophilic Substitution**
In general, the presence of electron withdrawing group like $-NO_2$, $>C=O$, $-COOH$, $-C\equiv N$, $-SO_3H$ etc. ortho-or-para with respect to the **halogen atom activates the aryl halides towards aromatic nuclephilic substitution.** This is evident from the following reactions of chloro benzene, as the member of electron withdrawing group $-NO_2$ attached to the ring increases, the reaction occurs more and more easily, as is clear form the less severity of the condition employed.



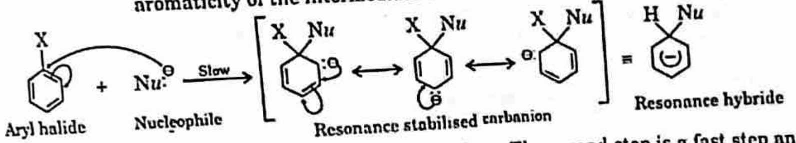
On the other hand, **presence of electron donating groups** like $-\ddot{O}H, -\ddot{O}R, -\ddot{N}H_2, -\ddot{N}HR, -\ddot{N}R_2, -R$ etc. deactivate the aryl halides towards aromatic nucleophilic substitution.

- **Mechanisms of Aromatic Nucleophilic Substitutions**
There are two possible mechanism :
(i) Addition – elimination mechanism
(ii) Benzyne mechanism
Both of these are being discussed as follows :

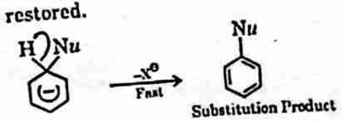
(a) Addition – Elimination Mechanism
(Or Bimolecular Displacement Mechanism)

According to this mechanism, aromatic nucleophilic substitution reaction occurs in two steps :

Step I. Formation of Carbonion : In the first step, the nucleophile attacks the aryl halide on the C–atom which carries the halogen to form a reasonance stabilised carbanion, which is also known as the **Meisenheimer complex.** The formation of the carbonion constitutes the **rate-determining step** of the mechanism. **It is to be noted that during the formation of carbonions the hybridisation of the concerned C-atom changes from sp^2 to sp^3** and aromaticity of the intermediate carbanion is lost.



Step II. : Elimination of halide ion : The second step is a fast step and involves the explusion of the halide ion form the carbanion to give the substitution product. During this step, the aromaticity of the benzene ring is also restored.



It is to be noted that the mechanism does not operate for simple aryl halides under ordinary conditions. It is operative only for those aryl halides which contain electron- withdrawing groups like $-NO_2$, $-C\equiv N$, $>C=O$, $-COOH$ etc. particularly at ortho – and para – positions w.r.t the halogen atoms.

300

(B) Elimination – Addition Mechanism (or Benzyne Mechanism) : The addition-elimination mechanism just discussed before proceeds for activated aryl halides, *i.e.*, aryl halides which contain an electron-with drawing group, while for unactivated or deactivated aryl halides reaction occurs only with very strong nucleophiles under forcing conditions and the mechanism followed is known as the elimination-addition mechanism or the benzyne mechanism (since the mechanism occurs via the formation of benzyne intermediate).

About the benzyne intermediate : Benzyne intermediate contains an additional bond between the two ortho carbons of the benzene ring. The two carbons involved are the carbon originally bearing the halogen and an ortho carbon carrying a hydrogen. The additional bond is formed by the sideways overlap of sp^2-orbitals of the two C-atoms and lies along the side of the ring. The electron could be of this additional bond which lies along the side of the ring and has very little interaction with the aromatic π-electron cloud which lies above and below the plane of the ring. As this additional bond is formed by the sideways overlapping of sp^2-orbitals, it is weak and hence is responsible for the high reactivity of the benzyne.

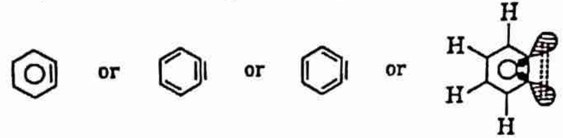
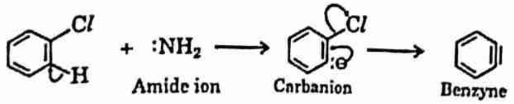


Fig. Representation of BENZYNE

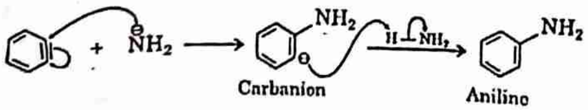
Mechanism

The reaction of chlorobenzene with strong nucleophile amide ion : $\overset{\ominus}{N}H_2$ in liquid NH_3 occurs through the addition elimination mechanism and proceeds through two steps :

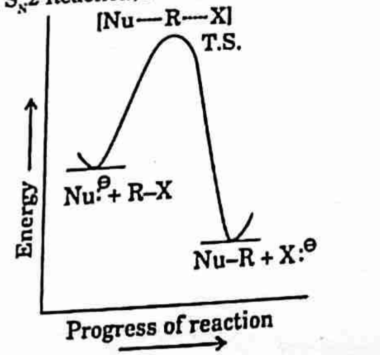
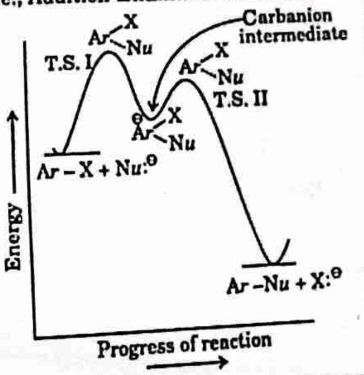
Steps 1 : Elimination : The amide ion first abstracts a proton from the carbon which is ortho with respect to the carbon carrying the halogen, leading to the formation of carbanion. This carbanion then expels a halide ion to form a benzyne.



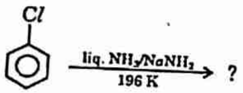
Step 2 : Addition : The amide ion then adds to the benzyne to give another carbanion which then abstracts a proton from liquid ammonia to give the final product, an aryl amine (in this case aniline).



Comparison of Aliphatic & Aromatic Nucleophilic Substitution Reactions

S.N.	Aliphatic Nucleophilic Substitution	Aromatic Nucleophilic Substitution
1.	SN' reactions involve the formation of carbocation in the rate-determining step. $R-X \xrightarrow[\text{Slow carbocation}]{-X^{\ominus}} R^{\oplus} \xrightarrow[Nu^{\ominus}]{\text{Fast}} R-Nu$ While no intermediate is involve in the single step S_N2 mechanism.	Aromatic nucleophilic substitution involve the formation of carbanion the rate-determining step. $Ar-X \xrightarrow[\text{Slow}]{Nu^{\ominus}} Ar\begin{smallmatrix}X\\Nu\end{smallmatrix} \xrightarrow[\text{Fast}]{-X^{\ominus}} Ar-Nu$
2.	S_N1 reactions are facilitated by the presence of electron donating groups, which help stabilise the carbocation. S_N2 reactions are not affected appreciably by electronic factors.	Aromatic nucleophilic substitutions are facilitated by the presence of electron withdrawing groups, which help stabilise the carbanion.
3.	Energy profile diagram for bimolecular aliphatic nucleophilic substitution (i.e., S_N2 Reaction) :  	Energy profile diagram for bimolecular aromatic nucleophilic substitution reaction (i.e., Addition-Elimination Mechanism 
4.	Aliphatic Nucleophilic substitutions are comparatively faster.	Aromatic Nucleophilic substitutions proceed at a comparatively slow rate. (reason discussed later)

QUESTIONS FOR PRACTICE

1. (a) Distinguish between S_N1 and S_N2 reactions.
   (b) Which is more reactive towards S_N1 reaction. Explain.
   CH_3-CH_2-Cl, $CH_2=CH-Cl$, $CH_2=CH-CH_2-Cl$
   (c) Complete the following reaction : (M.D.U. 2009)
   (i) 
2. Give the mechanism of dehydrohalogenation of alkyl halides. Explain the orientation and ease of formation of alkenes. (K.U.K. 2002)
3. (a) Vinylhalides are aliphatic halogen compounds but they resemble aryl halides in chemical reactivity. How do you account for this statement? (M.D.U. 2006)
   (a) Complete the following equations.

$$CH_3Br + Na\overset{+\ominus}{C}H(COOC_2H_5)_2 \longrightarrow$$

(M.D.U. 2006)

4. *(a) Discuss the mechanism of* S_N1 *reaction with energy profile diagram.* (K.U.K. 2013)
   (b) Write mechanism of chlorination of benzene. (K.U.K. 2005, K.U.K. 2011)
   (c) Explain the ortho and para directing nature of halogen.

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5. Explain the following :
   (i) S_N1 reactions of alkyl halides are accompanied by partial racemisation.
   (ii) Hydrolysis of ethyl chloride is S_N2 reaction but that *t*-butyl chloride is S_N1 reaction.
   (iii) S_N2 reaction proceeds by inversion of configuration.
   (iv) S_N2 mechanism of an alkyl halide is unlikely for an aryl halide.
   (v) Aryl halides are far less reactive than alkyl halides. (K.U.K. 2006)
   (vi) Mechanism of bimolecular nucleophilic aromatic substitution. (K.U.K. 2005, 06, 12)
6. (a) Why alkyl halides are more reactive than primary alkyl halides? or Compare the reactivity of alkyl halides vs aryl halides. (K.U.K. 2013)
   (b) Give the elimination-addition mechanism of conversion of chlorobenzene into aniline.
7. Discuss bimolecular displacement mechanism of aromatic nucleophilic substitution. (K.U.K. 2013)
8. Why does nucleophilic substitution of chlorobenzene take place through benzyne mechanism and that of *p*-nitrochloro benzene proceeds via addition-elimination mechanism? (M.D.U. 2007)
9. (a) Alkyl chloride undergo substitution reaction by S_N1 mechanism whereas *n*-propyl chloride reacts with S_N2 mechanism. Explain.
   (b) In E_2 elimination, trans-1, 2-dichloroethylene undergoes transformation to chloroacetylene twenty times faster than the corresponding *cis*-isomer.
      (i) *m*-Chlorotoluence from *p*-nitrotoluene
      (ii) *o*-Chlorotoluene from toluene
   (c) Convert the following :
      (i) Benzene diazonium chloride into chlorobenzene. (K.U.K. 2005)
10. Complete the following equation :
    (i) $C_2H_5MgBr + CH_3CN \longrightarrow$
    (ii) $C_3H_7Cl + NaNO_2 \longrightarrow$
    (iii) $C_2H_5Br + C_2H_5S\ Na \longrightarrow$
11. (a) Write chemical equations for the following :
    Write chemical equations for the following : Chlorobenzene reacts with ammonia in the presence of sodamide at 190 K.
    (b) Write a short note on (K.U.K. 2012, 2013)
       (i) Sandmeyer's reaction (K.U.K. 2013)
       (ii) Wurtz reaction (K.U.K. 2003)
    (c) Write a note on sigma (σ) and pi (π) complexes. (K.U.K. 2003)
12. (a) Discuss the factors affecting S_N2 reactions.
    (b) Give the elimination-addition mechanism of conversion of chlorobenzene into aniline. (K.U.K. 2011, M.D.U. 2003)
13. (a) Why aryl and viny halides are less reactive than alkyl halides? (K.U.K. 2011, M.D.U. 2004)
    (b) Explain the mechanism of nucleophilic aromatic substitution reaction (bimolecular displacement mechanism) (M.D.U. 2003)