HYDROCARBON

Introduction

Organic compounds containing carbon and hydrogen only are called hydrocarbons. These are widely distributed in nature in the form of petroleum, natural gas etc. Hydrocarbons are considered to be the parent organic compounds while all other compounds are thought to have been derived from them by replacement of one or more hydrogen atoms by other atoms or groups.

Classification

On the basis of carbon skelton, hydrocarbon are mainly two type

- I. Acyclic / open chain compound
- II. Cyclic / closed chain compounds

I. Acyclic / open chain compounds

Compounds contain open chains of carbon atoms in their molecules. They may be either straight or branched. Open chain compounds are also called aliphatic compounds

Aliphatic compounds are two types

- i. saturated hydrocarbon: compounds containing C-C.
 - Also known as alkanes / paraffins
- ii. unsaturated
 - a. Alkenes / olefins

compounds containing C = C

b. Alkynes / Acetylenes

compounds containing $C \equiv C$

II. Cyclic / closed chain compounds

Compounds containing closed chains / rings of carbon atoms.

Mainly two types

1) Homocyclic

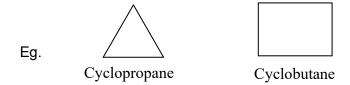
2) Hetero cyclic

1. Homocyclic

Rings are made up of only one kind of atom, mainly carbon atom so known as carbocyclic compounds; further divided in to

a) Alicyclic compounds

Rings are made up of 3 or more carbon atoms and properties resembles with aliphatic compounds



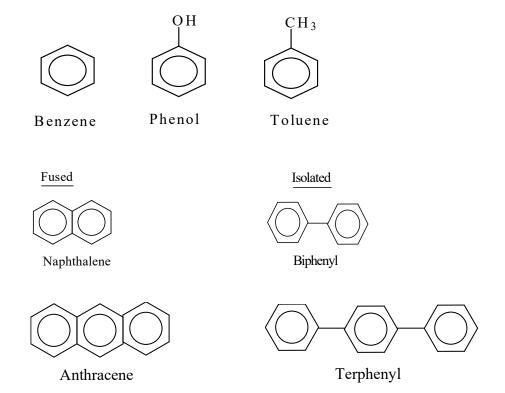
b) Aromatic compounds

From the word Aroma (Fragnent smell)

Two types

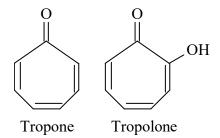
i) Benzenoid compound

Compounds containing one or more fused or isolated benzene rings.



ii) Non Benzenoid aromatic compounds

Compounds does not contains benzene ring but contain other highly unsaturated rings.

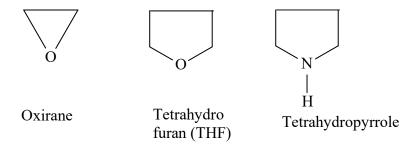


2. Heterocyclic compounds

Rings contains carbon and hetero atoms

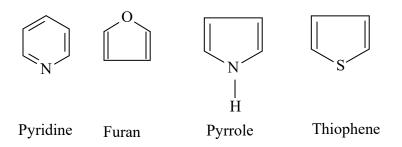
a) Alicyclic heterocyclic

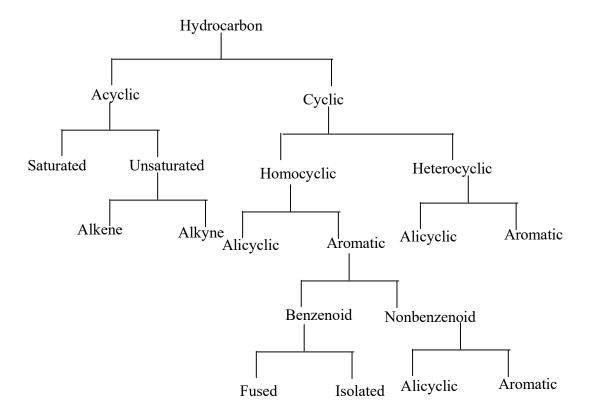
Alicyclic compounds contains hetero atoms



b) Aromatic hetero cyclic

Aromatic compounds containing heteroatoms





I. ALKANES / Paraffins

Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They are also called paraffins (Latin : Parum = little, affinis = affinity). They are unreactive towards most reagents.

Structure of Alkanes.

Carbon atoms in alkanes are sp³–hybridized, therefore, they have tetrahedral structures. The four bonds are directed towards the corners of a regular tetrahedron. The angle between any two adjacent bonds is 109.28° (tetrahedral angle).

Alkanes contain only carbon-carbon and carbon-hydrogen single bonds with average bond lengths of 154 pm and 110 pm respectively.

Structure of methane (CH₄)

General formula C_nH_{2n+2}

Preparation

1) From unsaturated hydrocarbon

Alkanes are obtained by hydrogenation of unsaturated hydrocarbons (alkenes / alkynes) in presence of catalyst.

$$CH_2 = CH_2 \xrightarrow{H_2} CH_3 - CH_3$$

Reaction known as sabatier & senderen reaction

$$CH_2 = CH_2 + H_2 \xrightarrow{\text{pt/pd}} CH_3 - CH_3$$

$$CH = CH + H_2 \xrightarrow{Ni} CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

$$CH_2 = CH_2 + H_2 \xrightarrow{\text{Raney Ni}} CH_3 - CH_3$$

2) From alkyl halide

a) Using Grignard reagent (R-Mg-x)

 $R-Mg-X \rightarrow$ First organometallic compound prepared by victor Grignard using R–X heated with Mg in present of dry ether.

$$R - X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

 $^{8-}$ $^{8+}$ $^{8-}$ $^{8-}$ is a source of carbanion so react with any H+ medium to form Hydrocarbon

$$R-Mg-X \xrightarrow{H_2O} R-H+Mg(OH)X$$

$$CH_3MgCl \xrightarrow{H_2O} CH_4 + Mg(OH)Cl$$

b) Wurtz reaction

An ether solution of alkylhalide is treated with sodium form hydrocarbon

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

This reaction is not suitable for the synthesis of alkane containing odd number of carbon atoms but the method is useful for the preparation of symmetrical alkanes

$$\begin{array}{c} \text{CH}_3-\text{Br}+2\text{Na}+\text{C}_2\text{H}_5-\text{Br} \xrightarrow{\text{dry ether}} \text{CH}_3-\text{CH}_3+\\ \\ \text{CH}_3-\text{CH}_2-\text{CH}_3+\\ \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3+2\text{NaBr} \\ \\ \text{Mixture of product, seperation not easy} \end{array}$$

Mechanism

Ionic: $2Na \longrightarrow 2Na^{\oplus} + 2e^{\Theta}$

$$2e + R - X \longrightarrow RNa^{\oplus} + NaX$$

Free radical: $2R - X + 2Na \longrightarrow 2R' + 2NaX$

$$2\dot{R} \longrightarrow R - R$$

Limitation: 1) Methane cannot be obtained

- 2) Tert alkylhalide does not give the reaction
- 3) Only for the preparation of symmetrical alkanes.

c) Frankland's reaction

Alkylhalide heated with Zn in presence of ether

$$2R - X + Zn \xrightarrow{\text{ether}} R - R + ZnX_2$$

d) Corey-House synthesis

Halo alkane react with Li form alkyl lithium

$$R-X+2Li \longrightarrow R-Li+LiX$$

Alkyl lithium react with cuprous iodide form Lithium dialkylcuprate

$$2R - Li + CuI \longrightarrow R_2CuLi + LiI$$

R₂CuLi react with R–X form hydrocarbon.

Gilman's reagent R, CuLi

$$R_2CuLi + R' - X \longrightarrow R - R' + R - Cu + LiX$$

$$CH_3 - Cl + 2Li \longrightarrow CH_3 - Li + LiCl$$

$$2CH_3 - Li + CuI \longrightarrow (CH_3)_2 - CuLi + LiI$$

$$\begin{array}{l} \left(\mathrm{CH_3}\right)_2^- - \mathrm{CuLi} + \mathrm{CH_3} - \mathrm{Cl} {\longrightarrow} \mathrm{CH_3} - \mathrm{CH_3} + \mathrm{CH_3}\mathrm{Cu} + \mathrm{LiCl} \\ \mathrm{symmetrical} \end{array}$$

$${\rm (CH_3)_2-CuLi+CH_3-CH_2-Cl} \longrightarrow {\rm CH_3-CH_2-CH_3+CH_3Cu+LiCl} \\ {\rm unsymmetrical}$$

e) Reduction of alkyl halide

Haloalkane react with metals dissolving in acid / base / alcohol

$$R-X \xrightarrow{Zn+HCl} R-H$$

$$R-X \xrightarrow{Zn+NaOH} R-H$$

$$R-X \xrightarrow{Zn+ROH} R-H$$

Haloalkane reduce with strong reducing agent $LiAlH_4$, R-H is formed

$$R - X \xrightarrow{LiAlH_4} R - H + \stackrel{\Theta}{X}$$

3) From carboxylic acid

a) using sodalime

Sodium salt of carboxylic acid decarboxylated with sodalime (NaOH + CaO), hydrocarbons having, one carbon less than parent acid is formed.

$$R - COONa + NaOH \xrightarrow{CaO} R - H + Na_2CO_3$$

$$CH_3 - COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

b) Kolbe's electrolytic decarboxylation

Aqueous sodium / potassium salt of mono carboxylic acid electrolysis, hydrocarbons are formed having twice the number of carbon atom in the parent alkyl group

$$2 R - COONa \longrightarrow 2R - COO + 2Na^{\oplus}$$

$$2H_2O \longrightarrow 2OH + 2H^{\oplus}$$

At Anode

At Cathode

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

Eg.
$$2CH_3COONa \xrightarrow{Electrolysis} CH_3 - CH_3$$

$$2\text{CH}_3\text{CH}_2\text{COONa} \xrightarrow{\quad \text{Electrolysis} \quad} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$$

4) Reduction of carbonyl compounds

a) Clemmensen reduction

Aldehyde and ketones reduced with amalgamated Zn and conc:HCl alkanes are formed

$$C = O \xrightarrow{Zn-Hg} CH_2$$

b) Wolf-Kishner reduction

Aldehydes and ketones reduced to hydrocarbon in presence of excess hydrazine and sodium alkoxide on heating

$$C = O \xrightarrow{NH_2 - NH_2} C = N - NH_2 \xrightarrow{C_2H_5ONa} CH_2$$

c) Mozingo method

 $m \dot{C} = O$ is converted into its dithioacetal or ketol using ethanedithiol in presence of Lewis

acid. Dithioacetal hydrogenated

get hydrocarbon in presence of Raney Ni

$$\begin{array}{c|c}
 & \text{HS-CH}_2 \\
 & \text{C} = \text{O} + \\
 & \text{HS-CH}_2
\end{array}$$

$$\begin{array}{c|c}
 & \text{S-CH}_2 \\
 & \text{S-CH}_2
\end{array}$$

$$\begin{array}{c|c}
 & \text{Raney} \\
 & \text{Ni}
\end{array}$$

$$\begin{array}{c|c}
 & \text{CH}_2 + \\
 & \text{HS-CH}_2
\end{array}$$

5) By action of water on Be / Al carbide

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

Physical properties

Amogst straight chain alkanes, the first four members (C1-C4) are gases, the next thirteen are liquids (C5-C17) and the higher members (C18 onwards) are colourless waxy solids.

Boiling points

The boiling points of straight chain alkanes increase fairly regularly by 20–30 K for the addition of each carbon atoms. This regular increase in the boiling point of straight chain alkanes is due to increase in molecular size and hence the surface area of the molecules. As result, the magnitude of the van der Waals forces of attraction increases.

Amongst isomeric alkanes, the branched chain isomer has lower boiling point than the corresponding n-alkane. This is due to the fact that with branching the shape of the molecule tends to approach that of a sphere. As a result, the surface area decreases and van der Waals forces of attraction become weaker. In case of isomeric alcohols branching increases boiling point decreases.

Melting points

The melting points of alkanes increase with increase in carbon content but the variation is not regular due to alternation effect.

Chemical Reactions

I. Substitution reaction

Replacement of H by another atoms / group

i) Halogenation

Replacement of H by halogen

$$\begin{array}{c|c} & & | \\ \hline - C - H + X_2 \xrightarrow{\begin{array}{c} light \\ 520 - 670 \end{array}} \begin{array}{c} | \\ C - X + HX \end{array}$$

Halogenation reaction depends on nature of halogen and type of H

$$F_2 > Cl_2 > Br_2 > I_2$$
 1°H < 2°H < 3°H
 $CH_4 + Cl_2 \xrightarrow{light} CH_3 - Cl + HCl$

Mechanism

Initiation: $Cl_2 \xrightarrow{\Lambda} 2Cl$

Propagation : $CH_4 + C1 \longrightarrow CH_3 + HC1$

$$\stackrel{\bullet}{\text{CH}_3} + \text{Cl}_2 \longrightarrow \text{CH}_3 - \text{Cl} + \text{Cl}$$

Termination : $2C1 \longrightarrow Cl_2$

$${}^{\bullet}$$
 2CH₃ \longrightarrow CH₃ -CH₃

$$\stackrel{\bullet}{\text{CH}_3} + \stackrel{\bullet}{\text{Cl}} \longrightarrow \stackrel{\bullet}{\text{CH}_3} - \stackrel{\bullet}{\text{Cl}}$$

In presence of excess Cl₂ all hydrogens are replaced by Cl,

$$\text{CH}_4 + \text{Cl}_2 \xrightarrow[-\text{HCl}]{\text{light}} \text{CH}_3 - \text{Cl} + \text{Cl}_2 \xrightarrow[-\text{HCl}]{\text{-HCl}} \text{CH}_2 \text{Cl}_2 \xrightarrow[-\text{HCl}]{\text{Cl}_2} \text{CHCl}_3 \xrightarrow[-\text{HCl}]{\text{Cl}_2} \text{CCl}_4$$

The relative reactivity of 1° , 2° and 3° H towards Cl_2 in the ratio $1^{\circ}: 2^{\circ}: 3^{\circ} = 1: 3.8: 5$

Towards bromination in the ratio 1:82:1600

The % yield of chlorination or bromination = $\frac{\text{Re lative amount}}{\text{Total amount}} \times 100$

1.
$$\begin{array}{c} CH_3-CH_2-CH_3+Cl_2 \xrightarrow{hu} CH_3-CH_2-CH_2-Cl+CH_3-CH-CH_3 \\ I & I & Cl & II \end{array}$$

No. of $1^{\circ}H = 6$

Relative amount =
$$6 \times 1 = 6 \% = \frac{6}{13.6} \times 100 = 44\%$$

II No. of $2^{\circ}H = 2$

R.A =
$$2 \times 3.8 = 7.6$$
 % = $\frac{7.6}{13.6} \times 100 = 56\%$

2.
$$CH_3$$
 CH_3 CH_3

I. No. of $1^{\circ}H = 9$

R.A =
$$9 \times 1 = 9$$
 % yield = $\frac{9}{1609} \times 100 = 0.6$ %

II. No of 3°H=1

R.A =
$$1 \times 1600 = 1600$$
 % yield = $\frac{1600}{1609} \times 100 = 99.4\%$

3.
$$\begin{array}{c} \operatorname{CH_3} & \operatorname{CH_3} & \operatorname{CH_3} \\ | & | & | \\ \operatorname{CH_3-CH-CH_2-CH_3+Cl_2} \xrightarrow{light} \operatorname{CH_3-CH-CH_2-Cl_+CH_3-CH-CH-CH_3} \\ | & | & | \\ (1) & | & | \\ & | & | \\ \end{array}$$

$$\begin{array}{cccc} & \text{CH}_{3} & \text{CH}_{2} - \text{Cl} \\ & & & \\ \text{CH}_{3} - \text{CH} - \text{CH}_{2} - \text{CH}_{3} + \text{CH}_{3} - \text{CH} - \text{CH}_{2} - \text{CH}_{3} \\ & & \\ \text{Cl} & (3) & (4) \end{array}$$

1) No. of $1^{\circ}H = 3$

R.A =
$$3 \times 1 = 3$$
 %yield = $\frac{3}{21.6} \times 100 = 14\%$

2) No. of $2^{\circ}H = 2$

R.A =
$$2 \times 3.8 = 7.6$$
 %yield = $\frac{7.6}{21.6} \times 100 = 35\%$

3) No. of 3° H = 1

R.A =
$$1 \times 5 = 5$$
 % yield = $\frac{5}{21.6} \times 100 = 23\%$

4) No. of $1^{\circ}H = 6$

R.A =
$$1 \times 6 = 6$$
 % yield = $\frac{6}{21.6} \times 100 = 28\%$

ii) Nitration

H atom replaced by nitro group

$$R - H + HONO_2 \xrightarrow{\text{High}} R - NO_2 + H_2O$$

Mechanism

$$HO - NO_2 \xrightarrow{\Delta} H \stackrel{\bullet}{O} + \stackrel{\bullet}{N} O_2$$

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

$$\overset{\bullet}{R} + \overset{\bullet}{N} O_2 \longrightarrow R - NO_2$$

Alkanes contain 6 or more carbon atom heating with fuming nitric acid yield nitroalkane

$$C_6H_{13} - H + HONO_2 \xrightarrow{\Delta} C_6H_{13} - NO_2 + H_2O$$

Mixture of vapour of an alkane and nitric acid is heated at $400^{\circ} - 500^{\circ}$ C nitro alkane is formed. This method is known as vapour phase nitration.

$$CH_3 - H + HONO_2 \xrightarrow{450^{\circ}C} CH_3 - NO_2 + H_2O$$

In alkane having 2 or more carbon atom, there is possibility of C-C bond breakage

$$C_{3}H_{8} \xrightarrow{HNO_{3} \atop 450^{\circ}C} CH_{3}CH_{2}CH_{2} - NO_{2} + CH_{3} - CH - CH_{3} + CH_{3}NO_{2} + CH_{3}CH_{2}NO_{2}$$

iii) Sulphonation

H atom replaced by SO₃H group

Higher alkanes contains six or more carbon atom heated with fuming H₂SO₄ at about 400°C

$$R-H+SO_3 \xrightarrow{H_2SO_4} R-SO_3H+H_2O$$

$$HO - SO_3H \xrightarrow{\Lambda} H\dot{O} + \dot{S}O_3H$$

$$R - H + \dot{O}H \xrightarrow{\Delta} \dot{R} + H_2O$$

$$\dot{R} + \dot{S}O_3H \longrightarrow R - SO_3H$$

II. Oxidation reaction

a) Complete oxidation / combustion reaction

$$\operatorname{CnH}_{2n+2} + \left(\frac{3n+1}{2}\right) \operatorname{O}_2 \longrightarrow \operatorname{n} \operatorname{CO}_2 + \left(n+1\right) \operatorname{H}_2 \operatorname{O}_2$$

Eg.:
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$$

b) Incomplete oxidation

In presence of limited supply of air / oxygen, alkanes give CO along with some unburnt carbon (soot) in the form of carbon black.

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$
Carbon black / soc

Carbon black is used for the preparation of black ink, paint etc.

When methane is react with superheated steam in presence of Ni at high temp, water gas is formed

$$CH_4 + H_2O_{(g)} \xrightarrow{N_i} CO + 3H_2$$

c) Catalytic oxidation

Different catalyst give different product

$$2CH_4 + O_2 \xrightarrow{\text{cu tube}} CH_3OH$$

$$CH_4 + O_2 \xrightarrow{MO_2O_3} HCHO + H_2O$$

$$2 R - CH_3 + 3O_2 \xrightarrow{Ag_{2O}} 2 R COOH + 2H_2O$$

Alkanes having 3°H are oxidise by oxidising agents to corresponding alcohol.

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} - C - OH$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} - C - OH$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

III. Isomerisation

When n-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under pressure (about 35 atmospheres) they are converted into branched chain alkanes.

$$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{An:AlCl}_{3+}} \text{CH}_3 - \text{CH} - \text{CH}_3$$

IV. Aromatisation

Alkanes contain 6 - 10 carbon atom are heated with metalic oxides and followed by dehydrogenation to form aromatic compounds

$$CH_{3} - (CH_{2})_{4}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} V_{2}O_{5}, 773 \text{ K}$$

$$CH_{3} - (CH_{2})_{5}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} V_{2}O_{5}, 773 \text{ K}$$

$$CH_{3} - (CH_{2})_{6}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} - (CH_{2})_{6}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} V_{2}O_{5}, 773 \text{ K}$$

$$CH_{3} - (CH_{3})_{6}CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} - (CH_{3})_{6}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} V_{2}O_{5}, 773 \text{ K}$$

$$CH_{3} - (CH_{3})_{6}CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} - (CH_{3})_{6}CH_{3} \xrightarrow{Cr_{2}O_{3}|Al_{2}O_{3}|} V_{2}O_{5}, 773 \text{ K}$$

$$CH_{3} - (CH_{3})_{6}CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

V. Pyrolysis

Decomposition of a compound by applying heat is known as pyrolysis

Pyrolysis of higher alkanes to give a mixture of lower alkanes, alkenes, etc. is called cracking. It is usually carried out by heating higher alkanes to high temperature (773–973 K) under a pressure of 6–7 atmospheres in presence or absence of a catalyst.

$$C_6H_{12} + H_2$$
 $C_6H_{14} \xrightarrow{773-} C_4H_8 + C_2H_6$
 $C_4H_4 + C_2H_4 + C_3H_6$

Isomerism in alkanes

Structural isomerism

Chain isomerism

$$\begin{array}{c} CH_3\\ \mid\\ C_4H_{10}-CH_3-CH_2-CH_2-CH_3\\ \quad n\ \ \text{butane} \end{array} \quad \begin{array}{c} CH_3\\ \mid\\ CH_3-CH-CH_3\\ \end{array}$$

$$C_{5}H_{12} \qquad CH_{3}-CH_{2}CH_{2}CH_{2}CH_{3} \qquad CH_{3}-CH-CH_{2}-CH_{3} \qquad CH_{3}-C-CH_{2} \\ CH_{3} \qquad CH_{3}-C-CH_{2} \qquad CH_{3}-C-CH_{2} \\ CH_{3} \qquad Neopentane \qquad Neopentane$$

Stereo isomerism

Isomers having the same structural formula but different relative arrangement of atoms or groups in space are called stereoisomers (Greek: stereo = space, meros = part) and the phenomenon is called stereoisomerism. Stereoisomers have the same molecular structure but different configurations. Stereoisomerism is of three types: (i) conformational isomerism (ii) geometrical isomerism and (iii) optical isomerism.

Optical isomerism

Alkanes with minimum 7 carbon atoms can show optical isomerism.

$$CH_3$$
Chiral carbon atom
 $CH_2CH_2CH_3$
 C_2H_5

Conformational isomerism

The infinite no. of spatial arrangements obtained due to the rotation around a C-C single bond is known as conformers. The phenomenon is known as conformational isomerism

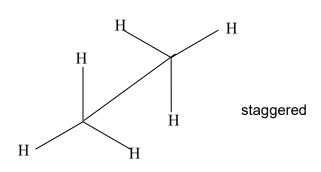
- It aries due to the free rotation around a C-C
- The energy of arrangement is max when bond pairs are very close to each other, such forms are called eclipsed conformation (Least stable)
- The energy of arrangement is min when bond pairs are far a part, such forms are called staggered conformation (more stable)
- Conformations between eclipsed and staggered is known as skew conformation

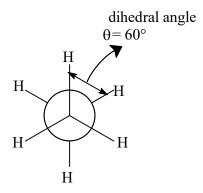
Conformations of ethane

$$CH_3 - CH_3$$

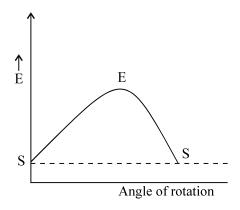
1) Saw - House projection

2) New - man projeciton





Energy level diagram



Conformations of butane

$$CH_3 - CH_2 - CH_2 - CH_3$$

Fully eclipsed

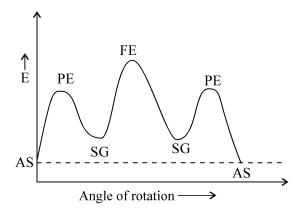
$$\begin{array}{c} CH_3 \\ H \\ H \end{array}$$

Staggered gauche

$$H_{\text{CH}^3}$$

Partially eclipsed

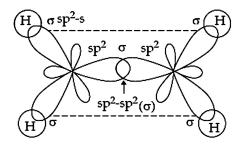
Energy level diagram



ALKENE

General formula $\mathbf{C}_{\mathbf{n}}\mathbf{H}_{\mathbf{2n}}$

3.1 Structure of Double Bond. The double bond in alkenes consists of one carbon-carbon σ -bond formed by head-on overlap of sp²-hybridised orbitals and a π -bond (284 kJ mol⁻¹) formed by lateral or sideways overlap of the two 2p-orbitals of the two carbon atoms



Orbital picture of ethene showing - bonds only

Orbital picture of ethene showing formation of (a) π -bonds (b) π -cloud and (c) bond angles and bond lengths

To have effective overlap, the p-orbitals move closer, therefore, a double bond is shorter (134 pm) than a single bond (154 pm). The presence of $\pi-bond$ makes alkenes less stable and more reactive than alkanes. Therefore, alkenes are readily attacked by (electrophiles) electrophilic reagents.

Isomerism in alkene

Geometrical isomerism

Two compounds having same molecular formula but different spatial arrangement around a carbon - carbon double bond. Such isomers are called geometrical isomers and the phenomenon is known as geometrical isomerism.

ullet If the identical atoms or groups are on same side of C=C is called cis isomer and they are on opposite side trans isomers

Eg. But - 2 - ene

Conditions:

- · Should contain at least 1 double bond
- No identical atoms or group are on same double bonded carbon atom

Preparation

I. From alkynes

Alkynes undergo partial reduction to form alkenes, Alkynes reduced with $\rm H_2$ in presence of Pd over $\rm CaCO_3$ or $\rm BaSO_4$ with added lead acetate and quinoline - is known as Lindlar catalyst

$$R - C \equiv C - R \xrightarrow{H_2 + Pd} H$$

$$R - C \equiv C - R \xrightarrow{H_2 + Pd} C = C$$
Sulpher or Quinoline
$$H$$

$$R$$

Alkynes on reduced with Li or Na in NH₃ give trans alkene: Birch reduction

$$R - C \equiv C - R \xrightarrow{\text{Na}} R$$

$$C = C$$

$$H$$

$$R$$

II From monohydric alcohols

Alcohols undergo dehydration in presence of protonic acid (conc. $H_2SO_4/Conc$: H_3PO_4) or heated with catalyst such as alumina or an. $ZnCl_2$ give alkenes

$$\begin{array}{c|c}
 & \beta & \alpha \\
 & C & C \\
 & \beta & \alpha \\
 & C & C
\end{array}$$

$$\begin{array}{c}
 & C & C \\
 & A
\end{array}$$

$$\begin{array}{c}
 & C & C \\
 & A
\end{array}$$

$$\begin{array}{c}
 & C & C \\
 & A
\end{array}$$

β - Elimination

Mechanism

$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow{\text{Protonation}} \text{CH}_3 - \text{CH}_2 \xrightarrow{\bigcirc} \text{H}_2 \xrightarrow{\text{Dehydration}} \text{CH}_3 - \text{CH}_2 \xrightarrow{\bigcirc} \text{Deprotonation} \\ -\text{H}^{\oplus} & \text{Deprotonation} \\ \text{CH}_2 = \text{CH}_2 \end{array}$$

Order of dehydration 3°>2°>1°

$$CH_3CH_2 - OH \xrightarrow{H^+} CH_4 = CH_2 + H_2O$$

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

$$\begin{array}{c|c} CH_{3} & CH_{3} \\ | & | \\ CH_{3} - C - OH \xrightarrow{H^{+}} CH_{3} - C = CH_{2} + H_{2}O \\ | & CH_{3} \end{array}$$

$$\mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{OH} \xrightarrow[-\mathrm{H}_2\mathrm{O}]{\mathrm{H}^+} \mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} + \mathrm{CH_2}$$

$$\xrightarrow{-H \text{ shift}} CH_3 - CH_2 - \overset{\oplus}{C}H - CH_3$$

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

$$CH_3 - CH = CH - CH_3$$

$$CH_3 - CH_2 - CH = CH_2$$

$$Major$$

$$CH_3 - CH_2 - CH = CH_2$$

$$Minor$$

In this case more than one product is formed, major product is determind by saytzeff's rule ie more substituted alkenes are the major product.

III. From alkylhalide

Haloalkane heated with strong bases such as sodiumethoxide, alc. KOH, tert -butoxide dehydrohalogenation to form alkenes

$$\begin{array}{c|c}
H & \alpha \\
C & C \\
\beta & A \\
\end{array}$$

$$\begin{array}{c}
A & \text{alc.KOH} \\
A & A \\
\end{array}$$

$$\begin{array}{c}
A & A \\$$

The leaving nature of halogens F < Cl < Br < I order of reactivity of R - X $3^{\circ} > 2^{\circ} > 1^{\circ}$ Reaction follows E² Mechanism.

$$CH_3 - CH_2 - CH_2CH_2 - Br \xrightarrow{alc.KOH} CH_3 - CH_2 - CH = CH_2 + HBr$$

In case of terminal halide, terminal alkenes are formed

$$\begin{array}{c} \operatorname{Br} \\ | \\ \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH} - \operatorname{CH}_3 \xrightarrow{\quad \text{alc.KOH} \quad} \operatorname{CH}_3 - \operatorname{CH} = \operatorname{CH} - \operatorname{CH}_3 + \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH} = \operatorname{CH}_2 \\ \operatorname{Maj} & \operatorname{Min} \end{array}$$

In case of non terminal halides major product is determind by saytzeff rule.

If the elimination carried out in presence of a bulky bases Hoffmann's elimination follows

$$\begin{array}{c|c}
& \text{Br} \\
& \downarrow \\
& \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \xrightarrow{\text{(CH}_3)_3 - \text{C} - \text{O}}
\end{array}$$

$$\begin{array}{c}
\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 \\
& \text{Maj}$$

E² elimination depends on periplanar geometry

Two types of periplanar

1. Syn periplanar - Both H and halogen are on same side



2) Anti periplanar - Both H and halogen are on opposite side

E₂eliminations are always antiperiplanar

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{\text{alc.KOH}} \text{No reaction}$$

$$\begin{array}{c|c}
CH_3 \\
Br & alc.KOH \\
\hline
Ph \\
\end{array}$$

4) From vicinal dihalides

$$\begin{array}{ccc}
C H_2 & & & & C H_2 \\
 & & & + Z n & \xrightarrow{eth er} & & | & \\
C H_2 & & & & | & \\
C H_2 & & & C H_2
\end{array}$$

5) From saturated dicarboxylic acids

Aqueous solution of sodium / pottasium salt of succinic acid undergo Kolbe's electrolytic decarboxylation to form alkene

succinic acid

$$\begin{array}{ccc} \text{CH}_2 & \text{COONa} & \text{CH}_2 & \text{COO} \\ | & & | & \\ \text{CH}_2 & \text{COONa} & \xrightarrow{\text{CH}_2} & \text{COO} \\ \end{array}$$

$$2H_2O \longrightarrow 2OH + 2H^{\oplus}$$

At Anode

At cathode

$$\begin{array}{ccc} CH_2 - COO^{\ominus} & CH_2 - COO \\ | & & & | & +2e^{\ominus} & 2H^{\oplus} + 2^{\bigodot} - \rightarrow H_2 \\ CH_2 - COO^{\ominus} & CH_2 - COO \\ & & & & | & -2CO_2 \\ & & & & & CH_2 = CH_2 \end{array}$$

6) Pyrolysis of ester

$$CH_3 - C - O - CH_2 - CH_3 \xrightarrow{\Delta} CH_2 = CH_2 + CH_3COOH$$

Mechanism

Cyclic 6 membered Transition state

Pyrolysis of esters are syn elimination reaction

$$CH_{3} - C - O - C - C - H$$

$$R$$

$$R$$

$$C = C + CH_{3}COOH$$

$$H$$

7) Pyrolysis of Quaternary ammonium salts

When quaternary ammonium salts are heated in presence of a base alkenes are formed.

$$CH_{3} - \overset{CH_{3}}{\overset{\ominus}{\longrightarrow}} CH_{2} \overset{\beta}{\overset{\ominus}{\longrightarrow}} CH_{2} \overset{CH_{3}}{\overset{\ominus}{\longrightarrow}} CH_{2} = CH_{2} + \overset{CH_{3}}{\overset{\ominus}{\longrightarrow}} CH_{3}$$

Properties

Physical properties

i) Physical state:

The first three members i.e., ethene, propene and butenes are colourless gases; the next fourteen (C5–C18) are liquids while the higher ones are solids. Except ethene which has pleasant smell, all other alkenes are colourless and odourless gases.

ii) solubility:

They are insoluble in water, buffairly soluble in non polar solvents such as benzene, petroleum ether, etc.

iii) Boiling points: Their boiling points increase regularly with increase in molecular mass. The boiling points generally increase by 20–30 K for the addition of each CH₂ group to the chain. Like alkanes, straight chain alkenes have higher boiling points than isomeric branched chain alkenes.

Stability

Stability of alkenes
$$^{\infty}$$
 No of alpha H atom $^{\infty} \frac{1}{\text{Heat of Hydrogenation}}$

Heat of Hydrogenation - The amount of energy release when an alkene is hydrogenated to form alkene

$$H_3C$$
 $C=C$
 H_3C
 CH_3
 H_3C
 $C=C$
 H_3C
 $C=C$
 H_3C
 H_3

$$CH_2 = CH_2$$

ΝοαΗ

Chemical Reactions

The π electrons in alkenes are loosely held and easily polarisable in presence of a polar solvent at low temperature heterolytic clevage take place and favour ionic mechanism.

In presence of a non polar solvents at high tempetrature homolytic clevage takes place and favour free radical mechanism

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IONIC MECHANISM

Alkenes show electrophilic addition reaction through 3 steps

$$\begin{array}{c|c} & & & E & Nu \\ \hline -C & -C & +Nu & \longrightarrow C - C \\ & & & & \end{array}$$
 formation of addition product

Important Addition Reactions

1) Addition of Hydrogen

Alkenes readily add dihydrogen in presence of Raney nickel (an active form of nickel), platinum or palladium as catalyst at room temperature or ordinary nickel at 523 – 573 to form alkanes (Sabatier and Senderen's reduction)

$$CH_2 = CH_2 \xrightarrow{H_2} CH_3 - CH_3$$

2) Addition of hydrogen halide

$$C - C + HX \xrightarrow{Dark} - C - C - Formation of alky halide$$
 $H \quad X$

Mechanism

$$HX \rightarrow H^{\oplus} + X^{\Theta}$$

$$\begin{array}{ccc}
H & H \\
C - C + HBr \longrightarrow CH_3 - CH_2 - Br \\
H & Ethyl bromide
\end{array}$$

$$CH_3 - CH = CH_2 + HC1 \xrightarrow{Dark} CH_3 - CH_2 - CH_2 - CI + CH_3 - CH - CH_3$$

$$CI$$

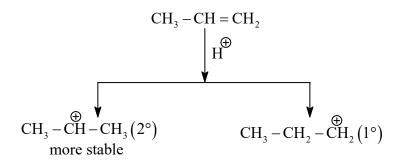
$$CI$$

$$(Major)$$

In this reaction morethan one product is formed therefore reaction is a regioselective reaction so the major product is determined by using "Markovnikov rule"

The rule states that addition of unsymmetrical reagent to an unsymmetrical alkene the negative part of the adding molecule attached to the carbon containing lesser number of H-atom

Proof for Markovnikov rule:



2°C is more stable hence it forms the major one. This reaction occurs due to electromeric shift. The reason for the repulsion of electrons to the next is due to +I effect of methyl thus providing a pushing force.

 Addition of HBr [not HF, HCl and HI] to an unsymmetrical alkene in presence of peroxide addition takes place against to Markovnikov rule known as Anti Markovnikov's Addition/ Peroxine Effect / Kharasch Effect.

$$CH_{3} - CH = CH_{2} + HBr \xrightarrow{Peroxide} \xrightarrow{Peroxide} CH_{3} - CH_{2} - CH_{2} - Br + CH_{3} - CH - CH_{3}$$

$$Major$$

$$Rr$$

Initiation

$$\begin{matrix} O & O & O \\ \parallel & \parallel & \parallel \\ C_6H_5-C-O-O-C-C_6H_5 & \longrightarrow 2C_6H_5-C-O \ Benzoyl \ free \ radical \end{matrix}$$

$$C_6H_5 - C \xrightarrow{O} C_6 \dot{H}_5 + CO_2$$

$$C_6 \overset{\bullet}{H}_5 + HBr \longrightarrow C_6 H_5 + \overset{\bullet}{B}r$$

Propagation

$$CH_3 - CH = CH_2 + \mathbf{\dot{B}r} \longrightarrow CH_3 - \mathbf{\dot{C}H} - CH_2 - Br$$

$$\mathrm{CH_3} - \mathrm{CH} - \mathrm{CH_2} - \mathrm{Br} + \mathrm{HBr} \longrightarrow \mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Br} + \mathrm{Br}$$

Termination

$$2Br \longrightarrow Br_2$$

$$\begin{array}{c} \overset{\bullet}{\operatorname{CH}}_3 - \overset{\bullet}{\operatorname{C}}\operatorname{H} - \operatorname{CH}_2 - \operatorname{Br} + \overset{\bullet}{\operatorname{Br}} - \longrightarrow \operatorname{CH}_3 - \overset{\bullet}{\operatorname{CH}} - \overset{\bullet}{\operatorname{CH}}_2 \\ | & | & | \\ & \operatorname{Br} & \operatorname{Br} \end{array}$$

3) Addition of H₂O

1. Acidic Hydration of Alkene

$$C = C \xrightarrow{H^+/H_2O} - C - C - C - H OH$$

$$CH_2 = CH_2 \xrightarrow{H^+/H_2O} CH_3 - CH_2OH$$

$$\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}^+ \ / \ \text{H}_2\text{O}} \text{CH}_3 - \text{CH}_2\text{OH} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH} + \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \text{OH}$$

$$\begin{array}{ccc}
CH_3 & CH_3 \\
CH_3 - C = CH_2 & CH_3 \\
\hline
CH_3 & C - CH_3
\end{array}$$

$$CH_3 & C - CH_3 \\
CH_3 & C - CH_3$$

Mechanism

$$H_2 \ddot{O} + H \longrightarrow H_3 O^+$$

$$C = C + \dot{H} - O \xrightarrow{\text{protonation}} C = C + \dot{H} -$$

$$H - C = C - \xrightarrow{\text{deprotonation}} C = C + H^{+}$$

$$H \longrightarrow H \longrightarrow H$$

Eg: 3, 3 dimethyl but -1- ene + dilute H_2SO_4

$$CH_{2} = CH - C - CH_{3} \xrightarrow{H^{\oplus}} CH_{3} - CH - C - CH_{3} \xrightarrow{-CH_{3} \text{ shift}} CH_{3}$$

$$\begin{array}{c} CH_3 \\ CH_3 - CH - C - CH_3 + H - O - H \xrightarrow{-H^+} CH_3 - CH - C - CH_3 \\ CH_3 & CH_3 & OH \end{array}$$

2. Hydroboration - Oxidation

When alkenes react with borane form trialkyl borane which on oxidised with H₂O₂in aqueous alkeline medium alchohols are formed Anti Markovnikov alchohol.

$$B_2H_6 \longrightarrow 2BH_3$$

$$CH_3 - CH - CH_2 \xrightarrow{H-BH_2} CH_3 - CH_2 - CH_2 - BH_2 \xrightarrow{CH_3-CH_2=CH_2}$$

$$3\text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{OH} \leftarrow \frac{\text{alkali}}{\text{H}_{2}\text{O}_{2}} \left(\text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} \right)_{3} \\ \text{B} \leftarrow \frac{\text{CH}_{3} - \text{CH}_{2} = \text{CH}_{2}}{\text{H}_{2}\text{O}_{2}} \left(\text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} \right)_{2} - \text{BH} \\ \text{H}_{3}\text{BO}_{3}$$

Syn addition

$$\begin{array}{c|c} \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 \\ & \downarrow \\ & \downarrow \\ & + - - - \operatorname{BH}_2 \end{array}$$

3. Oxymercuration - Demercuration

It is hydration of an alkene to form Markovnikov alchohol, there is no intermediate forming.

$$CH_3 - CH = CH_2 \xrightarrow{Hg(OAC)_2/H_2O} CH_3 - CH - CH_3$$

$$CH_3 - CH = CH_2 \xrightarrow{Hg(OAC)_2/H_2O} CH_3 - CH - CH_2 - D$$

$$OH$$

$$\mathrm{CH_3} - \mathrm{CH} = \mathrm{CH_2} \xrightarrow{\mathrm{Hg(OAC)_2/D_2O}} \mathrm{CH_3} - \mathrm{CH} - \mathrm{CH_2} - \mathrm{H}$$

$$\mathrm{OD}$$

Alkoxy Mercuration - Demercuration

$$CH_3 - CH = CH_2 \xrightarrow{Hg(OAC)_2/ROH} CH_3 - CH - CH_3$$

$$Record A = CH_2 \xrightarrow{NaBH_4} CH_3 - CH - CH_3$$

$$\stackrel{\text{OMDM}}{\longrightarrow} \stackrel{\text{OH}}{\longleftarrow}$$

$$\stackrel{\text{HBO}}{\longrightarrow} \stackrel{\text{OH}}{\longrightarrow}$$

Addition of Halogen

Formation of vicinal halide

$$C = C + X_2 \xrightarrow{CCl_4} - C - C - C$$

$$C = C + X - X \longrightarrow C - C \xrightarrow{X^{\Theta}} C - C \xrightarrow{X}$$

These are antiaddition reaction

$$\mathrm{CH_2} = \mathrm{CH_2} + \mathrm{Br_2} \xrightarrow{\mathrm{CCl_4}} \begin{array}{c} \mathrm{Br} \\ | \\ \mathrm{CH_2} - \mathrm{CH_2} \\ | \\ \mathrm{Br} \end{array}$$

The reddish brown colour of bromine is discharged and colourless vicinal dibromide is formed, this reaction is used for test for unsaturation.

Racemic Mixture

If alkenes containing nucleophilic center cyclisation takes place

$$OH + Br_2 \longrightarrow O + HBr$$

Mechanism

Addition of Carbene

Formation of cycloalkane

$$CH_2 = CH_2 + : CH_2 \xrightarrow{hv} CH_2 - CH_2$$

$$CH_{2}N_{2} \xrightarrow{hv} : CH_{2} + N_{2}$$

$$CH_{2} = C = O \xrightarrow{hv} : CH_{2} + CO$$

$$Ketene \longrightarrow Formation of Carbene$$

$$CHCl_{3} \xrightarrow{OH^{-} - CCl_{2} \longrightarrow : CCl_{2}} : CCl_{2}$$

$$\label{eq:ch3-CH3-CH2-CH2} \begin{split} \text{CH}_3-\text{CH} = \text{CH}_2 + \text{CHCl}_3 & \xrightarrow{\text{KOH}} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ & \text{CCl}_2 \\ \text{1, 1 dichloro 2 methyl cyclopropane} \end{split}$$

Addition of Hypohalous Acid

Formation of halohydrin

$$X_2 + H_2O \longrightarrow OH - X + HX$$

hypohalous acid

$$\label{eq:CH2} \begin{array}{c} \text{OH} \\ \text{CH}_2 = \text{CH}_2 + \text{X}_2 \xrightarrow{\quad +\text{H}_2\text{O} \quad} \text{CH}_2 - \text{CH}_2 \\ \\ \text{X} \end{array}$$

$$CH_{2} = CH_{2} + X - X \longrightarrow CH_{2} - CH_{2} \xrightarrow{H_{2}O} CH_{2} - CH_{2} \xrightarrow{\oplus} H$$

$$X \qquad \qquad \downarrow OH$$

$$HX + CH_{2} - CH_{2}$$

$$X \qquad \downarrow OH$$

$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow{H_2O} CH_3 - CH - CH_2$$

$$OH$$

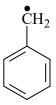
Alkenes substitution reaction

Higher alkenes are heated with halogen under higher temperature, H atoms from Alkyl / benzylic carbon replaced halogenation taking place and this halogenation is known as Alkylic / benzylic halogenation

$$CH_2 = CH - CH_3 + X_2 \xrightarrow{500^{\circ}C} CH_2 = CH - CH_2CI$$

$$CH_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2$$
 Allyl free radicals resonance stabilization

$$\begin{array}{c|c} CH_3 & CH_2\text{-}X \\ \hline \end{array} + X_2 \xrightarrow{\Delta} \begin{array}{c} CH_2\text{-}X \\ \hline \end{array} + HX$$



Allyl and benzyl radicals are resonance stabilised.

$$CH_2 = CH_2 + X_2 \xrightarrow{500^{\circ}C}$$
 not possible

$$CH_2 = CH - CH_3 + NBS \xrightarrow{425 \text{ K}} CH_2 = CH - CH_2Br + O$$

OXIDATION REACTION

1. Complete oxidation

$$CnH_2n + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

Eg.
$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

2. Incomplete / partial oxidation

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag_2} CH_2 - CH_2$$
 Epoxide

Epoxide undergo acidic hydrolysis give vicinal diol and reaction is known as hydroxylation. It is anti hydroxylation reaction

$$\begin{array}{c}
\text{OH} \\
\text{CH}_2 - \text{CH}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{CH}_2 - \text{CH}_2 \\
\text{OH}
\end{array}$$

Mechanism

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

$$\begin{array}{c|c} \text{OH} & \text{OH} \\ \text{CH}_3 - \text{CH} - \text{CH}_2 & \xrightarrow{\text{H}_2 \ddot{\text{O}}} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ & \text{OH} & \text{OH} \end{array}$$

$$CH_{2} = CH_{2} \xrightarrow{R-C-O-O-H} CH_{2} - CH_{2} + RCOOH$$

$$CH_{2} = CH_{2} \xrightarrow{Peroxy \ acid/peracid} CH_{2} - CH_{2} + RCOOH$$

$$CH_{3} - CH = CH_{2} \xrightarrow{CH_{3} - C - O - OH} CH_{3} - CH - CH_{2} + CH_{3}COOH$$

$$CH_{3} - CH = CH_{2} \xrightarrow{CH_{3} - C - O - OH} CH_{3} - CH - CH_{2} + CH_{3}COOH$$

$$CH_2 = CH_2 + m - CPBA \longrightarrow CH_2 - CH_2 + CH_$$

$$\begin{array}{c}
 & \xrightarrow{\text{M-CPBA}} & \xrightarrow{\text{M-CPBA}} & \xrightarrow{\text{H^+/H}_2\text{O}} & \xrightarrow{\text{H^+/H}_2\text{O}} & \\
 & \xrightarrow{\text{M-CPBA}} & \xrightarrow{\text{M-CPBA$$

Oxidation using Dil. /cold KMnO₄

$$2KMnO_4 \longrightarrow 2KOH + 2MnO_2 + 3[O] \longrightarrow$$

$$CH_2 = CH_2 \xrightarrow{KMnO_4} CH_2 - CH_2$$

$$OH OH$$

syn addition and vicinal diol

The purple colour / KMnO₄ is discharged and colourless, Vicinal diol is formed is known as

$$CH_{3}$$

$$C = C$$

$$H$$

$$CH_{3}$$

$$Syn \ addition$$

$$H$$

$$CH_{3}$$

$$OH$$

$$CH_{3}$$

$$CH_{3}$$

$$C = C \xrightarrow{\text{CH}_3} \xrightarrow{\text{dil.KMnO}_4} OH \xrightarrow{\text{CH}_3} OH OH \xrightarrow{\text{CH}_3} OH OH \xrightarrow{\text{CH}_3} OH$$

$$CH_3 \xrightarrow{\text{CH}_3} OH \xrightarrow{\text{CH}_3} OH OH \xrightarrow{\text{CH}_3} OH$$

Oxidation using Acidified or Alkaline hot KMnO₄/K₂Cr₂O7

$$CH_2 = CH_2 \longrightarrow 2CO_2 + 2H_2O$$

$$CH_3 - CH_2 = CH_2 \longrightarrow CH_3 - COOH + CO_2 + H_2O$$

Terminal can be converted into CO₂ and H₂O

$$CH_3 - CH = CH - CH_3 \longrightarrow 2CH_3 - COOH$$

Without terminal the respective acids will be formed

$$CH_3 - CH_2 - CH = CH - CH_3 \longrightarrow CH_3 - CH_2 - COOH + CH_3 - COOH$$

If no H is present on C then it becomes CO(Keto)

$$\begin{array}{c} \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \longrightarrow \text{CH}_3 - \text{C} = \text{O} + \text{CH}_3\text{COOH} \end{array}$$

$$\xrightarrow{\text{KMnO}_4} \text{HOOC} \xrightarrow{\text{(CH}_2)_4} \text{COOH}$$
adipic acid

Oxidation using OsO

Syn hydroxylation

$$\begin{array}{c} \xrightarrow{\text{H}_2\text{O}_2} \\ \text{OH} \end{array}$$

$$\begin{array}{ll} \mbox{dil. KMnO}_4 \left\{ \begin{array}{ll} \mbox{syn} & \mbox{epoxide} + \mbox{H}^+ \\ \mbox{OSO}_4 \end{array} \right. \left\{ \begin{array}{ll} \mbox{eyn} & \mbox{epoxide} + \mbox{H}^+ \\ \mbox{H}_2\mbox{O}_2 + \mbox{HCOOH} \end{array} \right. \left\{ \begin{array}{ll} \mbox{anti hydroxylation} \end{array} \right.$$

OZONOLYSIS REACTION

$$C = C + O_3 \longrightarrow C \qquad \xrightarrow{H_2O_2/AgO \text{Ozonide}} Oxidative ozonolysis$$

$$Zn \longrightarrow H_2O /Me_2S$$

Reductive Ozonolysis

$$CH_2 = CH_2 + O_3 \xrightarrow{Zn-H_2O} CH_2 \xrightarrow{CH_2} CH_2 \xrightarrow{-ZnO} 2H - C - H$$

$$CH_3 - CH = CH_2 + O_3 \xrightarrow{Zn - H_2O} CH_3 - C \xrightarrow{C} CH_2 \xrightarrow{-ZnO} CH_3CHO + HCHO$$

$$CH_3 - CH = CH - CH_3 + O_3 \longrightarrow CH_3 - CH \longrightarrow CH_3 - CH_3 \longrightarrow 2CH_3CHO$$

$$CH_3$$

 $CH_3 - C = C - CH_3 + O_3 \longrightarrow CH_3 - COCH_3 + CH_3CHO$

Oxidative ozonolysis

$$\begin{array}{c|c} \text{CH}_3 - \text{CH}_2 - \text{CH} & \text{CH}_2 - \text{CH}_3 \\ \hline \\ \text{O} & \text{O} \end{array} \\ \begin{array}{c|c} \text{CH}_3 - \text{CH}_2 - \text{CHO} + \text{CH}_3 \text{CHO} \\ \hline \\ \text{H}_2 \text{O}_2 \\ \hline \\ \text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{CH}_3 - \text{COOH} \\ \hline \end{array}$$

Polymerisation reaction

Polymerisation is a process by which a large number of simple molecules combine to form a large molecule. The simple molecules are called monomers while the large molecule is called a polymer

Conversion of monomer → polymer

At 473 k and 1500 atm

n
$$CH_2 = CH_2 \longrightarrow (CH_2 - CH_2)_n$$

ethene polythene

$$\begin{array}{c} \text{CH}_{3} \\ \text{n CH}_{2} - \text{CH} = \text{CH}_{2} \longrightarrow \underbrace{\text{CH}_{2} - \text{CH}_{2}}_{\text{polypropyne}} + n \end{array}$$

n
$$CH_2 = CH - Cl \longrightarrow n + (CH_2 - CH_2)$$
 polyvinyl chloride (pvc)

$$\begin{array}{ccc} \text{n (CH}_2\text{CH)} & \longrightarrow \text{n (CH}_2\text{-CH}_2\text{+}\\ & & \text{ph} & & \text{ph} \\ & & \text{Styrene} & & \text{Polystyrene} \end{array}$$

Acrylnitrile Polyacrylonitrile (PAN)

$$CF_2 = CF_2 \longrightarrow (CF_2 - CF_2)_n$$

$$\begin{array}{c|c} \text{CH}_3 & \text{CH}_3 \\ \text{n CH}_2 = \text{C} - \text{CH} = \text{CH}_2 & \xrightarrow{\text{TEFLON}} & \text{(CH}_2 - \text{C} - \text{CH} - \text{CH}_2)_n \\ \\ \text{Isoprene} & \text{Polyisoprene} \end{array}$$

Dimerisation reaction

$$CH_3$$
 $CH_3 - C - CH = CH_2 \xrightarrow{H_2SO_4} (CH_3)_3 - C - CH_2 = C - (CH_3)_2$

$$CH_{3} - C + CH_{2} = C - CH_{3} \longrightarrow CH_{3} - C - CH_{2} - C - CH_{3}$$

$$CH_{3} - C + CH_{2} = C - CH_{3} \longrightarrow CH_{3} - C - CH_{2} - C - CH_{3}$$

$$CH_{3} - C - CH_{2} = C + CH_{3}$$

$$(CH_{3})_{3} - C - CH_{2} = C + CH_{3})_{2}$$

Diels Alder Reaction

(4 + 2) Cycloaddition of conjugated alkene with an enophile (=/=)

$$\bigcirc \downarrow \downarrow \qquad \bigcirc$$

$$\begin{array}{c|c} & & & & & & & & & & & & & & & & \\ & & & & & & & & & & & & & & & & \\ & & & & & & & & & & & & & & \\ & & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ \\ & \\ & \\ \\ & \\ \\ & \\ \\ & \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ & \\ \\ &$$

ALKYNES

- General formula : C_nH_{2n-2}
- Less than 4 H atom corresponding paraffins
- Known as acetylene
- First member is acetylene others are derivatives of acetylene

Eg.
$$CH \equiv CH$$
 methylene

$$CH_3 - C \equiv C - CH_3$$

$$CH_3 - C \equiv C - CH_3$$
 $CH_3 - C \equiv C - CH_2 - CH_3$

$$CH_3 = C - CH_3$$

Dimethyl acetylene

$$CH_2 = CH - C \equiv C - CH_2 - CH = CH_2$$

Allyl vinyl acetylene

The four half filled orbitals on each C atom merge together to form a single electron cloud in a cylindrical cloud. The C - H bond is passing through the center of the cylinder its bond angle always remains 180° and linear geometry.

Alkynes are less reactive than alkenes due to

- 1. the cylindrucal geometry $\pi \bar{e}$ are not readily available for reactions.
- 2. Due to the sp hybridised C atom π i are tightly held by the nucleus thus π i are not readily available.

PREPARATION

1. addition of H₂O on CaC₂

$$CaC_2 + H_2O \longrightarrow CH = CH + Ca(OH)_2$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \xrightarrow{2000-3000^{\circ}C} CaC_2 + CO$$

- 2. from alkyl halide
- → from dihalide from vicinal di halides

$$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \xrightarrow{\quad \text{alc.KOH} \quad} \text{CH}_2 = \text{CH}_2 - X \xrightarrow{\quad \text{alc.KOH} \quad} \text{CH} \equiv \text{CH} + \text{HX} \\ X \end{array}$$

$$CH_2 = CH - \ddot{X} : \longrightarrow CH_2 - CH = \ddot{X}$$

Thus the reaction is very slow hence we can speed up the reaction by using NaNH₂ which is more basic

$$CH_2 = CH - X + \xrightarrow{NaNH_2} CH = CH + HX$$

There two step reaction can be concluded into one step using NaNH,

$$CH_2 - CH_2 \xrightarrow{2NaNH_2} CH = CH + 2HX$$
 X

From geminal halide

$$CH_3 - CH \xrightarrow{X} \qquad \xrightarrow{alc.KOH} CH_2 = CH - X \xrightarrow{alc.COH} CH \equiv CH$$

$$CH_3 = CHX_2 \xrightarrow{2NaNH_2} CH \equiv CH + HX$$

→ From Haloform

$$2CHX_3 \overset{+}{6}Ag \longrightarrow CH = CH + 6AgX$$

$$CHX_3 + 6Ag + X_3CH \longrightarrow CH_2 = CH + 6AgX$$

$$2CHCl_3 + 6Ag \longrightarrow CH \equiv CH + 6AgCl$$

Tetrahalide

$$\begin{array}{c|cccc} X & X & \\ & & \\ CH & -CH & +2Zn & \longrightarrow CH \Longrightarrow CH + 2ZnX \\ & & \\ X & & X & \end{array}$$

3. From unsaturated dicarboxylic acid

Aquarous Na/K salt of maleic/fumeric acid undergoes kolbe electrolytic decarboxylation.

$$H_2O \longrightarrow H^+ + OH^-$$

At anode At cathode

4. From C and H

Berthlot method

Passing H₂ gas through an electric arc stuck between carbon electrode

$$2C + H_2 \xrightarrow{3000^{\circ}C} CH \equiv CH$$

5. Preparation of higher alkynes using acetylenes

Acetylene react with metals form metal acetylide. These metal acetyldes reawct with haloalkenes form higher alkynes

$$2CH = CH + 2Na \longrightarrow 2CH = C - Na + H_{2}$$

$$2CH = C - Na + 2R - X \xrightarrow{SN_{2}} 2CH = C - R + 2NaX$$

$$CH = CH - Na + CH_{3} - C1 \longrightarrow CH = CH - CH_{3} + NaC1$$

$$CH = CH + 2NaX \longrightarrow Na - C = C - Na + 2HX$$

$$Na - C = C - Na + 2R - X \longrightarrow R - C = C - R + 2NaX$$

$$Na - C = C - Na + 2CH_{3} - C1 \longrightarrow CH_{3} - C = C - CH_{3} + 2NaC1$$

Physical properties

- Acetylene is a colourless odourless gas
- First 3 members are gas next 8 members are liquid remaining are solids.

Melting and boiling point

 Melting and boiling points are higher than alkenes due to symmetrical and more polar in nature.

When size or mol mass is high, boiling point melting point will be high

Solubility

Insoluble in H₂O and soluble in organic solvents

Chemical reactions

Acidic character of an alkenes

1. Formation of alkalimetal acetylide

Thermal alkynes react with alkali metals and forms alkali metal acetalides and there acetalides react with H₂O and regenerate acetylene. This shows water is more acidic than acetylene.

$$2R - C \equiv CH + 2Na \longrightarrow 2R - C \equiv CNa$$

$$R - C \equiv CNa + H_2O \longrightarrow R - C \equiv CH + NaOH$$

2. Formation of heavy metal acetylide

Acetaline react with Tollens reagent $\left[2Ag(NH_3)_2\right]OH^-$ ammoniacal silver nitrate form silver acetalide.

$$CH = CH + 2\left[Ag(NH_3)_2\right]^+OH^- \longrightarrow Ag - C = C - Ag + 4NH_3 + 2H_2O$$

Acetylene reacted with ammoniacal cuprous chloride.

$$CH = CH + 2\left[Cu\left(NH_3\right)_2\right]^+OH^- \longrightarrow Cu - C = C - Cu + 4NH_3 + 4H_2O$$

There reagents are used for the detection of terminate alkynes to alkenes.

$$Ag - C \equiv C - Ag + 2HCl \longrightarrow CH \equiv CH + 2AgCl$$

Thus acetylene are weaker than mineral acids

3. Formation of alkynyl grignard reagent

$$CH \equiv CH + R - MgX \longrightarrow CH \equiv C - MgX + RH$$

Reason for acidic

In acetylene C is $sp \rightarrow so$ more s character so highly electronegative. Thus it withdraws electrons from C–H bonds and thus releases H $^{+}$ atom.

Addition reaction

Addition of hydrogen

$$CH \equiv CH + H_2 \xrightarrow{N_i} CH_2 = CH_2 \qquad \Delta H = -196 \text{ kj/mol}$$

$$CH_2 \equiv CH_2 + H_2 \xrightarrow{N_i} CH_3 - CH_3 \qquad \Delta H = -138 \text{ kJ/mol}$$

Catalytic hydrogenation of alkynes is more spontaneous then catalytic hydrogenation of alkanes to alkenes.

$$CH_3 - C \equiv C - CH = CH_2 \xrightarrow{H_2 - pd} CH_3 - CH = CH - CH = CH_2$$

2. Addition of halogen

$$CH = CH + X_2 \xrightarrow{CCl_4} HC = CH \xrightarrow{X} X$$

$$X \longrightarrow X$$

$$CH \equiv CH + Cl_2 \xrightarrow{CCl_4} CH = CH \xrightarrow{Cl} Cl_2 \xrightarrow{Cl} CH \xrightarrow{Cl} CH$$

$$\downarrow CH = CH \xrightarrow{CH} CH \downarrow \downarrow CH$$

$$\downarrow CH = CH \xrightarrow{CH} CH$$

1,1,2,2 tetrachloroethene westron

$$\text{Eg}: \text{CH} = \text{CH} + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{CH} = \text{CH} \xrightarrow{\text{Br}} \text{Br} & \text{Br} & \text{Br} \\ | & | & | \\ | & \text{CH} = \text{CH} \\ | & | & | \\ | & \text{Br} & \text{Br} \\ | & \text{Br} & \text{Br} \\ | & \text{Br}$$

Reddish brown

Colourless

3. Addition of hydrogen halide

$$CH \equiv CH + HX \longrightarrow CH_2 = CH - X + HX \longrightarrow CH_3 - CH - X$$

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

1,2,dibromoethane

Addition of H₂O

Due to low reactivity of alkynes it reacts in presence of mercuric ion.

$$CH = CH \xrightarrow{\text{dil.H}_2SO_4} CH_2 = CHOH \longrightarrow CH_3 - C - H$$

$$\begin{array}{c} Hg_2^+ \\ CH = CH \xrightarrow{H_2O} CH = CH - Hg^+ \longrightarrow CH = CH - Hg^+ \longrightarrow OH \\ H & OH \end{array}$$

$$\begin{array}{c} H-C-CH_2-Hg^+ \xrightarrow{H^+} H-C-CH_2-Hg^+ \xrightarrow{-Hg^{2+}} H-C=CH_2 \longrightarrow H-C-CH_3 \\ O \qquad \qquad O \longrightarrow H \end{array}$$

$$CH_3$$
— C = CH_4 CH_3 — CH_3 — CH_4 CH_5 CH_5 CH_5 CH_5 CH_6 CH_7 CH_7 CH_7 CH_8 $CH_$

$$CH_3$$
— CH_2 — $C\equiv C$ — CH_3 — $\frac{dil.H_2SO_4}{HgSO_4}$ CH_3 — CH_2 — CH_2 — C — CH_3

Addition of acetic acid

Addition of alcohol

$$CH = CH + C_2H_5OH \longrightarrow CH_2 = CH - O - C_2H_5 \xrightarrow{H^+/H_2O} CH_3 \longrightarrow C \longrightarrow H + C_2H_5O_{11}$$

NUCLEOPHILIC ADDITION REACTION

Due to the presence of sp hybridised carbon alkynes can show nucleophilic addition reaction.

$$CH \equiv CH \xrightarrow{CH_3O^{-}} CH = CH - OCH_3 \longrightarrow CH_2 = CH - OCH_3$$

$$\begin{array}{c}
Nu \\
Nu + R - C = C - R \\
\end{array}$$

$$\begin{array}{c}
Nu \\
C = C - R \\
- Nu \\
\end{array}$$

$$\begin{array}{c}
Nu \\
- Nu \\
R
\end{array}$$

$$\begin{array}{c}
C = C \\
R
\end{array}$$

Hydroboration - Oxidation reaction

$$CH_{3}-C \equiv CH \xrightarrow{H-BH_{2}} CH_{3}-CH = C - BH_{2} \xrightarrow{CH_{3}-C} \equiv CH$$

$$(CH_{3}-CH = C \xrightarrow{})_{2}BH \xrightarrow{} CH_{3}-C \equiv CH$$

$$0$$

$$\parallel$$

$$3CH_{3}-CH_{2}-CH \xleftarrow{} 3CH_{3}-CH = CH-OH \xleftarrow{} \frac{H_{2}O_{2}}{\Theta} (CH_{3}-CH = C)_{3}B$$

$$aq.OH$$

To avoid the multiple addition of alkene bulky borones like dissamyl borane (1, 2 dimethyl propyl borane) is used

$$CH_3$$
— $C\equiv CH$ R_2BH CH_3 — CH CH BR_2

Where
$$R = \begin{pmatrix} CH_3 - CH - CH - CH - BH \\ | & | \\ CH_3 & CH_3 \end{pmatrix}$$
 disiamyl

$$CH_3$$
— CH_2 — $C=C$ — CH_3 — CH_3 — CH_2 — CH_2 — CH_3 — C

Hydroboration - Alkylation

$$\left(CH_3 - CH_2 - CH_2 \xrightarrow{} B \xrightarrow{3R-COOH} CH_3 - CH_2 - CH_3 \right)$$

$$\left(\text{CH}_3 - \text{CH} = \text{CH} \xrightarrow{}_{3} \text{B} \xrightarrow{\text{3R-COOH}} \text{CH}_3 - \text{CH} = \text{CH}_2\right)$$

Addition of HCN

$$CH = CH + HCN \longrightarrow CH_2 = CH$$

$$CH = CH + HCN \longrightarrow CH_2 = CH$$

$$CN$$

$$\begin{array}{c|c}
nCH_2 & \xrightarrow{Poly} & \leftarrow CH_2 & \xrightarrow{CH} & \rightarrow \\
CN & & CN & n
\end{array}$$
PAN

OXIDATION REACTION

1. Complete oxidation

$$2CH \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

When acetylenes are burnt with air/oxygen under higher pressure they burn to form CO_2 and H_2O atoms with blue flame having higher temperature around 3000°C and this flame is used for cutting and welding metals.

2. Oxidation using dilute KMnO

CH
$$\equiv$$
 CH $\xrightarrow{\text{dil.KMnO}_4}$ OH $\xrightarrow{\text{C}}$ C $\xrightarrow{\text{C}}$ OH

CH₃—C \equiv CH $\xrightarrow{\text{CH}_3}$ —C —COOH

CH₃—C \equiv C —CH₃ $\xrightarrow{\text{C}}$ CH₃—C —C—CH₃
 \parallel \parallel \parallel OOO

3. Oxidation using acidified alkaline/KMnO₄/K₂Cr₂O₇

OZONOLYSIS

$$CH = CH + O_3 \longrightarrow CH \xrightarrow{CH} CH \xrightarrow{Zn-H_2O} H - C - C - H$$

$$0 \quad 0 \quad Glyoxal$$

$$CH_{3}-C = CH \xrightarrow{C} CH_{3} - C \xrightarrow{C} CH \xrightarrow{C} CH_{2}O \xrightarrow{C} CH_{3} - C \xrightarrow{C} CH$$

POLYMERISATION REACTION

1. Linear polymerisation

$$2CH \equiv CH \xrightarrow{NH_4CI/CuCl} CH_2 = CH - C \equiv CH \xrightarrow{CH \equiv CH} CH_2 = CH - C \equiv C - CH = CH_2$$

Cyclic polymerisation

$$3CH \equiv CH \xrightarrow{\text{Red} \atop \text{Hot Fe} \atop \text{Tube}} CH \xrightarrow{\text{CH}} CH$$

$$CH \downarrow CH$$

$$CH \downarrow CH$$

$$3CH_{3} - C \equiv CH \xrightarrow{R.H.} CH$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$4CH \equiv CH \xrightarrow{Ni(CN)_4} CH \equiv CH$$

$$CH \qquad CH$$

$$CH \qquad CH$$

$$CH \qquad CH$$

$$CH \equiv CH$$

$$CH \equiv CH$$

$$CH \equiv CH$$

ISOMERISATION

$$CH_3 - C \equiv C - CH_3 \xrightarrow{NaNH_2} CH_3 - CH_2 - C \equiv CH$$

$$CH_3 - CH_2 - C \equiv CH \xrightarrow{\text{alc.KOH}} CH_3 - C \equiv C - CH_3$$

BENZENES

- C₆H₆
- Less than 8H corresponding paraffins

- Highly unsaturated system
- 8 observations that suggest benzene
- 1. Benzene and 3 molecules of H on presence of Rency Ni and cyclohexane

$$C_6H_6 + 3H_2 \xrightarrow{\text{Rency Ni}} C_6H_{12}$$

2. Benzene add 3 molecule of chlorine and form benzene hexachloride

$$C_6H_6 + 3Cl_2 \xrightarrow{hv} C_6H_6Cl_6$$

3. Benzene add 3 molecules of ozone and form benzene triozonide

$$C_6H_6 + 3O_3 \longrightarrow C_6H_6(O_3)_2$$

Two observations that suggest benzene shows saturated properties.

- 1. Benzene resist $\equiv KMnO_4$ oxidation like alkane
- 2. Benzene does not decolourise Br₂ in CCl₄ but benzene give monosubstitution product with bromine in presence of FeBr₃

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5 - Br + HBr$$

In 1865 Fredrich Augast Kekule suggest structure of benzene based on his dream According to Kekule, benzene containing 6C atom join each of alternatively single and double bond and each C atom goin with hydrogen.

$$\begin{array}{c|c} H & H \\ | & | \\ C & C \\ | & | \\ H & C \\ \\ H \\ H$$

Objection against Kekule structure

- 1. Kekule cannot explain benzene stability against KMnO₄ oxidation
- 2. Kekule structure explained two type of bond ie single and double bond. But X-ray diffraction shows that benzene have only 1 bond length (ie) 139 pm and is b/w C=C and C-C.
- 3. Kekule only explained the monosubstitution product but in case of disubstitution product there is two possibilities.

$$\begin{array}{c|c} & & & & & & & \\ Br & & & & & \\ \hline \end{array}$$

There is a double bond between C contaiing two Br

There is a single bond between C carrying Br

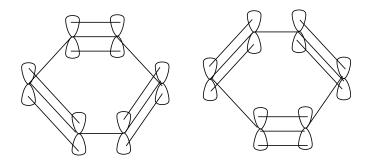
If Kekule's structure was correct there structures exist with two different properties but only one desubstitution product are known. Kekule suggest and equilibrium between there two structures and the position of single and double bond is not fixed

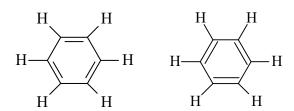
THE STRUCTURE OF BENZENE IS EXPLAINED BY USING

1) MOT

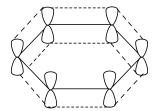
2) Resonance theory

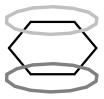
In benzene each C atom form two C–C σ bond with neighbouring two C so there is total 6 C–C σ bond. Each carbon atom forms σ bond with H so there is total 6CH σ bond. The C–C bond angle is 120° so molecule is in planar geometry and each C atom is sp² hybridised. Each C atom left on one unhybridised p orbital and there unhybridised p orbitals sidewise overlapping to form there carbon π bond on two ways.





The participation of each π orbitals to form more than one π bond is known as delocalisation and this delocalised π electrons are shown above and below the plane.





According to resonance theory there π electrons are completely delocalised and there delocalised structures are called cannonical structures.

CHEMISTRY -2020

PREPARATION

1. From acetylene

$$3CH \equiv CH \xrightarrow{\text{red hot}}$$

2. From normal hexane

$$C_6H_{14} \xrightarrow{V_2O_5}$$
 $\xrightarrow{3H_2}$

3. From sodium benzoate

COOH
$$Na_2CO_3$$
 $NaOH+C_2O$

4. From phenol

$$OH \longrightarrow Z_{n-dust} \longrightarrow Z_{n}$$

5. From chlorobenzene

$$\begin{array}{c}
C1 \\
\hline
Ni-Al alloy \\
NaOH
\end{array}$$
+ HC

6. From benzene diazonium chloride

$$+ H_3PO_2 + H_2O \xrightarrow{Cu^{2+}} N_2 + HCI + H_3PO_3$$

7. From benzene sulphonic acid

$$+ H_2O \longrightarrow + H_2SO_4$$

8. From grignard reagent

$$C_6H_5MgX \xrightarrow{H_2O} C_6H_6 + Mg(OH)X$$

$$C_6H_6CH_2MgX \xrightarrow{H_2O} C_6H_5CH_3 + Mg(OH)X$$

9. Wurtz Fittig Reaction

Haloalkenes react with haloalkenes in presence of disodium in dry ether aralkyl compounds are formed

$$X + 2Na + X - R - A$$

$$R-X+2Na+X-R \xrightarrow{\quad \ \ \, } R-R+2NaX$$
 - Wurtz reaction

$$X + 2Na + X \longrightarrow A \longrightarrow Fitting reaction$$

PHYSICAL PROPERTIES

As size increases melting point and boiling point increses. In benzene each π electrons are equally attracted by all carbon atoms so dipole moment is zero.

- .. So boiling point depends only on size.
- In case of isomeric, P isomers having high melting point than M and O due to symmetric geometry.
- Benzene insoluble in water but soluble in organic solvent

CHEMICAL REACTIONS

 More reactive than alkanes and less reactive than alkenes and alkynes due to complete delocalisation of electron.

ELECTROPHILIC SUBSTITUTION REACTION

1. E - Nu
$$\xrightarrow{\text{ionise}} \stackrel{\bigoplus}{E} + N \stackrel{\bigoplus}{U}$$

2.
$$E^{\oplus}$$
Arenium ion

3.
$$\begin{array}{c} & & \\ & & \\ & & \end{array}$$

- 1. Generation of electrophile
- 2. Formation of arenium ion
- 3. Formation of sub product

1. HALOGENATION

$$+ Cl_2 \xrightarrow{\text{anhy:AlCl}_3} + HC$$

$$Cl - Cl + AlCl_3 \longrightarrow Cl^+ + Al^-Cl_4$$

$$\begin{array}{c} Cl - Cl \\ \hline AlCl_3 \\ \hline \end{array} \begin{array}{c} H \\ Cl \\ + AlCl_4 \\ \hline \\ Cl \\ \hline \end{array} \\ + HCl + AlCl_3 \\ \end{array}$$

AICI₃ acts as a halogen carries as well as electrophilic producer. If a halogen carries is present and no light then benzene goes subtraction.

$$+ Br_{2} \xrightarrow{FeBr_{3}} + HBr$$

$$+$$
 Br - Br $FeBr_3$ $+$ HBr +

$$\begin{array}{c}
Cl \\
Cl \\
Cl
\end{array}$$

$$\begin{array}{c}
Cl \\
Cl
\end{array}$$

$$\begin{array}{c}
Cl \\
Cl
\end{array}$$

$$\begin{array}{c}
Cl \\
Cl
\end{array}$$

hexachlorobenzne

2. Nitration

$$\xrightarrow{\text{conc:H}_2 \text{SO}_4} \text{NO}_2 \\
+ \text{H}_2 \text{O}$$

$$H_2SO_4 \Longrightarrow H^+ + HSO_4$$

$$OH \longrightarrow NO_2 \xrightarrow{H} O \longrightarrow NO_2 \longrightarrow H_2O + NO_2$$

$$\downarrow H$$

$$+ NO_2 \longrightarrow H \longrightarrow HSO_4 \longrightarrow NO_2$$

$$+ H_2SO_4$$

3. Sulphonation

$$\underbrace{\hspace{1cm} \begin{array}{c} \text{conc. } H_2SO_4/\\ \hline H_2S_2O_7 \text{ Oleum} \end{array}} \begin{array}{c} SO_3H \\ \end{array}$$

$$2H_2SO_4 \longrightarrow SO_3 + H_3O + \overset{\Theta}{H}SO_4$$

$$\begin{array}{c|c}
O \\
H \\
O \\
O \\
\end{array} + H_2O$$

FRIEDEL CRAFT REACTION

1. ALKYLATION

$$R \longrightarrow Cl$$

$$R \longrightarrow R$$

2. ACYLATION

$$\begin{array}{c|c}
O & C \\
C - R \\
R - C - Cl \\
\hline
An.AlCl_3 + HCl
\end{array}$$

BENZENE ADDITION REACTION

$$+ 3Cl_2 \xrightarrow{hv} H Cl H Benzene hexachloride$$

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

When benzene burn with air/oxygen under pressure, they burn with an yellow sooty flame. This flame indicate presence of higher carbon content in benzene and is used for distinguishing diphetic and aromatic compound.

Incomplete oxidation

Oxidation with KMnO₄

Benzene resist KMnO₄ oxidation but alkyl benzenes give benzoic acid due to high reactivity of benzylic hydrogen oxidaiton taking place at benzylic carbon.

$$+3O_3 \longrightarrow 0 \longrightarrow 0 \longrightarrow 0$$

$$\longrightarrow 2n-H_2O \longrightarrow 3H-C-C-H$$

$$\bigcirc O \bigcirc O$$

AROMATICITY

According to molecular orbital theory compounds containing $(4n + 2)\pi$ electrons are completely delocalised. Such compounds are called aromatic compounds.

Conditions:

- Cyclic
- Planar
- Conjugated
- Satisfy $(4n + 2)\pi$ rule

$$4n + 2 = 6$$

$$n = 1$$

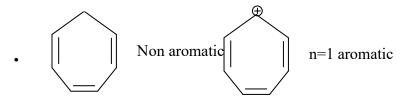
Compounds satisfying $4n\pi e^{-}$ rule \rightarrow antiaromatic

Others are non aromatic

$$4n + 2 = 10$$

$$n = 2 \quad aromatic$$

•
$$4n+2=0$$
 $n=0$ aromatic



aromatic
$$N$$
 Aromatic $n = 1$

• antiaromatic

Directive Influence of substituents

It is the ability of atoms ie group to direct the incoming group to a particular position in benzene ring

1. Ortho-para directing group

Atoms or group which donate electrons towards benzene ring and increases electron density in o and p positions. These group are ring activating groups.

All electron donating groups are o and p and ring activators.

META DIRECTING GROUP

Atoms or group which withdraw electron from benzene rings and decreases electron density at o and p positions. These groups are ring deactivating group. All electron withdrawn groups are metal directing and electron withdrawing.

Here N too have *I* pair but act as M-group because look at the atom near the *I*-pair if it is high electronegative then it act as M-group.

Polynuclear hydrocarbon

Compounds containing more than one fused benzene ring. These can generate cancer in living tissues so they are known as carcenogenic compound and the nature is called carcinogenicity. The main source of polynuclear hydrocarbon is coal tar.

$$PNH \xrightarrow{O_2} PNH \xrightarrow{H_2O} PNH \xrightarrow{H_2O} PNH \xrightarrow{PNH} CANCER$$

1, 2 benzanthracene

9,10 dimethyl benzanthracene

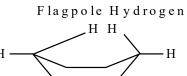
Melting point of alkane

The mp of n - alkanes are not a regular pattern. Alkanes having even number of C atom have higher mp than corresponding alkane with odd no. of carbon ie next & previous. This effect is known as alternating effect / oscillating effect.

Conformations of cyclohexane

Several 3D shapes that a cyclohexane molecule can assume while maintaing the stability of its chemical bonds cyclohexane ring tend to assume certain non planar conformations and which bond angle closer to 109°.5 and lower the strain energy.

Two type Hydrogen atoms-Axial and equatorial



Stability order

Chair > Twist boat > Boat > Half Chair

1,2	Cis	1a	2e	
1,2	Trans	1e	2e	MS
		1a	2e	LS
1,3	Cis	1e	3e	MS
		la	3a	LS
1,3	Trans	1a	3e	
1,4	Cis	1a	He	
1,4	Trans	1e	4e	MS
		1a	4a	LS

- MS- More stable
- LS-Least stable