CHAPTER - 12 **HYDROCARBON**

Organic compounds which contains both Carbon and Hydrogen.

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

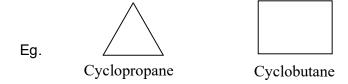
- 1) Homocyclic
- 2) Hetero cyclic

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

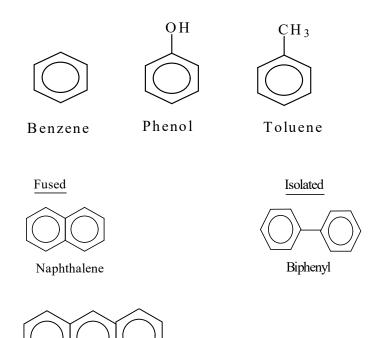
From the word Aroma (Fragnent smell)

Two types

i) Benzenoid compound

Anthracene

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.



OH

Tropolone

Tropone

2. Heterocyclic compounds

Rings contains carbon and hetero atoms

a) Alicyclic heterocyclic

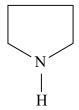
Alicyclic compounds contains hetero atoms







Tetrahydrofuran(THF)



Tetrahydropyrrole

b) Aromatic hetero cyclic

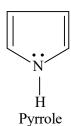
Aromatic compounds containing heteroatoms



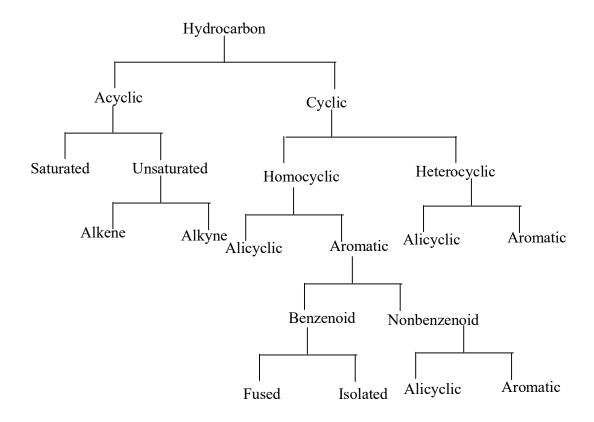
Pyridine



Furan







I. Alkanes / Paraffins

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.

$$CH_2 = CH_2 \xrightarrow{\text{Ni } 200-300^{\circ}C} CH_3 - CH_3$$

Reaction known as sabatier & senderen reaction

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

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

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

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.

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

 $\overset{8-}{R}-\overset{8+}{M}\overset{8-}{g}-\overset{8-}{X}$ 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

$$CH_3 - Br + 2Na + C_2H_5 - Br \xrightarrow{dry \text{ ether}} CH_3 - CH_3 + \\ CH_3 - CH_2 - CH_3 + \\ CH_3 - CH_2 - CH_2 - CH_3 + 2NaBr$$
 Mixture of product, seperation not easy

Limitation: 1) Methane cannot be obtained

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

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

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

$$2CH_3CH_2COONa \xrightarrow{Electrolysis} CH_3 - CH_2 - CH_2 - CH_3$$

- 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

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

Properties

1) Physical properties

1st four members (C_1-C_4)

- colourless, odourless, gases

 $\underset{\left(C_{5}-C_{17}\right)}{\text{Next}}\underset{\left(C_{5}-C_{17}\right)}{\text{13}}\text{ - colourless, odourless, liquids}$

From C₁₇

- colourless, odourless, solids

Boiling points:

Bp of n - alkanes increases regularly with increasing number of carbon atoms.

In case of isomeric alkanes branching increases bp decreases

Chemical Reactions

I. Substitution reaction

Replacement of H by another atoms / group

i) Halogenation

Replacement of H by halogen

$$--- C - H + X_2 \xrightarrow{\text{light} \atop \Delta} - C - X + HX$$

$$520 - 670 \text{ K} (x = \text{Cl, Br})$$

Halogenation reaction depends on nature halogen and type of H

$$F_2 > Cl_2 > Br_2 > I_2$$
 1°H < 2°H < 3°H

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3 - Cl + HCl$$

Mechanism

Initiation: $Cl_2 \xrightarrow{\Lambda} 2C1$

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

$$CH_3 + Cl_2 \longrightarrow CH_3 - Cl + Cl$$

Termination : $2C1 \longrightarrow C1_2$

$$2CH_3 \longrightarrow CH_3 - CH_3$$

$$CH_3 + C1 \longrightarrow CH_3 - C1$$

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

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

ii) Nitration

H atom replaced by nitro group

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

Mechanism

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

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

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

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

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

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.

$$\text{CH}_3 - \text{H} + \text{HONO}_2 \xrightarrow{450^{\circ}\text{C}} \text{CH}_3 - \text{NO}_2 + \text{H}_2\text{O}$$

iii) Sulphonation

H atom replaced by SO₃H group

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

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

$$\begin{array}{c|c} HO - SO_3H & \longrightarrow & H \dot{O} + \dot{S}O_3H \\ \hline R - H + \dot{O}H & \stackrel{\Delta}{\longrightarrow} & \dot{R} + H_2O \end{array} | \dot{R} + \dot{S}O_3H & \longrightarrow & R - SO_3H \\ \end{array}$$

- II. Oxidation reaction
- a) Complete oxidation / combustion reaction

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

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 / soot

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

$$CH_4 + H_2O_{(g)} \xrightarrow{Ni} CO + 3H_2$$
(Reaction reversible)

c) Catalytic oxidation

Different catalyst give different product

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

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

$$2 R - CH_3 + 3O_2 \xrightarrow{\text{(CH}_3COO)_2Mn} 2 R COOH + 2H_2O$$

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

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

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

III. Isomerisation

Alkanes when heated in presence of an : AlCl₃ and HCl at about 200°C and 35 atm

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} \xrightarrow{An:AlCl_{3+} \atop HCl.200^{\circ}C} CH_{3} - CH - CH_{3}$$

IV. Aromatisation

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

$$CH_3 - (CH_2)_4 CH_3 \xrightarrow{Cr_2O_3|MO_2O_3|} V_2O_5, 773 \text{ K}$$

$$n \text{---hexane}$$

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

$$n \text{heptane}$$

V. Pyrolysis

Decomposition of a compound by applying heat is known as pyrolysis

Pyrolysis of alkane to lower members is known as thermal cracking

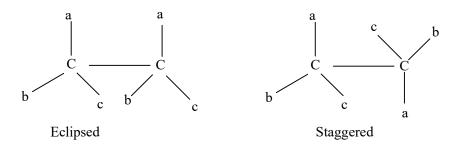
$$C_6H_{14} \xrightarrow{773-} C_4H_8 + C_2H_6$$
 $C_4H_4 + C_2H_4 + C_3H_6$

Isomerism in alkanes

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

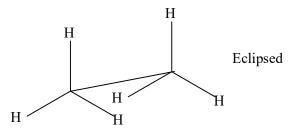
- It aries due to the free rotation around a C-C
- The energy of arrangement is max when bond pairs are very close to each other, such forms are called eclipsed conformation (Least stable)
- The energy of arrangement is min when bond pairs are far a part, such forms are called staggered conformation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



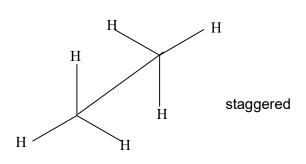
Conformations of ethane

$$CH_3 - CH_3$$

1) Saw - House projection

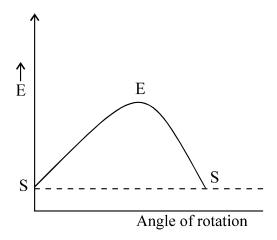


2) New - man projection



dihedral angle
$$\theta = 60^{\circ}$$
H
H
H
H

Energy level diagram



Conformations of butane

<u>Alkene</u>

General formula C_nH_{2n}

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.

• 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 carbon atom

Preparation

I. From alkynes

Alkynes undergo partial reduction to form alkenes, Alkynes reduced with H_2 in presence of Pd over CaCO $_3$ or BaSO $_4$ with added lead acetate and quinoline - is known as Lindlar catalyst

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

$$R - C \equiv C - R \xrightarrow{BaSO_4, CaCO_3} H$$

$$C = C$$
Sulpher or Quinoline H

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

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

$$C = C$$

$$H$$

$$R$$

$$Ph - C \equiv C - Ph$$

$$Ra$$

$$Liq.NH_3$$

$$Ph$$

$$C = C$$

$$H$$

$$C = C$$

$$H$$

$$C = C$$

$$H$$

$$Trans$$

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

$$\begin{array}{c|c}
 & \beta & \alpha \\
 & C & C \\
 & \beta & C
\end{array}
\xrightarrow{Conc:H_2SO_4} C = C + H_2O$$

β - Elimination

Mechanism

$$CH_{3}-CH_{2}-OH \xrightarrow{Protonation} CH_{3}-CH_{2}-OH_{2} \xrightarrow{Dehydration} CH_{3}-CH_{2} \xrightarrow{Dehydration} CH_{3}-CH_{2}$$

$$-H^{\oplus} Deprotonation$$

$$CH_{2}=CH_{2}$$

Order of dehydration $3^{\circ} > 2^{\circ} > 1^{\circ}$

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

$$CH_3$$

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

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

$$\mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{OH} \xrightarrow[-H_2\mathrm{O}]{}^{\mathrm{H^+}} \mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2}$$

$$\xrightarrow{-\text{H shift}} \text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{CH}} - \text{CH}_3$$

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

$$CH_3 - CH = CH - CH_3$$

$$CH_3 - CH_2 - CH = CH_2$$

$$Major$$

$$CH_3 - CH_2 - CH = CH_2$$

$$Minor$$

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

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

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

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

$$\begin{array}{c}
 & C = C \\
 & + Hx
\end{array}$$

Also known β-Elimination

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

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

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

$$\begin{array}{c} \operatorname{Br} \\ \mid \\ \operatorname{CH_3-CH_2-CH-CH_3} \xrightarrow{\quad (\operatorname{CH_3})_3-\operatorname{C-O}^{\Theta}} \operatorname{CH_3-CH} = \operatorname{CH-CH_3} + \operatorname{CH_3-CH_2-CH} = \operatorname{CH_2} \\ \operatorname{Maj} \end{array}$$

E² elimination depends on periplanar geometry two types of periplanar

Properties

Physical properties

First 3 members are gases

Next 14 members are liquids

Others are solids

Melting and Boiling points

Molecular mass increases mp and bp increases

$$H_3C$$
 CH_3
 CH_3

Cis isomer having more bp than trans due to more polar nature

Trans isomer having higher mp than cis due to more symmetry.

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

IONIC MECHANISM

Alkenes show electrophilic addition reaction through 3 steps

$$E - Nu \xrightarrow{ionise} E^{\oplus} + N \xrightarrow{\Theta} Generation of electrophile$$

$$C = C + E \xrightarrow{\bigoplus} C - C \xrightarrow{\bigoplus} Formation of carbocation$$

IMPRORTANT ADDITION REACTION

1) Addition of Hydrogen

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

2) Addition of hydrogen halide

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

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

$$CH_3 - CH = CH_2$$

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

$$\mathbf{CH_3} - \mathbf{CH} = \mathbf{CH_2} + \mathbf{HBr} \xrightarrow{\mathbf{Peroxide}} \mathbf{CH_3} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{HBr} + \mathbf{CH_3} - \mathbf{CH} - \mathbf{CH_3}$$

$$\mathbf{Major}$$

Initiation

$$\begin{array}{c|c} O & O & O \\ \parallel & \parallel & \parallel \\ C_6H_5-C-O-C-C_6H_5 {\longrightarrow} 2C_6H_5-C-O \text{ Benzoyl free radical} \end{array}$$

Benzoyl peroxide

$$C_6H_5 - C - O \longrightarrow C_6H_5 + CO_2$$

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

Propagation

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

$$\mathrm{CH_3} - \mathbf{\dot{C}}\,\mathrm{H} - \mathrm{CH_2} - \mathrm{Br} + \mathrm{HBr} \longrightarrow \mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Br} + \mathbf{\dot{B}}\,\mathrm{r}$$

Termination

$$2Br \longrightarrow Br_2$$

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

$$\begin{array}{cccc} \operatorname{CH}_3 - \dot{\operatorname{C}} \operatorname{H} - \operatorname{CH}_2 - \operatorname{Br} & \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 - \operatorname{Br} \\ & & \downarrow \\ \operatorname{CH}_3 - \dot{\operatorname{C}} \operatorname{H} - \operatorname{CH}_2 - \operatorname{Br} & \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 - \operatorname{Br} \end{array}$$

- 3) Addition of H₂O
- 1. Acidic Hydration of Alkane

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

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

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

$$\begin{array}{c|c} \operatorname{CH_3} & \operatorname{CH_3} \\ \mid & \mid \\ \operatorname{CH_3} - \operatorname{C} = \operatorname{CH_2} \xrightarrow{\quad +\operatorname{H}/\operatorname{H_2O} \quad} \operatorname{CH_3} - \operatorname{C} - \operatorname{CH_3} \\ \mid & \mid \\ \operatorname{OH} \end{array}$$

ADDITION OF HALOGEN

Formation of vianal halide

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

These are antiaddition so forming vicinal dihalides

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} CH_2 - CH_2$$

$$Br \quad Br$$

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

ALKENES SUBSTITUTION REACTION

Higher alkenes are heated with halogen under higher emperature, H atoms from alkyl / benzylic carbon

replaced halogenation taking place and this halogenation is known as Alkylic / benzylic halogenation

$$CH_2 = CH - CH_3 + X_2 \xrightarrow{500^{\circ}C} CH_2 = CH - CH_2C1$$

$$CH_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2$$

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

Allyl and benzyl radicals are resonance stabilised.

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

$$CH_2 = CH - CH_3 + NBS \xrightarrow{425 \text{ K}} CH_2 = CH - CH_2C1 + \bigvee_{O} N - H$$

$$\begin{array}{c} \text{NBS} \to \text{CH}_2 - \text{C} \\ \text{CH}_2 - \text{C} \\ \text{O} \end{array} \qquad \text{--Br N - Bromo Succinamide}$$

OXIDATION REACTION

1. Complete oxidation

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

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

Oxidation using dilute/cold KMnO₄

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

$$CH_2 = CH_2 \xrightarrow{KMnO_4} CH_2 - CH_2 \text{ vicinal diol}$$

$$OH \quad OH \quad Syn \text{ addition}$$

The purple colour / KMnO₄ is discharged and colourless, Vicinal diol is formed is known as Baeyer's test for unsaturation

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 ultimately it becomes CO(Keto)

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

$$\xrightarrow{\text{KMnO}_4} \text{HOOC-} \left(\text{CH}_2\right)_{\cancel{4}} \text{COOH}$$
adipic acid

OZONOLYSIS REACTION

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

$$Zn - H_2O/Me_2S$$

Reductive Ozonolysis

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

$$O$$

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

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

$$O \longrightarrow O$$

Oxidate ozonolysis

POLYMERISATION REACTION

Conversion of monomer \rightarrow polymer

• At 473 k and 1500 atm

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

ethene polythene

n
$$CH_2 - CH = CH_2 \longrightarrow (CH_2 - CH_2)_n$$
propyne polypropyne

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

Tests for unsaturation

Theory

Organic compounds containing > C = C < and / or -C = C - bonds are called unsaturated compounds. These compounds undergo addition reaction with bromine water or the solution of bromine in carbon tetrachloride, chloroform or glacial acetic acid. Addition of bromine to an alkene results in the formation of vicinal dibromide. The reddish orange colour of the solution of bromine in carbon tetrachloride disappears on reaction with an alkene. The reaction is as follows:

$$\begin{array}{c|c} & \text{Br } H \\ \downarrow & \downarrow \\ H_2\text{C} = \text{CH}_2 + \text{Br}_2 \rightarrow H - \text{C} - \text{CH} \\ \downarrow & \downarrow \\ H & \text{Br} \\ \text{(colourless)} \end{array}$$

Alkenes decolourise the neutral/alkaline $KMnO_4$ solution and vicinal glycols are formed (**Bayer's test**). Reaction takes place as follows:

$$3CH_2 = CH_2 + 4H_2O + 2MnO_4^- \rightarrow 3CH_2 - CH_2 + 2OH^- + 2MnO_2$$
 (purple) OH

Both the above reactions are used as tests for unsaturation.

Test tubes : Two

Test tube holder : One

•

• Potassium hydroxide

solution : 1–2 mL

Carbon tetrachloride/

chloroform : 2 mL

 Bromine water/solution of bromine in CCl₄ or

chloroform : 2 mL

• Potassium permanganate

solution : As per need Compound to be tested : As per need

Procedure

A. Bromine water test

Dissolve 0.1 g or 5 drops of organic compound in 2 mL of carbon tetrachloride in a test tube and add 2% solution of bromine in carbon tetrachloride or bromine water drop by drop with continuous shaking. Decolourization of bromine solution indicates the presence of unsaturation in organic compound.

Potassium hydroxide







B. Bayer's test

Dissolve 25-30 mg of organic compound in 2 mL of water or acetone (free of alcohol) and add 1% potassium permanganate solution containing equal volume of 1% sodium carbonate solution. The discharge of the colour of more than one drop of potassium permanganate indicates the presence of unsaturation in the organic compound. Carrying out the reaction under alkaline conditions removes the possibility of confusion due to substitution in aromatic compounds.

Chloroform













- **Note:** (i) Unsaturation in an organic compound is confirmed only when both of the above tests are positive.
 - (ii) In place of CCl_4 any other solvent such as $CHCl_3$ /dioxan and even water can be used to dissolve the organic compound for carrying out the reaction.

Precautions

- (a) The tests should be performed at room temperature.
- (b) Handle bromine solution carefully. Do not inhale the vapours and also avoid its contact with the skin.

ALKYNES

 \bullet 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

Methyl acetylene

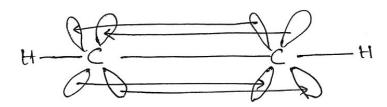
$$CH_2 = CH - C \equiv C - CH_2 - CH = CH_2$$

$$H \xrightarrow{\sigma} C \xrightarrow{\pi} C \xrightarrow{\sigma} H$$

$$sp 121 pm 106 pm$$

Alkyl 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 $\pi \overline{e}$ 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

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

This product formed $CH_2 = CH_2 - X$ is resonance stabilised

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

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

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

There two step reaction can be concluded into one step using NaNH₂

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

From geminal halide

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

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

Tetrahalide

$$X$$
 X $|$ $CH = CH + 2ZnX_2$ $|$ X X

5. Preparation of higher alkynes using acetylenes

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

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

$$2CH \equiv C - Na + 2R - X \xrightarrow{SN_2} 2CH \equiv C - R + 2NaX$$

$$CH \equiv CH - Na + CH_3 - C1 \longrightarrow CH \equiv CH - CH_3 + NaC1$$

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

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

$$Na - C \equiv C - Na + 2CH_3 - Cl \longrightarrow CH_3 - C \equiv C - CH_3 + 2NaCl$$

Physical properties

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

MELTING POINT 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

1. Acidic character of an alkenes

1. Formation of alkalimetal acetalides

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 $\left\lceil 2Ag\left(NH_{_{3}}\right)_{_{2}}\right\rceil OH^{-}$ ammoniacal silver nitrate from silver acetalide.

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

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 electronegativity. Thus it withdraws electrons from C–H bonds and thus releases H $^{+}$ atom.

ADDITION REACTION

1. Addition of hydrogen

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

$$CH_2 \equiv CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3 \qquad OH = -138 \text{ kJ/mol}$$

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

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

Therefore alkynes are more reactive than alkenes.

In hydrogenation alkynes are more stable hence whenever add H to $_{\equiv}$ as to form more stable compounds.

2. Addition of halogen

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

1,1,2,2 tetrachloroethene

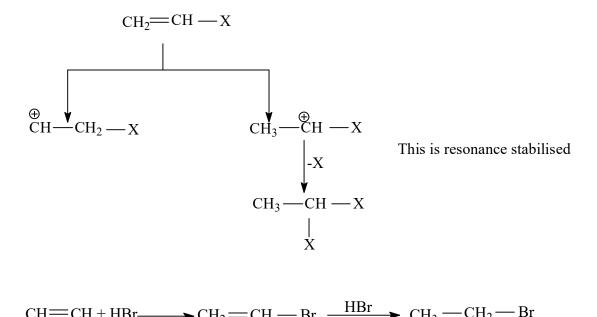
Eg: CH
$$\Longrightarrow$$
 CH + Br $\xrightarrow{\text{CCl}_4}$ CH \Longrightarrow Br \Longrightarrow CH \Longrightarrow CH

Reddish brown

Colourless

3. Addition of hydrogen halide

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



CH
$$\equiv$$
CH + HBr \longrightarrow CH₂ \equiv CH \longrightarrow Br \longrightarrow CH₃ \longrightarrow CH₂ \longrightarrow Br \longrightarrow 1,2,dibromoethane

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

Therefore alkynes are more reactive than alkenes. In hydrogenation alkynes are more stable hence whenever add H to \equiv as to form more stable compounds.

2. Addition of halogen

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

1,1,2,2 tetrachloroethene

Eg: CH
$$=$$
 CH + Br $\xrightarrow{CCl_4}$ CH $=$ CH \xrightarrow{Br} Br $=$ Br $=$ $|$ $|$ $|$ $|$ CH $=$ CH $=$

3. Addition of hydrogen halide

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

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

CH
$$\equiv$$
CH + HBr \longrightarrow CH₂ \equiv CH \longrightarrow Br $\xrightarrow{\text{HBr}}$ CH₃ \longrightarrow CH₂ \longrightarrow Br 1,1 dibromoethane

$$CH_3$$
— C \equiv $CH + 2HBr$ \longrightarrow CH_3 — C — CH_3
 \downarrow
 Br

2, 2 dibromopropane

ADDITION OF H,O

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

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

$$CH_3 - C = CH \xrightarrow{\text{dil.H}_2SO_4} CH_3 - C - CHHg \longrightarrow CH_3 - C - CH_2Mg \longrightarrow CH_3 - C - CH_3$$

$$0 \\ CH_3 - CH_2 - C = C - CH_3 \xrightarrow{\text{dil.H}_2SO_4} CH_3 - CH_2 - CH_2 - C - CH_3$$

$$0 \\ CH_3 - CH_2 - C = C - CH_3 \xrightarrow{\text{dil.H}_2SO_4} CH_3 - CH_2 - CH_2 - C - CH_3$$

$$0 \\ CH_3 - CH_2 - C = C - CH_3 \xrightarrow{\text{dil.H}_2SO_4} CH_3 - CH_2 - CH_2 - C - CH_3$$

OXIDATION REACTION

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 KMnO₄

CH
$$\equiv$$
 CH $\xrightarrow{\text{dil.KMnO}_4}$ OH $\xrightarrow{\text{O}}$ OH $\xrightarrow{\text{O}}$ OH $\xrightarrow{\text{C}}$ CH $=$ CH₃ $=$ CC $=$ COOH

3. Oxidation using acidified alkaline/KMnO₄/K₂Cr₂O₇

$$\equiv \text{CH} \Rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

$$\text{RC} \equiv \Rightarrow \text{RCOOH}$$

$$CH \equiv CH \longrightarrow 2CO_2 + 2H_2O$$

$$CH_3 - C \equiv CH \longrightarrow CH_3COOH + CO_2 + H_2O$$

$$CH_3 - C \equiv C - CH_3 \longrightarrow 2CH_3COOH$$

OZONOLYSIS

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

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

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

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

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH$$

$$CH_{3}$$

$$CH_{3}$$

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

$$CH \qquad CH$$

$$CH \qquad CH$$

$$CH \qquad CH$$

$$CH \equiv CH$$

$$CH \equiv CH$$

$$CH \equiv CH$$

ISOMERISATION

$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{NaNH}_2} CH_3 - CH_2 - C \equiv CH$$

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

BENZENES

- C₆H₆
- Less than 8H corresponding paraffins

Highly unsaturated system

$$C_6H_6 + 3O_3 \longrightarrow C_6H_6(O_3)_3$$

PREPARATION

1. From acetylene

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

$$\begin{array}{c|c} CH & H \\ CH & CH \\ \parallel & H \\ CH & H \\ \end{array}$$

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

2. From normal hexane

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

3. From sodium benzoate

4. From phenol

$$\begin{array}{c}
OH \\
\xrightarrow{Zn-dust} \\
n
\end{array}$$
+ ZnO

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

$$\begin{array}{c} SO_3H \\ \hline \\ + H_2O \longrightarrow \end{array} + H_2SO_4$$

8. From grignard reagent

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

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

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

$$\delta^+$$
 δ^+ Cl Cl $AlCl_3$

$$\begin{array}{c}
Cl - Cl \\
AlCl_3
\end{array}$$

$$\begin{array}{c}
Cl \\
+ AlCl_4
\end{array}$$

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

$$\begin{array}{c}
Cl \\
+ HCl + AlCl_3
\end{array}$$

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

$$+ \operatorname{Br}_{2} \xrightarrow{\operatorname{FeBr}_{3}} + \operatorname{HBr}$$

$$+$$
 Br - Br $+$ Br $+$ Br $+$ 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

$$\xrightarrow{\text{conc:H}_2\text{SO}_4}
\xrightarrow{\text{HNO}_3}
+ \text{H}_2\text{CO}_2$$

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

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

$$+ NO_2 \longrightarrow H \longrightarrow NO_2 + H_2SO_4$$

Sulphonation

$$\xrightarrow[H_2S_2O_7\ \text{Oleum}]{} SO_3H$$

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

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

$$+ H_2O$$

FRIEDEL CRAFT REACTION

1. ALKYLATION

$$R - Cl \longrightarrow H + HCl$$

$$R - Cl \longrightarrow R - Cl \longrightarrow R - Cl \longrightarrow R + HCl + AlCl_3$$

$$R - Cl \longrightarrow R - Cl \longrightarrow R + HCl + AlCl_3$$

2. ACYLATION

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

$$R \longrightarrow C \longrightarrow C \longrightarrow Alc 1_3$$

BENZENE ADDITION REACTION

$$+ 3Cl_{2} \xrightarrow{hv} H \qquad Cl \qquad Benzene hexachloride$$

$$H \qquad Cl \qquad H$$

OXIDATION REACTION

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

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

$$\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
O \\
\parallel \\
CH - COOH
\end{array}
\end{array}$$

$$\begin{array}{c}
CH - COOH
\end{array}$$

$$\begin{array}{c}
CH - COOH
\end{array}$$

$$\begin{array}{c}
CH - CH - CH
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$$CH - CH$$

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.

$$\begin{array}{c} \text{CH}_{3} & \text{COOH} \\ \hline \\ \text{H}^{\prime\prime}/\text{OH} \\ \hline \end{array}$$

$$\begin{array}{c} \text{CH}_{3} & \text{COOH} \\ \hline \\ \text{KMnO}_{4} & \text{No reaction due to the absence of benzyl hydrogen} \\ \hline \\ \text{H}^{\prime\prime}/\text{OH} & \text{COOH} \\ \hline \\ \text{O} & \text{O} & \text{O} \\ \hline \end{array}$$

AROMATICITY

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

Conditions:

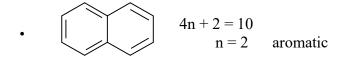
- Cyclic
- Planar
- Conjugated
- Satisfy $(4n + 2) \pi$ rule

$$4n + 2 = 6$$

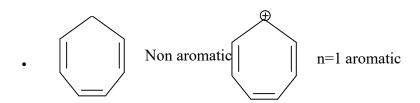
$$n = 1$$

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

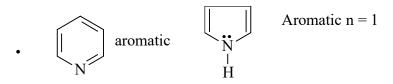
Others are non aromatic



- not conjugated ∴ non aromatic
- 4n+2=0 n=0 aromatic



• aromatic n = 1



• antiaromatic

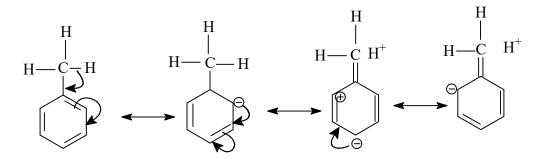
Directive Influence of substituents

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

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

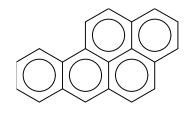
Compounds containing more than one fused benzene ring. These can generate cancer in living tissues so they are known as carcenogenic compound and the nature is called carcinogenicity. The main source of polynuclear hydrocarbon is coal tar.

$$PNH \xrightarrow{O_2} PNH \xrightarrow{H_2O} PNH \xrightarrow{hydroxy \text{ epoxides}} \longrightarrow CANCER$$

1-2 benzanthracene

9-10 dimethyl benzanthracene

Methylchlolanthrene



Benzpyrene



Pyrene