

Hydrocarbons

Hydrocarbons are chemical compounds made up of only carbon and hydrogen atoms. Saturated hydrocarbons contain only single bonds (C-C and C-H) between the carbon atoms. When the carbon atoms form an open chain, they are called alkanes. When they form a closed chain or ring structure, they are called cycloalkanes. Unsaturated hydrocarbons contain one or more double or triple bonds between the carbon atoms $(-C = C - \text{or} - C \equiv C -)$, in addition to single bonds. Aromatic hydrocarbons contain carbon atoms bonded in flat, ring-like structures called aromatic rings. The carbon-carbon bonds in aromatic rings have properties between single and double bonds.

Alkanes

Preparation -

- From alkyl halides -
- a) Alkyl halides (except fluorides) are reduced to alkanes using zinc and hydrochloric acid.

$$CH_3Cl + H_2 \xrightarrow{Zn,H^+} CH_4 + HCl$$

b) Wurtz reaction – Alkyl halides produce higher alkanes when treated with sodium in dry ether solution.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{Ether} CH_3 - CH_3 + 2NaBr$$

- From carboxylic acids –
- a) **Decarboxylation** Heating sodium salts of carboxylic acids with soda lime produces alkanes with one less carbon than the original acid.

$$CH_{3}COO^{-}Na^{+} + NaOH \xrightarrow{\quad CaO\quad \\ \Delta \quad} CH_{4} + Na_{2}CO_{3}$$

b) Kolbe's electrolytic method – Electrolysis of an aqueous solution of a Na/K carboxylic acid salt produces an alkane with an even number of carbons at the anode.

At cathode:

At anode:

$$H_2O+e^- \rightarrow OH+H$$

$$2 \stackrel{\bullet}{H} \rightarrow H_2 \uparrow$$

Physical properties -

• The non-polar nature causes alkanes to be insoluble in the polar solvent water, following the principle that "like dissolves like".

- Boiling Point of linear chain alkanes increases with an increase in molecular mass.
- An increase in branching causes the molecule to attain the shape of a sphere. As such there is a decrease in boiling point.

Chemical properties -

- Substitution reactions
- a) Halogenation The rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is 3° > 2° > 1°. Fluorination is too violent to be controlled.
- **b)** Controlled oxidation Heating alkanes with regulated oxygen or air at high pressure in the presence of catalysts produces various oxidation products.

$$2CH_{4} + O_{2} \xrightarrow{Cu/523K/100atm} 2CH_{3}OH$$

$$CH_{4} + O_{2} \xrightarrow{Mo_{2}O_{3}} HCHO + H_{2}O$$

$$2CH_{3}CH_{3} + 3O_{2} \xrightarrow{(CH_{3}COO)_{2}Mn} 2CH_{3}COOH$$

Tertiary alkanes can be selectively oxidized to the corresponding alcohols using potassium permanganate, while primary and secondary alkanes generally resist oxidation.

$$(CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3C - OH$$

c) Aromatization -

Conformations –

- In the **staggered conformation**, the electron clouds of the carbon-hydrogen bonds are farthest apart, minimizing repulsive forces between them. This results in lower torsional strain and greater stability.
- When the molecule changes to the eclipsed conformation, the electron clouds come closer together. This increases repulsive interactions between them.
- Torsional strain is required to overcome these increased repulsions, so the eclipsed form has higher energy and less stability than the staggered form.
- The magnitude of torsional strain depends on the dihedral angle between carbon atoms.

Alkenes -

• Orbital Picture -

• **Geometrical Isomerism** – The isomer, in which two identical atoms or groups lie on the same side of the double bond is called cis isomer, and the other isomer in which identical atoms or groups lie on the opposite sides of the double bond is called trans isomer.

Dipole moment of cis-but-2-ene is 0.33 Debye, whereas, the dipole moment of the trans form is almost zero.

Preparation -

• From alkyl halides – This reaction is known as Dehydrohalogenation. It is a typical example of β - elimination.

The rate is in the order I > Br > Cl and for the alkyl group Tert > Secondary > Primary.

From alcohols by acidic dehydration –

$$\begin{array}{ccc} H & H \\ H - C - C - C - H & \frac{\text{Conc. H}_2\text{SO}_4}{\Delta} & \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \\ \downarrow & \downarrow & \text{Ethene} \\ H & \text{OH} \end{array}$$

Chemical properties -

- Addition of hydrogen halides The order of reactivity of the hydrogen halides is HI > HBr > HCl.
- Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule) The rule states that in the addition reaction of an unsaturated hydrocarbon and a hydrogen halide, the halogen atom will preferentially bond to the carbon atom of the alkene that already has the greater number of hydrogen atoms attached.

Less stable carbocation More stable carbocation

$$\begin{array}{c} \stackrel{\textstyle \stackrel{\frown}{Br} \stackrel{\downarrow}{\downarrow}}{\downarrow} \\ H_3C-CH-CH_3 & \longrightarrow \begin{array}{c} H_3C-CH-CH_3 \\ & Br \end{array}$$

 Anti-Markovnikov addition or peroxide effect or Kharash effect — In the presence of peroxide, HBr adds to unsymmetrical alkenes like propene following the Anti-Markonikov rule. This happens only with HBr but not with HCl and HI.

$$CH_3-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2}CH_3-CH_2$$

$$| CH_aBr$$

The reaction follows free radical mechanism.

 Oxidation – Reaction of alkenes with cold, dilute potassium permanganate (Baeyer's reagent) yields vicinal glycols. Decolorization of the permanganate solution serves as a test for unsaturated carbon-carbon double bonds.

$$CH_2 = CH_2 + H_2O + O \xrightarrow{\text{dil. KMnO}_4} CH_2 - CH_2$$

$$OH OH$$

■ Ozonolysis – Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by $Zn-H_2O$ to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.

Alkynes – Preparation –

• From vicinal dihalides – This reaction is a typical example of Dehydrohalogenation.

$$\begin{array}{c} H \\ \downarrow \\ H_2C - C - H + KOH & \underline{alcohol} \\ \downarrow \\ Br & Br \end{array} \xrightarrow{-KBr} \begin{array}{c} H \\ C = C \\ H \\ Br \end{array}$$

$$\begin{array}{c} C = C \\ H \\ Br \end{array}$$

$$\begin{array}{c} Na^{\dagger}NH_2^{-} \downarrow - NaBr \\ -NH_3 \end{array}$$

$$CH \equiv CH$$

Chemical properties –

• Acidic character of alkyne – Order of acidity

$$HC \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$

$$HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$$

Aromatic Hydrocarbon –

- Aromatic compounds containing Benzene ring are known as Benzenoid and those not containing Benzene ring are called Non-Benzenoid.
- Hückel Rule For a compound to be Aromatic. It should –
- be Planar

Aldehydes, Ketones and Carboxylic Acid

- have complete delocalization of π electrons.
- have a $(4n+2)\pi e^-$ where n is the integer (n = 0,1, 2,...)

Preparation of Benzene -

Decarboxylation of aromatic acids –

COONa + NaOH
$$\xrightarrow{\text{CaO}}$$
 + Na₂CO₃

Chemical properties -

- Electrophilic substitution reactions -
- a) Friedel-Crafts alkylation reaction When benzene is treated with an alkyl halide in the presence of anhydrous Aluminium chloride to form alkyl-substituted benzene derivative known as an alkylbenzene.

b) Friedel-Crafts acylation reaction — When benzene is treated with an acyl halide or acid anhydride in the presence of a Lewis acid such as Aluminium chloride to form an acylsubstituted benzene derivative known as an Acyl Benzene.

$$+ CH_3COC1 \xrightarrow{Anhyd. AlCl_3} + HCl$$
Acetylchloride
$$Acetophenone$$

Directive influence of a functional group in monosubstituted benzene -

Ortho and para-directing groups – The groups that activate the Benzene ring for the attack of an electrophile are activating groups. Example – OH, –NH₂, –NHR, –NHCOCH₃, –OCH₃, –CH₃

Aldehydes, Ketones and Carboxylic Acid

• **Meta-directing groups** – The groups that direct the incoming group to the meta position are called meta-directing groups.

$${\sf Example - -} NO_2, -CN, -CHO, -COR, -COOH, -SO_3H$$