AIKANE
(Part-II)

By

Dr. JYOTI CHANDRA

Assistant Professor

Department of Chemistry

Email ID- jyotic09@gmail.com

B.Sc-Ist Year (SEM-II)

Patna Women's College

Patna University

Preparation of Alkane

- Alkanes can be prepared by following methods :

1) From unsaturated hydrocarbons: Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called **hydrogenation.** These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H} + 2H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

2) From alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$

Chloromethane — Methane

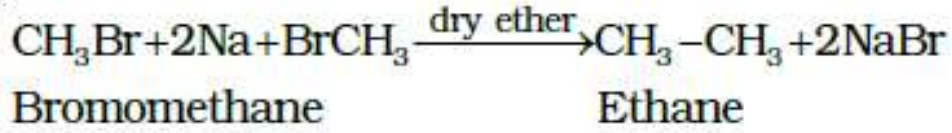
$$C_2H_5-Cl + H_2 \xrightarrow{Zn,\ H^+} C_2H_6 + HCl$$

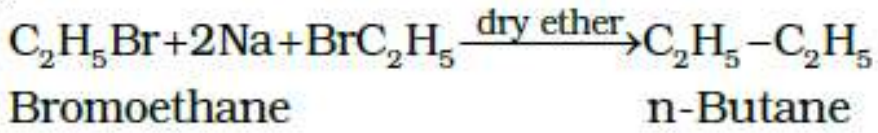
Chloroethane — Ethane

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow{Zn,\ H^+} CH_3CH_2CH_3 + HCl$$

1-Chloropropane — Propane

ii) **Wurtz reaction:** Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction and is used** for the preparation of higher alkanes containing even number of carbon atoms.





Mechanism of Wurtz reaction :

Two types of mechanism are possible for Wurtz reaction:

- **Free Radical Mechanism**
- **Ionic Mechanism**
- **Free Radical Mechanism**: This involves 3 steps

Step 1: The transfer of an electron from the sodium metal to the halogen leads to the formation of an alkyl free radical along with the metal halide. This reaction can be written as follows.

R-X + Na → R• + NaX

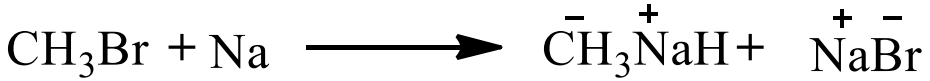
Step 2: A different sodium atom now donates a single electron to the alkyl radical, leading to the formation of an alkyl anion

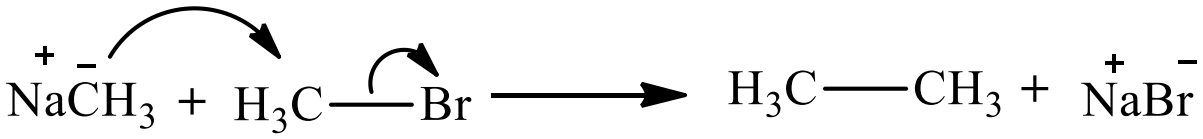
$$R\bullet + Na \rightarrow R^-$$

Step 3: The carbon belonging to the alkyl anion having a nucleophilic nature proceeds to displace the halogen in the alkyl halide via an S_N2 reaction and form a covalent bond with the carbon which was bonded with the halogen.

$$R^- + R\text{-}X \rightarrow R\text{-}R + NaX$$

▪**<u>Ionic Mechanism</u>:** This involves the intermediate formation of metal alkyls. Thus methyl bromide reacts with two atoms of sodium to produce methyl sodium and sodium and sodium bromide. Methyl sodium then reacts with another molecule of methyl bromide to give ethane and sodium bromide.





- For carrying out Wurtz reaction, the alkyl bromides and iodides may also be used. Order of reactivity of alkyl halides is RCI < RBr < Rl.
- Wurtz reaction is a good method of building up higher alkanes from lower members.

❑ Limitations of the Wurtz Reaction

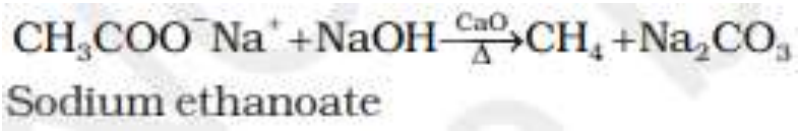
- Only symmetric alkanes (R-R type)can be synthesized via this method since a mixture of alkane products are formed and these mixtures are very difficult to separate because of little difference in their boiling points.
- There exists a side reaction via which an alkene product is formed.
- Methane cannot be synthesized via the Wurtz reaction since the product of an organic coupling reaction must have at least two carbon atoms.
- The Wurtz coupling method generally fails when tertiary alkyl halides are used.
- The reaction medium should be free from moisture and oxygen otherwise sodium (Na) will be destroyed b reacting with water and oxygen as follows:

$$Na + H_2O \longrightarrow NaOH + H_2$$

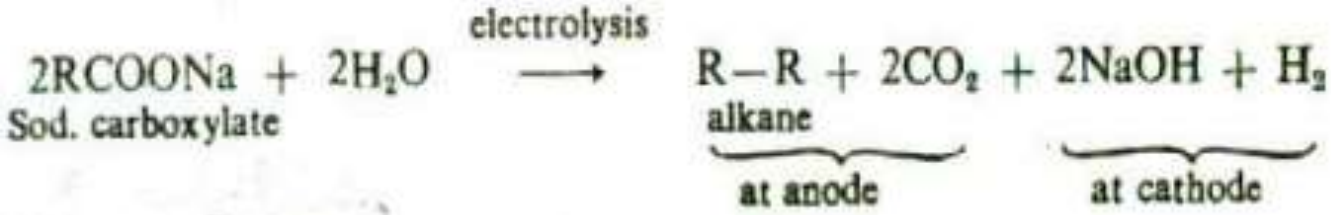
$$Na + O_2 \longrightarrow Na_2O$$

3) From carboxylic acids

(i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as decarboxylation.



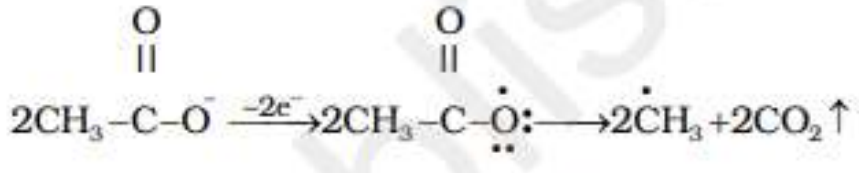
(ii) Kolbe's electrolytic method: An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode and sodium hydroxide and hydrogen at the cathode.



- **Mechanism of Kolbe's method**

When an electric current is passed through a solution of sodium acetate, the acetate ions ($CHCOO^-$) migrate to the anode and give up one electron to produce acetate free radical. The acetate free radical in turn decomposes to give a methyl free radical and carbon dioxide. Two of the resulting methyl free radicals then combine to form ethane.

At anode:



At cathode :