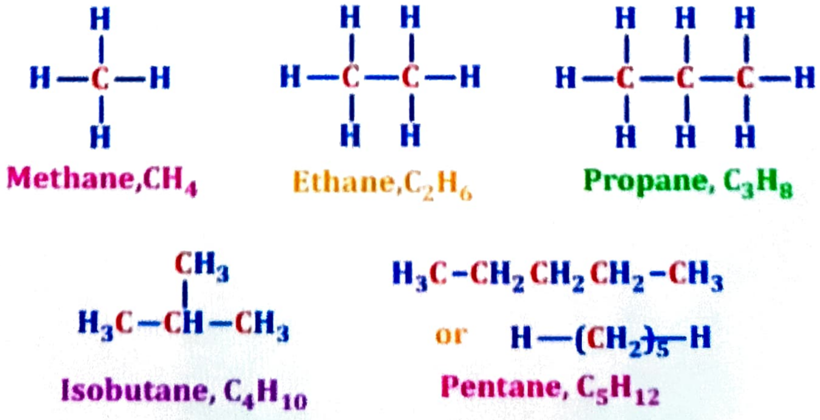
ALKANES

Points to be covered in this topic

- **1. INTRODUCTION**
- **2. GENERAL METHODS OF PREPARATION**
- **3. sp^3 HYBRIDIZATION IN ALKANES**
- **4. HALOGENATION OF ALKANES**
- **5. PARAFFIN**

☐ INTRODUCTION

- An alkane consists of **hydrogen and carbon atoms** arranged in **a tree structure** in which all the **carbon-carbon bonds are single**.
- Alkanes have the general **chemical formula = C_nH_{2n+2}**
- Alkanes contain **strong C-C and C-H covalent bonds**;
- Therefore, this class of hydrocarbons are relatively **chemically inert**.
- They are referred to as **Paraffins** (Latin, Parumaffinis = little affinity)
- Alkanes belongs to the class of hydrocarbons where all the carbons present in the molecule are linked through single bond (σ bonds) only and thus referred as saturated hydrocarbons.



Methane, CH_4

Ethane, C_2H_6

Propane, C_3H_8

Isobutane, C_4H_{10}

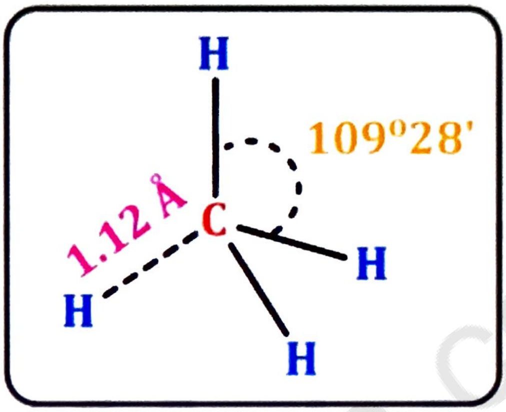
$H_3C-CH_2CH_2CH_2-CH_3$ or $H-(CH_2)_5-H$

Pentane, C_5H_{12}

Example of few alkane

❖ Alkanes have following structural characteristics:

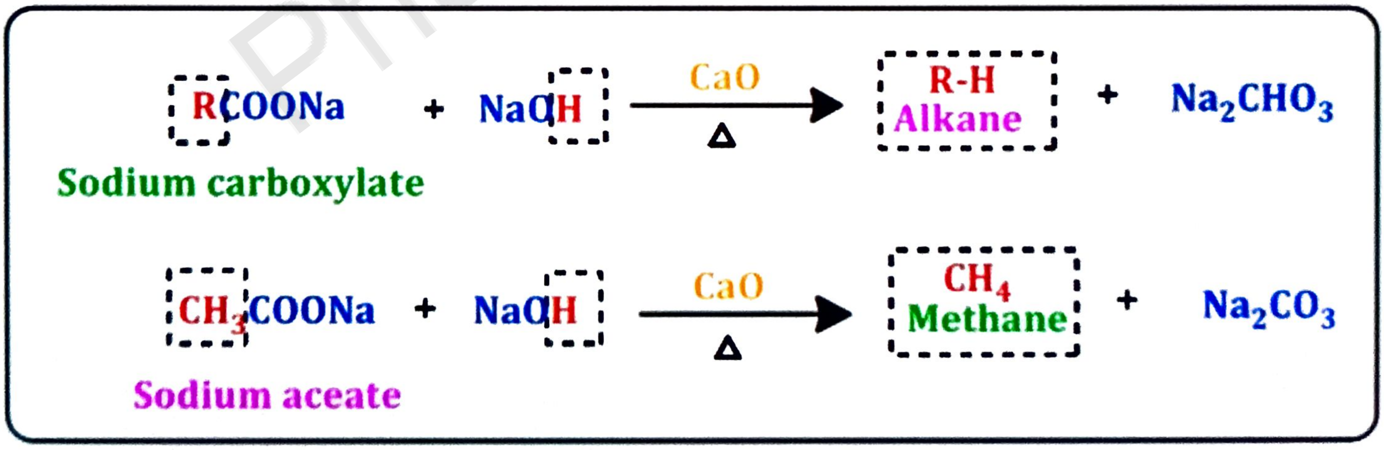
1. Every carbon atom is **sp^3 hybridized**, its four bonding orbitals are directed towards the **four corners of a regular tetrahedron.**
2. All the carbon-carbon and carbon-hydrogen bonds are strong **sigma bonds**.
3. The bond lengths between carbon-carbon and carbon hydrogen are 1.54 Å and 1.12 Å respectively.
4. The bond angles in alkanes are **tetrahedral angles** having a value of **109.5° (109°28′).**



❑ GENERAL METHODS OF PREPARATION

1. Decarboxylation of Carboxylic Acids:

- Alkanes are prepared by heating a mixture of anhydrous sodium salt of carboxylic acid with soda lime (NaOH + CaO).



$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Alkane}}{R\text{-}H} + Na_2CHO_3$$

Sodium carboxylate

$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

Sodium aceate

2. Reduction of Alkenes or Alkynes:

- Hydrogenation of unsaturated hydrocarbons in the presence of Nickel at 570 K yields alkanes.
- This reaction is called **Sabatier Senderens reaction.**
- Examples for other hydrogenating agents are platinum and palladium.

➤ Reduction of alkenes

$$\underset{\text{Alkene}}{\boxed{C_nH_{2n}}} + \boxed{H_2} \xrightarrow[570K]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Alkene}}{\boxed{R-CH=CH_2}} + \boxed{H_2} \xrightarrow[570K]{Ni} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

$$\underset{\text{Ethylene}}{\boxed{H_2C=CH_2}} + \boxed{H_2} \xrightarrow[570K]{Ni} \underset{\text{Ethane}}{H_3C-CH_3}$$

➤ Reduction of alkynes

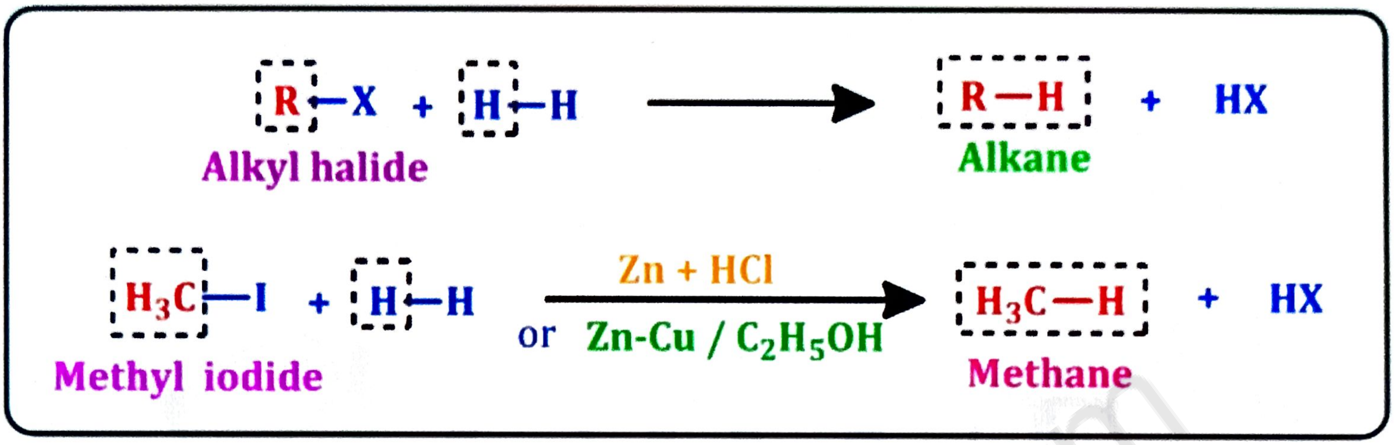
$$\underset{\text{Alkyne}}{\boxed{C_nH_{2n-2}}} + \boxed{2H_2} \xrightarrow[570K]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Alkyne}}{\boxed{R-C\equiv CH}} + \boxed{2H_2} \xrightarrow[570K]{Ni} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

$$\underset{\text{Acetylene}}{\boxed{HC\equiv CH}} + \boxed{2H_2} \xrightarrow[570K]{Ni} \underset{\text{Ethane}}{H_3C-CH_3}$$

3. Reduction of Alkyl Halides:

- Reduction of alkyl halides with nascent hydrogen yields alkanes.
- **Common reducing agents** used are: Zn/HCl, Zn/CH_3COOH, Zn/Cu, Ni, Pt, $LiAlH_4$, H_2 (gas), C_2H_5OH/Na, HI/P .



$$R-X + H-H \longrightarrow R-H + HX$$

Alkyl halide

Alkane

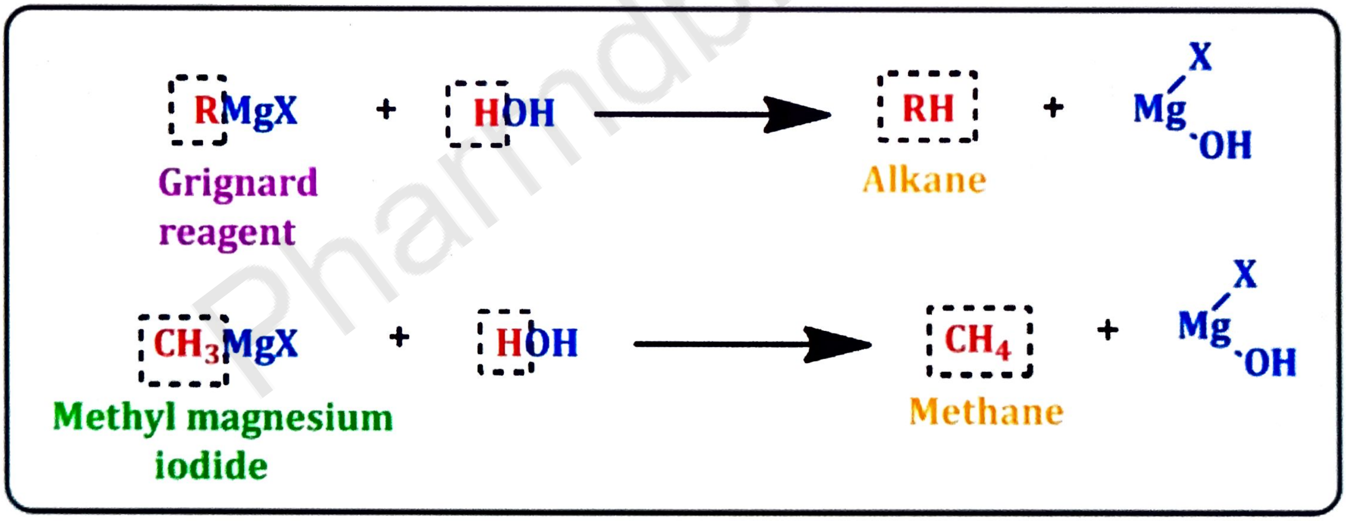
$$H_3C-I + H-H \xrightarrow[\text{or Zn-Cu / } C_2H_5OH]{\text{Zn + HCl}} H_3C-H + HX$$

Methyl iodide

Methane

4. Hydrolysis of Grignard Reagents :

- Upon hydrolysis, Grignard reagent **(alkyl magnesium halide)** yields concerned alkanes



$$RMgX + HOH \longrightarrow RH + Mg{<}^{X}_{OH}$$

Grignard reagent

Alkane

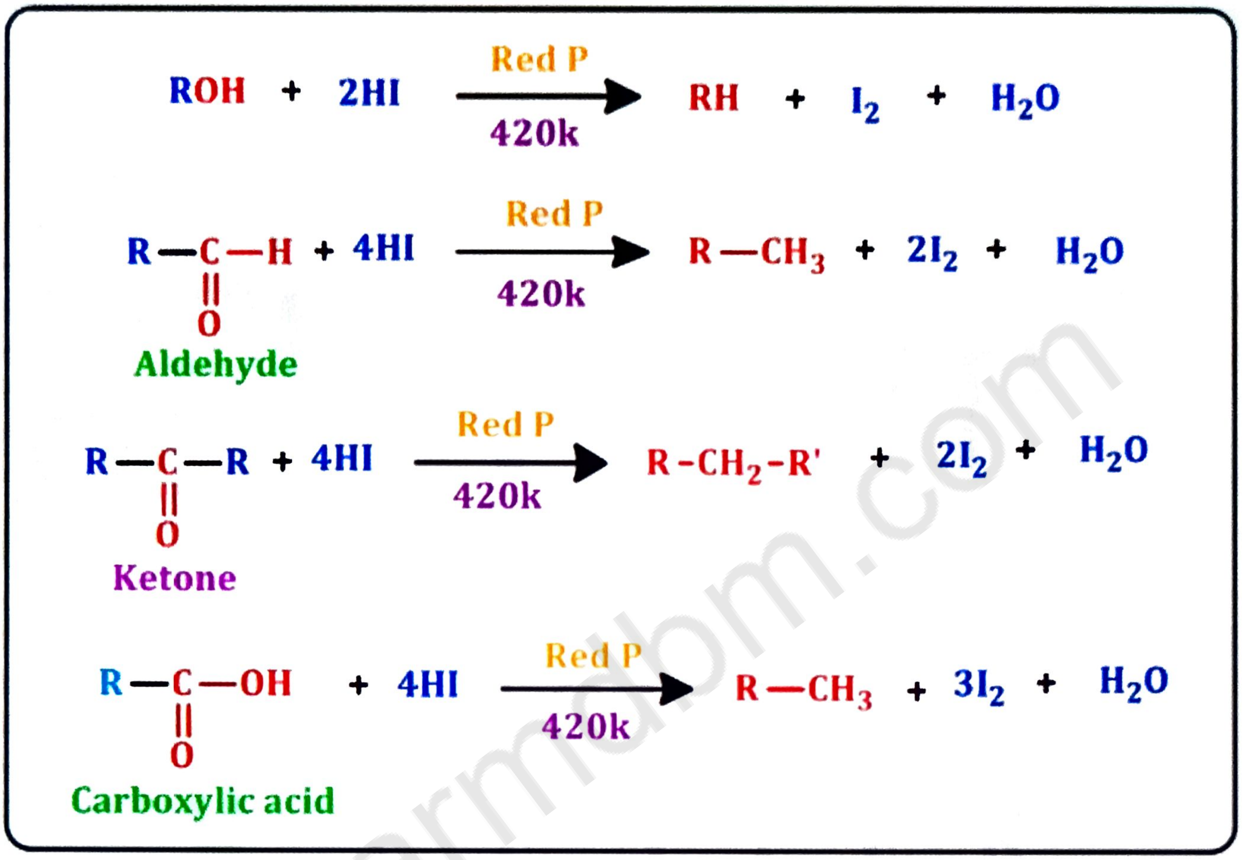
$$CH_3MgX + HOH \longrightarrow CH_4 + Mg{<}^{X}_{OH}$$

Methyl magnesium iodide

Methane

5. Reduction of Alcohols, Aldehydes, Ketones or Carboxylic acids:

- Reduction of alcohols, aldehydes ketones or carboxylic acids with excess of **hydroiodic acid** at **high temperature** in a **sealed tube in presence** of **red phosphorous yields alkanes** .



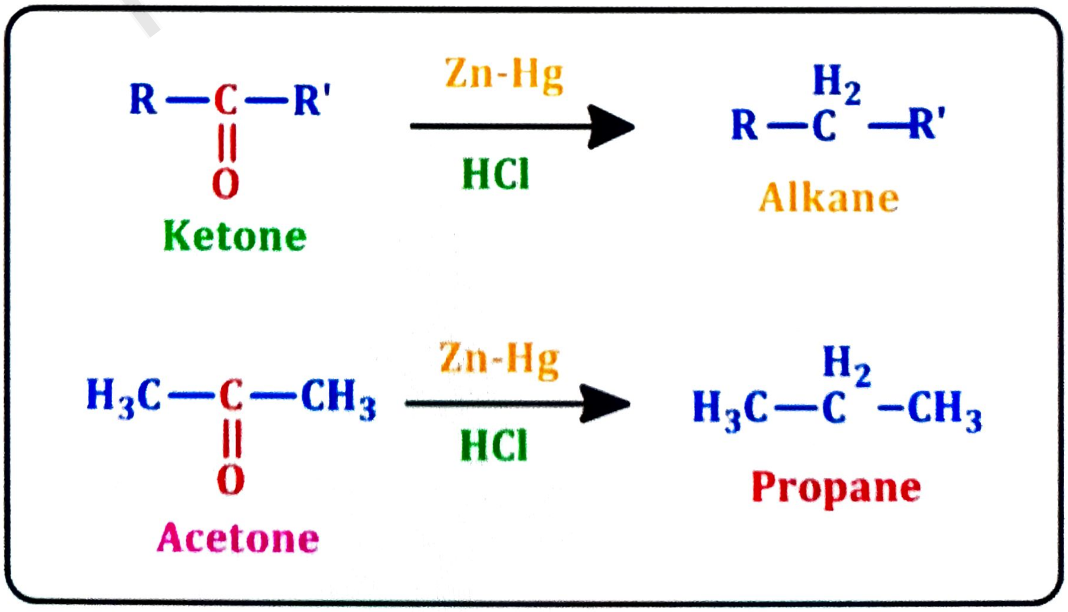
$$ROH + 2HI \xrightarrow[420k]{Red\ P} RH + I_2 + H_2O$$

$$R-\underset{\substack{\| \\ O}}{C}-H + 4HI \xrightarrow[420k]{Red\ P} R-CH_3 + 2I_2 + H_2O$$

$$R-\underset{\substack{\| \\ O}}{C}-R + 4HI \xrightarrow[420k]{Red\ P} R-CH_2-R' + 2I_2 + H_2O$$

$$R-\underset{\substack{\| \\ O}}{C}-OH + 4HI \xrightarrow[420k]{Red\ P} R-CH_3 + 3I_2 + H_2O$$

✓ **Carbonyl compounds**, especially ketones can be reduced with Zn/Hg and conc. HCl. This reaction is known as **Clemmensen reduction** .



$$R-\underset{\substack{\| \\ O}}{C}-R' \xrightarrow[HCl]{Zn\text{-}Hg} R-\overset{H_2}{C}-R'$$

$$H_3C-\underset{\substack{\| \\ O}}{C}-CH_3 \xrightarrow[HCl]{Zn\text{-}Hg} H_3C-\overset{H_2}{C}-CH_3$$

6. Wurtz Synthesis:

- Reaction between a solution of alkyl halide (especially alkyl bromide or alkyl iodide) and metallic sodium in the presence of dry ether yields alkanes.

$$\underset{\text{Alkyl halide}}{RX + 2Na + RX} \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R{-}R} + 2NaX$$

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + 2Na + \underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{H_3C{-}CH_3} + \underset{\substack{\text{Sodium}\\\text{iodide}}}{2NaI}$$

7. Corey-house Synthesis:

- Eliminating the limitations of Wurtz synthesis and coupling of two halides are carried out by corey-house synthesis.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + \underset{\substack{\text{Lithium}\\\text{dimethyl cuprate}}}{Li(CH_3)_2Cu} \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + \underset{\substack{\text{Methyl}\\\text{lithium}}}{CH_3Li} + CuBr$$

8. Kolbe's method or Kolbe's electrolysis:

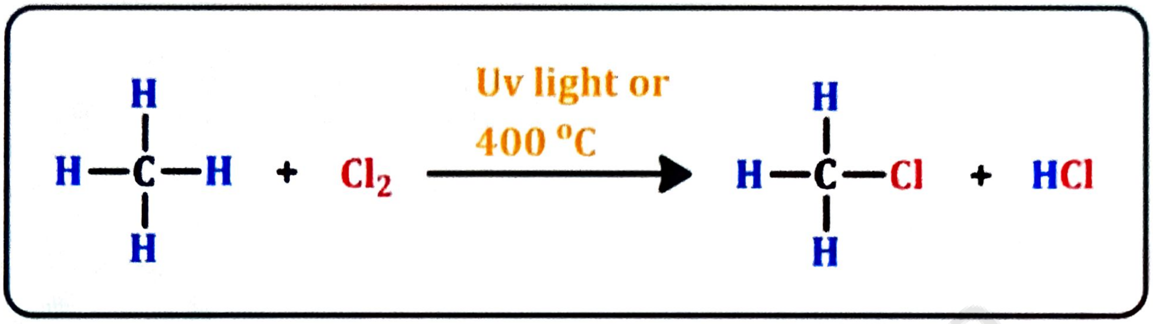
- By electrolysis of sodium or potassium salts of fatty acids: Electrolysis of a concentrated aqueous solution of either sodium or potassium salts of saturated mono-carboxylic acids yields higher alkanes at anode.

$$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Alkane}}{R\text{-}R} + 2CO_2 + KOH$$

CHEMICAL PROPERTIES OF ALKANES

1. HALOGENATION OF ALKANES

- The reaction of a **halogen with an alkane** in the **presence of ultraviolet** (UV) light or heat leads to the formation of a haloalkane (alkyl halide).
- An example is the **chlorination of methane**.



$$CH_4 + Cl_2 \xrightarrow[400\ ^\circ C]{Uv\ light\ or} CH_3Cl + HCl$$

- When the **alkane and halogen** reactants are **not exposed to UV light** or heat, the **react does not occur**.

❖ Halogenation mechanism

- In the **methane** molecule, the **carbon-hydrogen bonds** are **low-polarity covalent** bonds.
- A **free radical** is an atom or group that has a **single unshared electron**.

➤ 1. Chain initiation step :-

- The originally bonded atoms **receives one electron**

$$Cl:Cl \xrightarrow[\Delta]{Uv\ light} \dot{Cl} + \dot{Cl}$$

Chlorine free radical

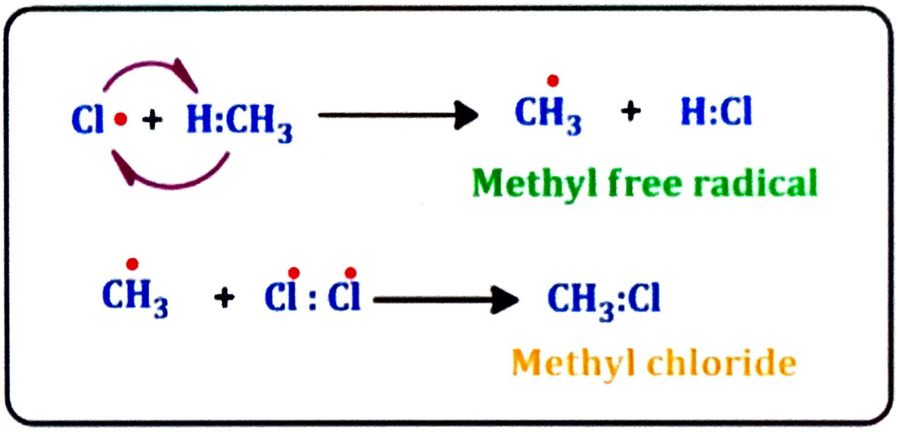
➤ 2. Chain propagation:

$$\dot{Cl} + \dot{CH_3} \longrightarrow CH_3\text{-}Cl$$

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl\text{—}Cl$$

$$\dot{CH_3} + \dot{CH_3} \longrightarrow H_3C\text{—}CH_3$$

3. Chain termination step:



$$\text{Cl}\bullet + \text{H:CH}_3 \longrightarrow \dot{\text{C}}\text{H}_3 + \text{H:Cl}$$

Methyl free radical

$$\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{l} : \dot{\text{C}}\text{l} \longrightarrow \text{CH}_3\text{:Cl}$$

Methyl chloride

2. Nitration:

- Substitution of hydrogen atom of alkanes with nitro (-NO) group is called as nitration.
- The reaction between alkanes and nitric acid takes place in vapour phase at 400-500 °C yields nitro alkanes.

$$\text{CH}_4 + \text{HNO}_3 \xrightarrow[\text{Pressure}]{400\text{-}500\,^{\circ}\text{C}} \text{CH}_3\text{NO}_2 + \text{H}_2\text{O}$$

Nitromethane

3. Sulphonation:

- **Substitution of hydrogen atom of alkanes** with -SO,H **group** is called as Sulphonation. The reaction does not take place at room temperature and **lower alkanes up to pentane cannot sulphonated.**
- From hexane, the alkanes react with oleum [Fuming sulphuric acid and sulphur trioxide and from alkane sulphonic acid.

$$\text{R—H} + \text{OH—SO}_3\text{H} \longrightarrow \text{R—SO}_3\text{H} + \text{H}_2\text{O}$$

Alkane — Fuming sulphuric acid — Alkane sulphonic acid

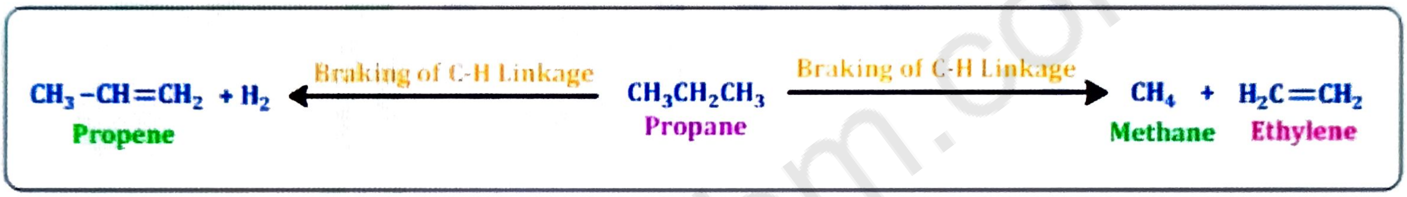
4. Oxidation (Combustion reactions): Oxidation of alkanes in presence of excess of oxygen forms carbon dioxide water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 213\ KCal/Mol$$

5 . Thermal Decomposition or Pyrolysis or Cracking:

- Upon heating alkanes at high temperature (500°C - 600°C) in the absence of air, pyrolysis or thermal decomposition occurs and large alkane molecules are broken into smaller alkanes, alkenes and hydrogen with the cleavage of C-C bond and C-H bond in alkanes

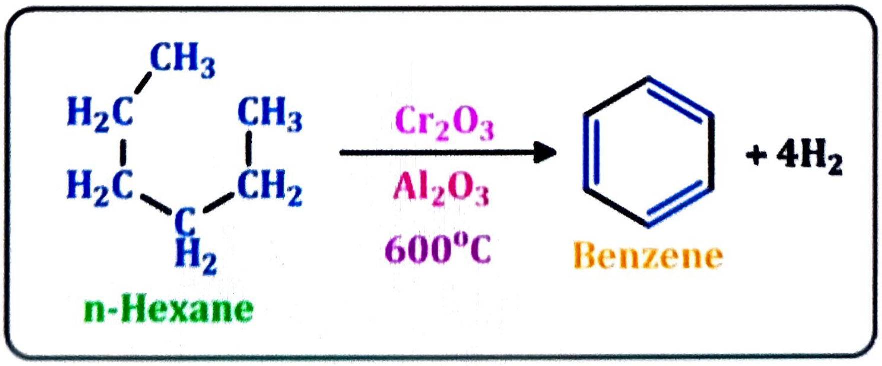
- **Mechanism:** It follows free radical mechanism.



$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xleftarrow{\text{Braking of C-H Linkage}} \underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{\text{Braking of C-H Linkage}} \underset{\text{Methane}}{CH_4} + \underset{\text{Ethylene}}{H_2C=CH_2}$$

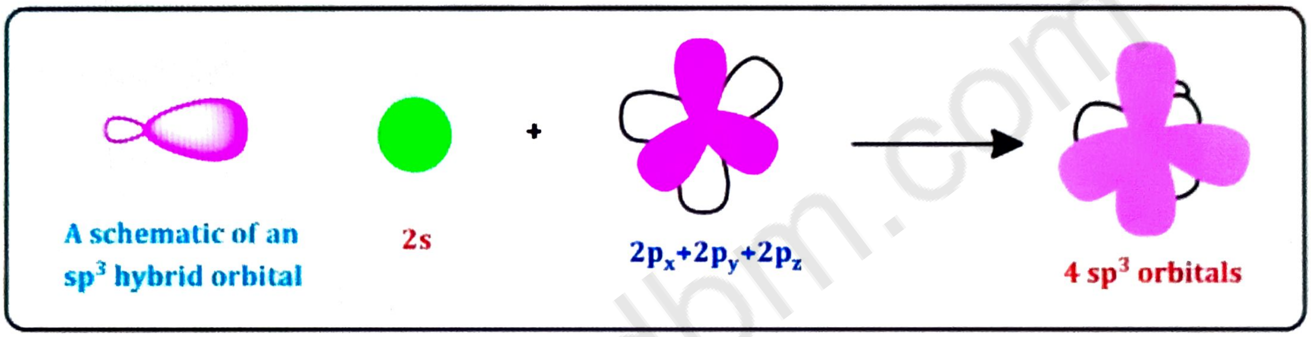
6. Aromatisation:

- Alkanes containing **six or more carbons** when heated under **pressure in presence** of catalyst yields **cyclised and dehydrogenated product** called aromatic compounds and the process of formation of aromatic compounds **in this reaction** is called aromatisation.



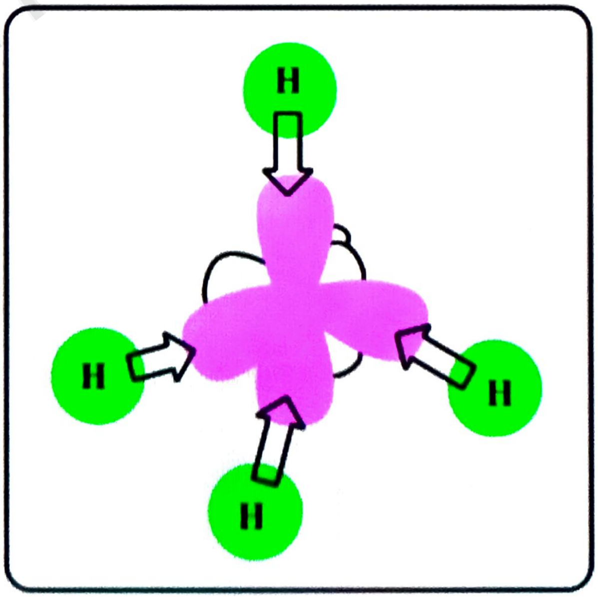
sp^3 HYBRIDIZATION IN ALKANES

- In **sp^3 hybridization**, **one s orbital combines** with all the **three p orbitals** to form **four equivalent sp^3 hybrid** orbitals.
- Each hybrid sp^3 orbital displays **25 % s-orbital** characteristics and **75% p-orbital** characteristics.
- They have a **tetrahedral arrangement** and the **angle between two orbitals is 109.5** degrees.
- Shape of the molecule in which **central atom is sp^3- hybridized is tetrahedral.**



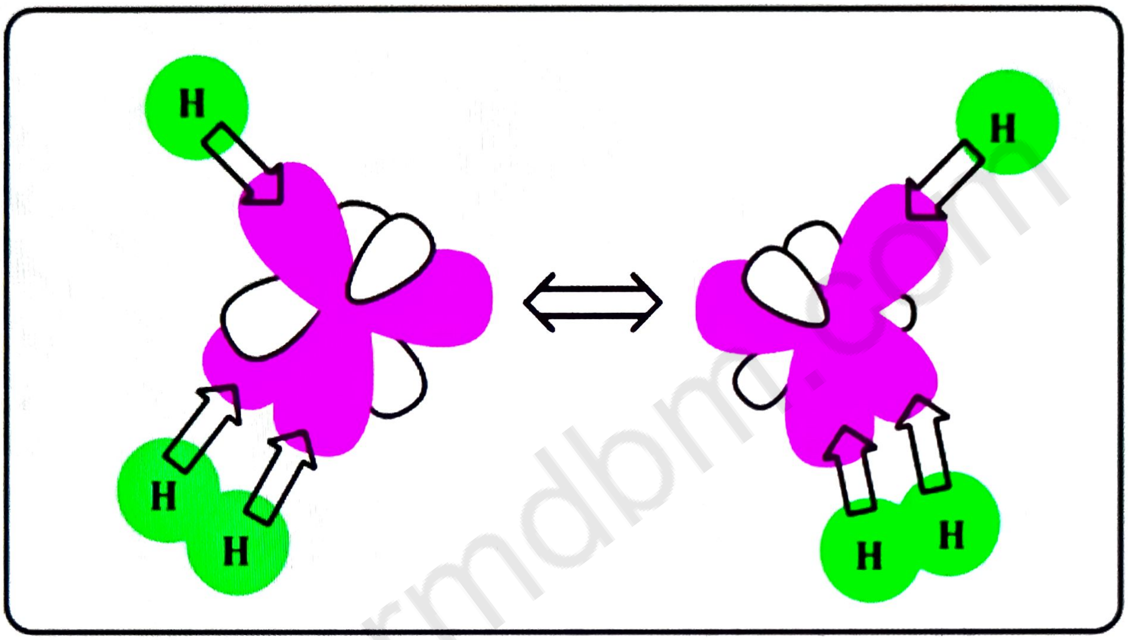
For methane:

- 4 equivalent C-H σ bonds can be made by the interactions of C sp^3 with a H 1s.



Now in methane, $H_2C\text{-}CH_3$ the hybridization can be explained as:

- Both Care sp^3 hybridized.
- 6C-H σ bonds are made by the interaction of C sp^3 with H1s orbitals (indicated by re arrows).
- 1C-C σ bond is made by the interaction of C sp^3 with another C sp^3 orbital (indicated by green arrow).



☐ PARAFFIN

- The saturated hydrocarbons are called **paraffins** (Latin: parum = little; affinis = affinity) as they are relatively inert towards chemical reagents. In IUPAC nomenclature, **paraffins are termed alkanes**.
- Paraffin is also known as **liquid paraffin**, paraffin oil or kerosene, is a combustible hydrocarbon liquid that is burned as a fuel.
- It is a mixture of different types of simple hydrocarbons, it is **less volatile than gasoline** and it boils at **302-527 degrees Fahrenheit**

➤ Application or uses of paraffin

1. Used as Liquid Paraffin Fuel

- One of the primary uses of liquid paraffin is fuel. Liquid paraffin is a **highly distilled** and **refined** form of **kerosene** that can be **burned in lamps and other devices**.

2. Used for Industrial and Textile purposes

- Liquid paraffin is mainly used as a lubricant in various **industrial settings**.
- The uses of liquid paraffin in the **textile industry** mostly involve lubrication. Liquid paraffin is an oil component used for spinning, weaving and meshing materials.

3. Used for Medicinal and Cosmetic purposes

- Liquid paraffin passes through the **body's intestinal tract** without **being absorbed** it can be **used as a laxative** to limit the amount of **water removed** from the **stool** and **ease constipation.**
- It is **used** in the **penicillin production process** and is also used in some **eye lubricants**.
- The **cosmetic industry** also makes good use of liquid paraffin. The substance is used in various **beauty products, including detergent creams, cold creams, hydrated creams, bronzed oils and makeup products**. It can also be used as an emollient lotion to treat dry skin.

4. Other uses of paraffin

- For example, it is an ingredient in many agricultural insecticides.
- Liquid paraffin is a component in the manufacture and containment of reactive gases like sulfur dioxide and chlorine.

ALKENES

Points to be covered in this topic

- **1. INTRODUCTION**
- **2. METHODS OF PREPARATION**
- **3. CHEMICAL REACTIONS**

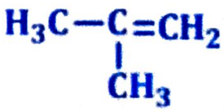
❑ INTRODUCTION

- **Alkenes** belong to the class of **hydrocarbons** containing **carbon-carbon double bond** and the **hydrocarbons** which have **less number of hydrogen atoms** than the corresponding **alkanes** (or saturated hydrocarbons) are **unsaturated hydrocarbons.**
- Alkanes follows the general formula C_nH_{2n}, Where **n = 1, 2, 3 etc.**
- The **first member** of this series is $CH_2{=}CH_2$, **ethene** commonly known as **ethylene.**
- The **alkenes are also called as Olefins** (**Latin: *oleum* means oil** and ***fiant* means producing**)
- **Alkenes** are **more reactive** than **alkanes** due to the **presence of the double bond**

$H_2C{=}CH_2$

Ethene

Old name- Ethylene



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

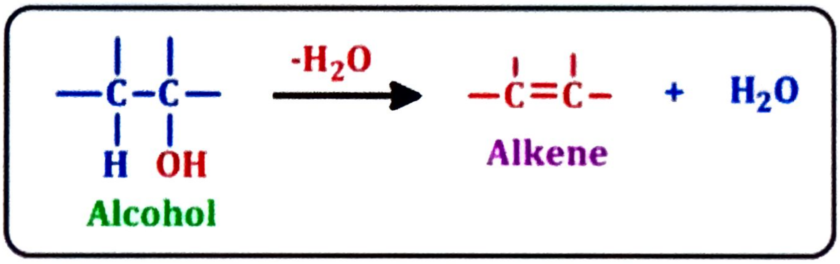
Isobutene or 2-methylpropane

Old name- Isobutylene

☐ METHOD OF PREPARATION

1. By dehydration of alcohols:

- An **alcohol is converted into an alkene by dehydration**, i.e., elimination of a molecule of water.



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \xrightarrow{-H_2O} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

➤ **The dehydration of alcohols is generally carried out in either of two ways:**

i. **Heating the alcohol with acid catalyst** like concentrated sulphuric acid or phosphoric acid H_3PO_4 or p-toluene sulphonic acid or P_2O_5 to temperatures as high as 200°C

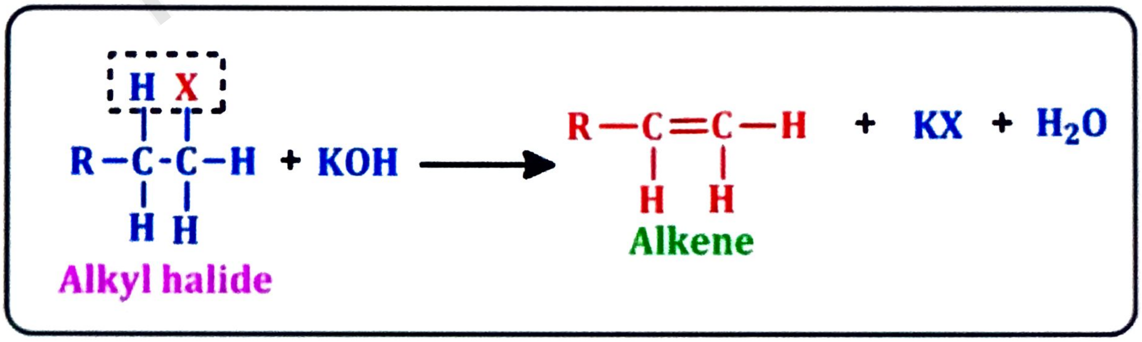
ii. **Passing the vapor's of alcohol over alumina** (Al_2O_3) at 350- 400°C, (Al_2O_3 serves as a Lewis acid).

The ease of dehydration follows the following order:

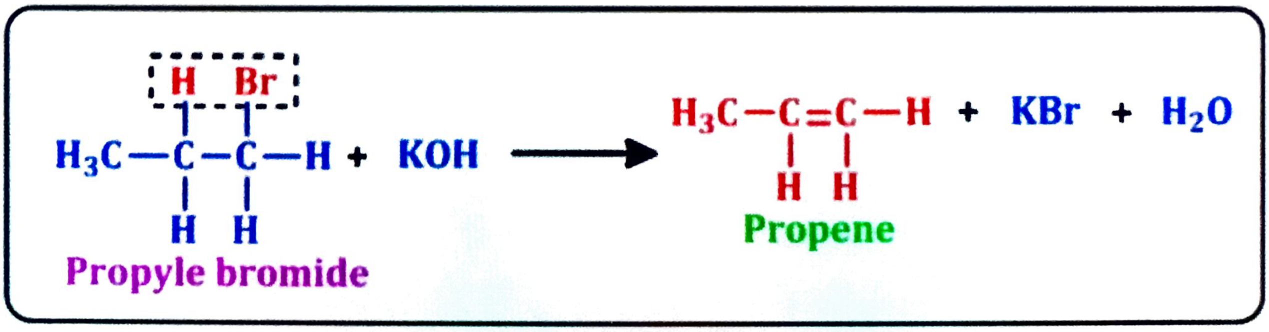
Tertiary (3°) > Secondary (2°) > Primary (1°)

2. By dehydrohalogenation of alkyl halides

- When heated with alcoholic solution of potassium hydroxide **(alcoholic potash)**, alkyl halides eliminate a hydrogen and **halogen atom from adjacent carbon atoms to form alkenes***.



$$R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{X}{C}}-H + KOH \longrightarrow R-\underset{H}{C}=\underset{H}{C}-H + KX + H_2O$$



$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-H + KOH \longrightarrow H_3C-\underset{H}{C}=\underset{H}{C}-H + KBr + H_2O$$

- This is probably the **most important method** for preparing alkenes in the laboratory.
- In the preparation of **alkenes from alkyl halides**, as a rule, **iodides are most reactive and chlorides are least so.**

✓ **Saytzeff's Rule,** states that in the **dehydration of alcohols** or the **dehydrohalogenation of alkyl halide,** hydrogen atom is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms.

The ease of dehydrohalogenation in alkyl halide is in the order

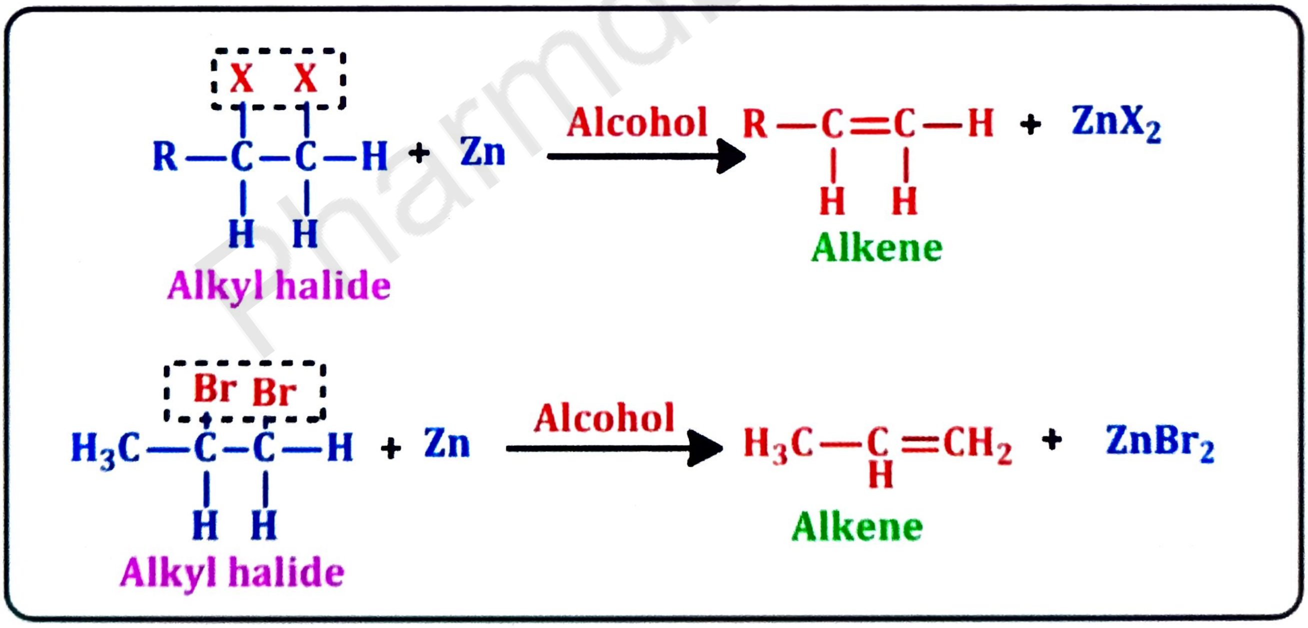
Tertiary > Secondary > Primary

The ease of dehydrohalogenation for different halogens is in the order

Iodide > Bromide> Chloride

3. By dehalogenation of dihaloalkanes with zinc

- When **dihalogen derivatives of alkenes** having the **two halogen atoms on adjacent carbons** are heated with an **active metal** like zinc the latter removes the halogen atoms to form **alkenes.**



$$R-\overset{X}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-H + Zn \xrightarrow{\text{Alcohol}} R-\underset{H}{C}=\underset{H}{C}-H + ZnX_2$$

$$H_3C-\overset{Br}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H + Zn \xrightarrow{\text{Alcohol}} H_3C-\underset{H}{C}=CH_2 + ZnBr_2$$

4. By partial hydrogenation of alkynes

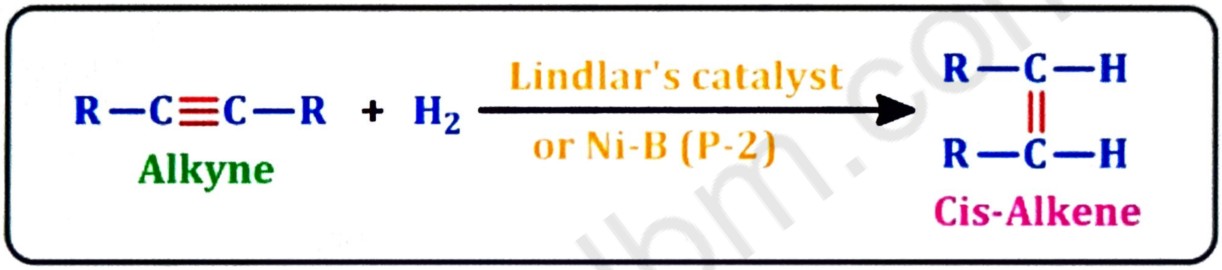
- **Alkynes react with hydrogen** when passed over heated catalyst **(Lindlar's catalyst)**-Palladium poisoned with **$CaCO_3$ or $BaSO_4$** and partially poisoned by **addition of $PbCO_3$, S or quinoline** to form predominantly **cis-alkenes (as high as 98%)**

$$\underset{\text{Alkyne}}{R-C\equiv C-H} + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} \underset{\text{Alkene}}{R-CH=CH_2}$$

$$\underset{\text{Propyne}}{H_3C-C\equiv C-H} + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} \underset{\text{Propene}}{H_3C-CH=CH_2}$$

$$\underset{\text{Acetyline}}{H-C\equiv C-H} + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} \underset{\text{Ethylene (Ethene)}}{H_2C=CH_2}$$

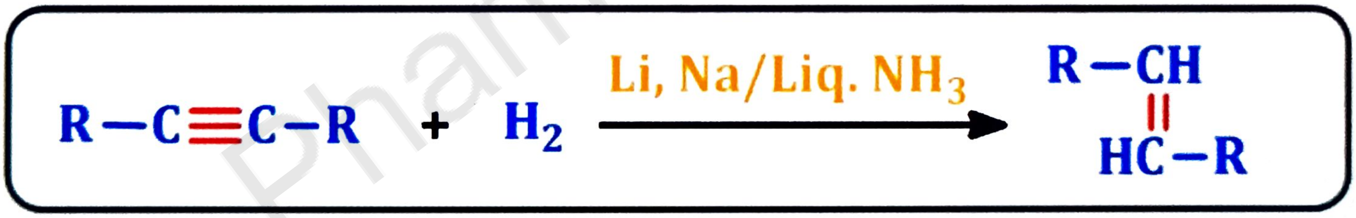
(a) **Hydrogenation of alkynes** with **Lindlar's catalyst** or a nickel boride called **P-1 catalyst** yields only **cis-alkene.**



$$\underset{\text{Alkyne}}{R-C\equiv C-R} + H_2 \xrightarrow[\text{or Ni-B (P-2)}]{\text{Lindlar's catalyst}} \begin{matrix} R-C-H \\ \| \\ R-C-H \end{matrix}$$

Cis-Alkene

(b) But **reduction of alkynes** with **lithium or sodium in liquid NH_3** **(Birch: reduction)** yields predominantly **trans-alkene**



$$R-C\equiv C-R + H_2 \xrightarrow{\text{Li, Na/Liq. }NH_3} \begin{matrix} R-CH \\ \| \\ HC-R \end{matrix}$$

5. By Cracking or Pyrolysis

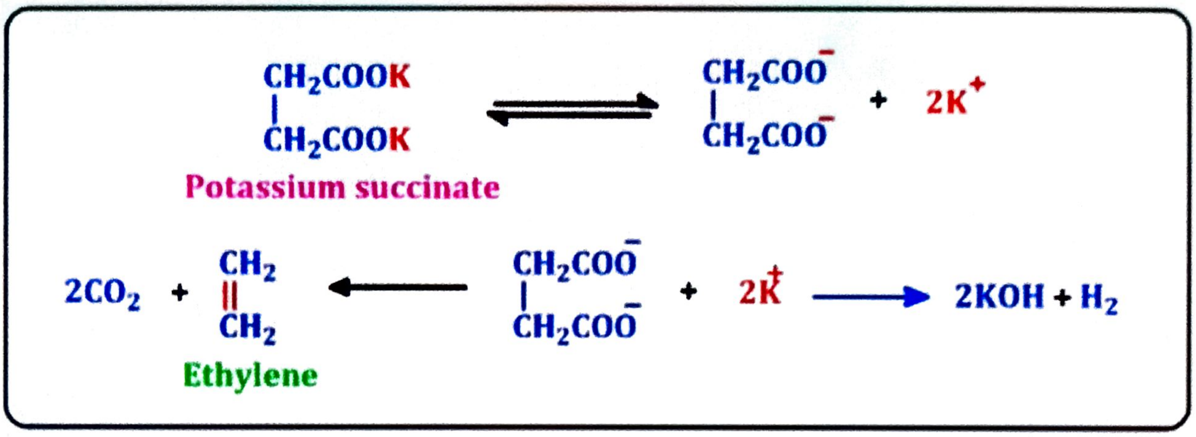
- The **higher alkanes** when heated to a **high temperature** decompose to give a **lower alkene** along with a **lower alkane.**
- The **first three alkenes** are thus obtained by the **cracking** of the **petroleum hydrocarbons.**

$$\underset{\text{Higher alkane}}{R'-CH_2-CH_2-R} \xrightarrow{\text{Cracking}} \underset{\text{Alkene}}{R'-CH=CH_2} + \underset{\text{Lower alkane}}{RH}$$

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{\text{Cracking}} \underset{\text{Propene (Propylene)}}{H_3C-CH=CH_2} + \underset{\text{Methane}}{CH_4}$$

6. By electrolysis of salts of dicarboxylic acids

- **Alkenes** are formed by the **electrolysis of aqueous solutions** of **potassium salts of dibasic acids** of the succinic acid series. Thus :



$$\begin{array}{c}CH_2COOK\\|\\CH_2COOK\end{array} \rightleftharpoons \begin{array}{c}CH_2CO\bar{O}\\|\\CH_2CO\bar{O}\end{array} + 2K^+$$

Potassium succinate

$$2CO_2 + \begin{array}{c}CH_2\\||\\CH_2\end{array} \longleftarrow \begin{array}{c}CH_2CO\bar{O}\\|\\CH_2CO\bar{O}\end{array} + 2K^+ \longrightarrow 2KOH + H_2$$

Ethylene

7. By pyrolysis of quaternary ammonium compounds

- Many **alkenes** are conveniently prepared by heating **quaternary ammonium compounds.**

$$(C_2H_5)_4\overset{+}{N}OH^- \xrightarrow{Heat} (C_2H_5)_3N + C_2H_4 + H_2O$$

Tetraethyl ammonium hydroxide

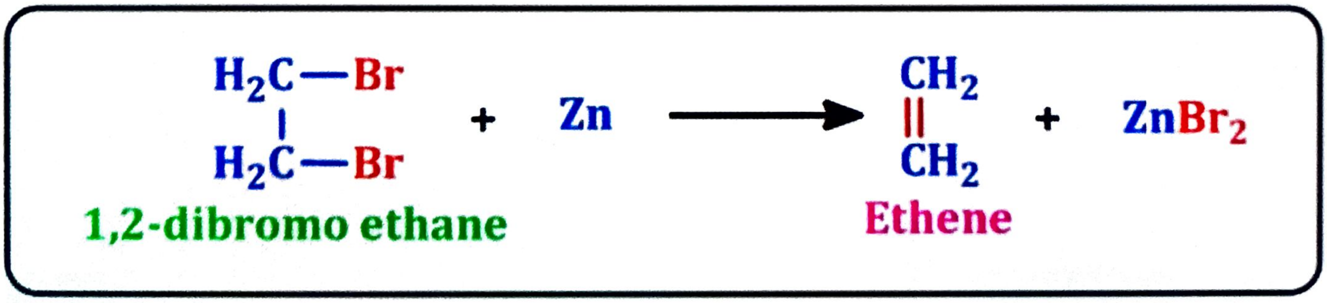
Triethyl amine

Ethane

- It is called **Hoffmann elimination** with the **formation of an amine** having smaller alkyl groups on the **π-bonded carbon.**
- This reaction is **E_2 elimination** with an amine as **leaving group**

8. Dehalogenation of vicinal dihalides

- A compound having **two halogen atoms** on the **two adjacent carbon** atom is called **vicinal dihalide.** When any such compound, preferably **vicinal dibromide is heated with zinc,** a corresponding **alkene is formed.** Thus :



$$\begin{array}{c}H_2C-Br\\|\\H_2C-Br\end{array} + Zn \longrightarrow \begin{array}{c}CH_2\\||\\CH_2\end{array} + ZnBr_2$$

1,2-dibromo ethane

Ethene

9. From gem dihalides

$$H_3C-CHBr_2 + 4Na + Br_2CHCH_3 \longrightarrow CH_3CH{=}CH\,CH_3 + 4NaBr$$

1,1-Dibromoethane

But-2-ene

☐ CHEMICAL REACTION

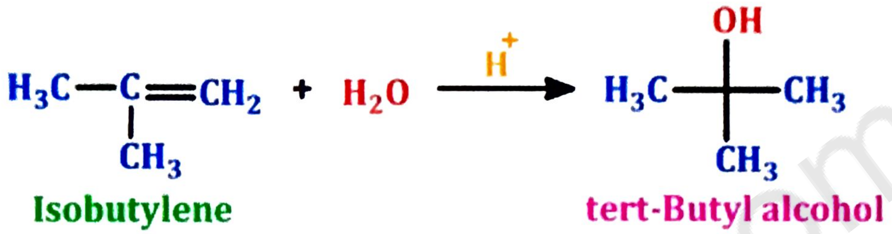
i. Addition reaction

1. Addition of hydrogen

$$H_2C{=}CH_2 + H_2 \longrightarrow H_3C{-}CH_3$$

Ethylene Ethane

2. Addition of water



$$H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} H_3C{-}\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3$$

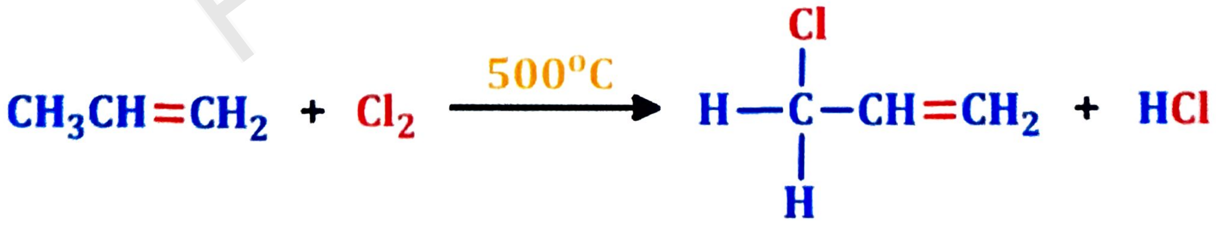
Isobutylene tert-Butyl alcohol

3. Addition of HNO_3

$$H_2C{=}CH_2 + HNO_3 \longrightarrow CH_2OHCH_2NO_2$$

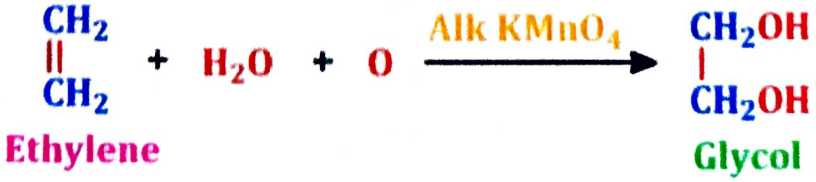
Ethene 2-Nitroethaol

ii. Substitution reaction



$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow{500^\circ C} H{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}{-}CH{=}CH_2 + HCl$$

iii. Oxidation reaction



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + O \xrightarrow{Alk\ KMnO_4} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

Ethylene Glycol

ALKENES

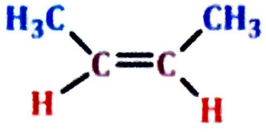
Points to be covered in this topic

1. STABILITIES OF ALKENES
2. sp^2 HYBRIDIZATION OF ALKENES
3. ISOMERISM IN ALKENES
4. E_1 AND E_2 REACTIONS
5. E_1 VERSUS E_2 REACTIONS
6. FACTORS AFFECTING E_1 AND E_2 REACTIONS
7. ORDER OF REACTIVITY OF ALKYL HALIDES
8. REARRANGEMENT OF CARBOCATIONS

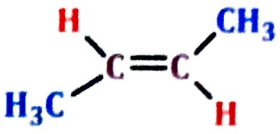
☐ STABILITY OF ALKENES

- The relative **thermodynamic stabilities** of various alkenes can be **determined by heats of hydrogenation.**
- **For example**, the reactions of **1-butene** and **both cis- and trans-2-butene** with dihydrogen afford the same product, butane.
- Consequently, **differences in heats of hydrogenation** accurately reflect the differences in thermodynamic stabilities of these **three alkenes**.
- **These heats** are: **1-butene**, -30.3 kcal/mol; **cis-2-butene**, **-28.6 kcal/mol**; **trans-2-butene** -27.6 kcal/mol.
- The order of stabilities is therefore **1-butene least stable** and **trans-2-butene most stable**. The stability difference between **1-butene and trans-2-butene is 2.7 kcal/mol.**

- **There are two factors which affect the stability order**



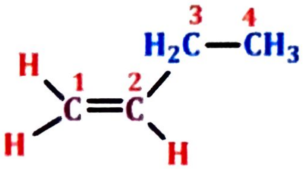
cis-2-butene



trans-2-butene

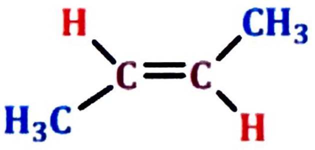
1. **First,** The presence of **alkyl groups** directly attached to the **double bond** tends to stabilize the system. We regard **1-butene** as a **monoalkyl substituted double bond,**

✓ Since it has **one methyl group attached to the double bond**



1-Butene

2. **The second** factor is relevant to the relative stability order of the two **di-substituted double bonds,** i.e., **cis- and trans-2-butene.**
   - The **methyl groups** of the **cis isomer** are relatively close in space, so that a **steric repulsion of 1.0 kcal/mole** results, as was mentioned previously.
   - The **trans isomer,** which has **no such steric effect,** is therefore the **more stable isomer.**



trans-2-butene

❑ SP^2 HYBRIDIZATION OF ALKENES

- The simplest **alkene**, **ethene**, has a planar structure, where the **two carbon atoms** and **four hydrogens atoms** that are attached to these carbon **atom lie in a plane.**
- The **carbon to carbon** and **carbon to hydrogen bonds** are arranged as **far apart in space** as possible Thus, these **bonds are at 120°** to each other.
- The **geometry** of this structure **cannot be explained** using the **shape of atomic orbitals** on the carbon atom.