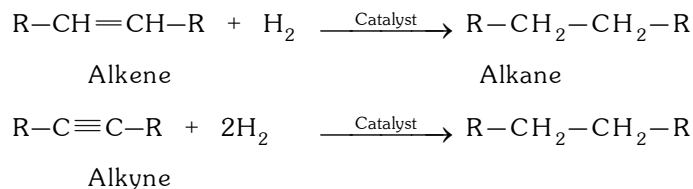# HYDROCARBON

ALKANE

❑ **Introduction** :

(i)   Branched and unbranched aliphatic saturated hydro carbons are called member of alkane. The structural formula of alkane have only single bonds or all bonds in alkane is only σ bonds.

(ii) Alkanes does not reacts with chemical reagants such as dil. and conc. HCl, dil. & conc. H_2SO_4, dil. & conc. HNO_3, Caustic soda, acidic & basic $K_2Cr_2O_7$, $KMnO_4$ etc. That is why alkanes are called paraffins. (Parum=little, affins = reactivity).

Property	Characteristics of alkane	Property	Characteristics of alkane
General formula	C_nH_{2n+2}	C—C Bond length	1.54 A
C—C Bond energy	82.67 kcal/mole	C—H Bond length	1.112 A
C—H Bond energy	98.67 kcal/mole	Hybridisation on C	sp^3
Bond angle	109 .28'	shape	Tetrahedral

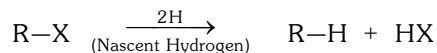❑ **General Methods of Preparations** :

1.   **From alkenes and alkynes (Sabatier and Sandrens reaction) or (By hydrogenation of alkenes and alkynes)** : Alkenes and alkynes on catalytic hydrogenation gives alkanes.

$$R-CH=CH-R \ + \ H_2 \ \xrightarrow{\text{Catalyst}} \ R-CH_2-CH_2-R$$
$$\text{Alkene} \qquad\qquad\qquad \text{Alkane}$$

$$R-C\equiv C-R \ + \ 2H_2 \ \xrightarrow{\text{Catalyst}} \ R-CH_2-CH_2-R$$
$$\text{Alkyne}$$

Catalyst :

(a)   Pd/Pt at ordinary temp. and pressure

(b)   Ni, 200–300 C (sabatier)

(c)   Raney Nicker at room temp.

(d)   Raney nickel is obtained by boiling Ni/Al with NaOH. Al dissolved & Ni obtained in finally divided state.

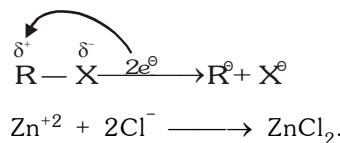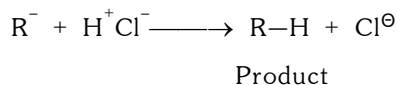(e)   Methane can not be prepared by this method (From unsaturated hydrocarbon).

2.   **From alkyl Halides (By reduction)** :

$$R-X \ \xrightarrow[\text{(Nascent Hydrogen)}]{2H} \ \ R-H \ + \ HX$$

Catalyst :

(i) Zn + HCl　　　　　　　(ii) Zn + CH_3 COOH　　　　(iii) Zn—Cu couple in C_2H_5OH

(iv) Red P + HI　　　　　　(v) Al + Hg + ethanol

◆   **Mechanism** : Zn $\longrightarrow$ Zn^{+2} + $2e^{\ominus}$ 　　　　$\overset{\delta^+}{R} - \overset{\delta^-}{X} \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$

R^- + $H^+Cl^- \longrightarrow$ R–H + $Cl^{\ominus}$ 　　Zn^{+2} + $2Cl^- \longrightarrow$ $ZnCl_2$.

Product

(a) Alkyl halides can also be reduced to alkane by H_2/Pd or $LiAlH_4$ or H_2/Ni.

(b) Reduction is due to the electron transfer from the metal to the substrate (R- X)

(c) If any alkyl halide is asked, the H-atom of any carbon atom of given alkane is removed by halogen atom.

3. **From alkyl halide (By Wurtz reaction):**
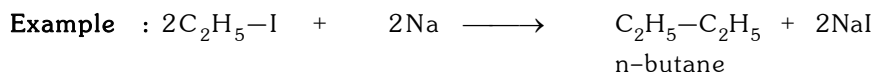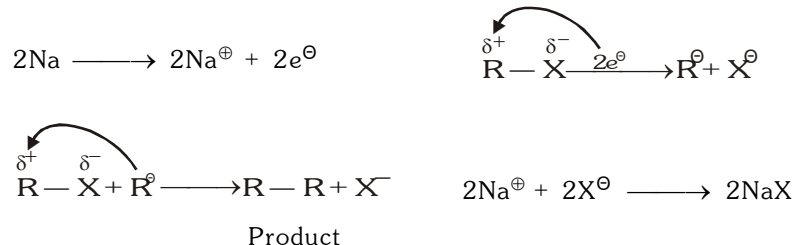A solution of alkyl halide in ether on heating with sodium gives alkane.

$$R - X + 2Na + X - R \xrightarrow[\text{ether}]{\text{Dry}} R - R + 2NaX$$
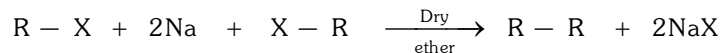
(a) Two moles of alkyl halide treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

$$2Na + H_2O \longrightarrow 2NaOH + H_2$$
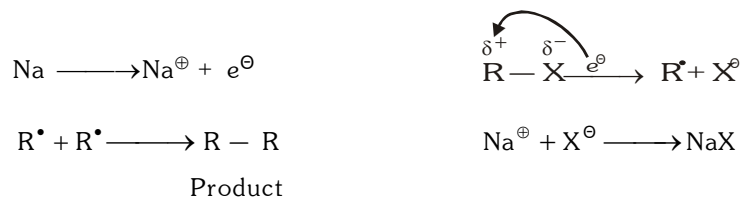$$CH_3I + NaOH \longrightarrow CH_3OH + NaI$$
$$\text{Methanol}$$
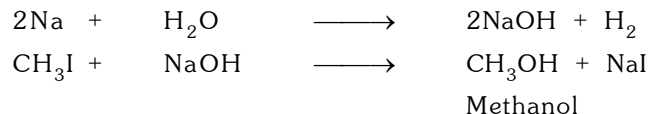
(b) Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.

(c) Two different alkyl halides, on wurtz raction give all possible alkanes.

(d) The seperation of mixture in to individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

(e) This reaction generally fails with tertiary alkyl halide.

◆ **Mechanism :** Two mechanism have been proposed for this reaction.

(a) Ionic Mechanism:

$$2Na \longrightarrow 2Na^{\oplus} + 2e^{\ominus} \qquad \overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$$

$$\overset{\delta+}{R} - \overset{\delta-}{X} + R^{\ominus} \longrightarrow R - R + X^{-} \qquad 2Na^{\oplus} + 2X^{\ominus} \longrightarrow 2NaX$$
$$\text{Product}$$

Example : $2C_2H_5 - I + 2Na \longrightarrow C_2H_5 - C_2H_5 + 2NaI$
$$\text{n–butane}$$

(b) Free radical mechanism :

$$Na \longrightarrow Na^{\oplus} + e^{\ominus} \qquad \overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow{e^{\ominus}} R^{\bullet} + X^{\ominus}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R \qquad Na^{\oplus} + X^{\ominus} \longrightarrow NaX$$
$$\text{Product}$$

Free radicals also undergo Disproportionation i.e. one radical gains hydrogen at the expense of the other which loss hydrogen.

$$\overset{H}{\underset{CH_2}{|}} - \dot{C}H_2 + \dot{C}_2H_5 \longrightarrow C_2H_6 + C_2H_4$$
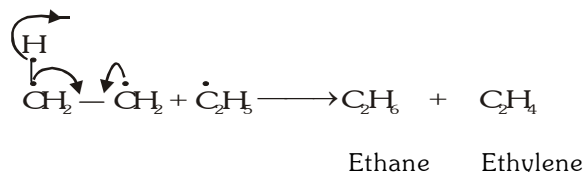
$$\qquad\qquad\qquad\qquad\text{Ethane} \quad \text{Ethylene}$$

This explains the presence of ethylene and ethane in the butane obtained by Wurtz reaction.

Ex. If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.

Sol. 2, 3-Dimethyl butane.

Ex. If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.

Sol. n-Butane, 2-Methyl butane and 2, 3-Dimethyl butane.

Ex. Which of the following compound can not obtained from wurtz reaction.

(A) ethane   (B) butane   (C) isobutane   (D) hexane

Sol. (C) **[Hint :** In wurtz reaction unsymmetrical alkane can not be obtained.
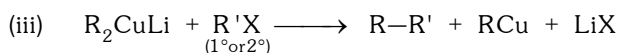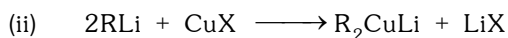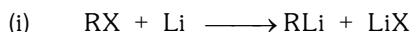
Ex. When ethyl chloride and n-propyl chloride undergoes wurtz reaction which is not obtained.

(A) n–butane   (B) n–pentane   (C) n–hexane   (D) isobutane

Sol. (D) $C_2H_5-Cl + C_3H_7Cl \xrightarrow[\text{dry ether}]{\text{Na}} C_2H_5 -C_2H_5 + C_3H_7-C_3H_7 + C_2H_5-C_3H_7$

4. Corey-House Synthesis :

This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R—R'

(i) $RX + Li \longrightarrow RLi + LiX$

(ii) $2RLi + CuX \longrightarrow R_2CuLi + LiX$

(iii) $R_2CuLi + \underset{(1°or2°)}{R'X} \longrightarrow R-R' + RCu + LiX$

Note : In Corey-house reaction symmetrical and unsymmetrical alkane both can be formed.

5. From Frankland Reagent: If Zn is used in place of Na, the reaction is named as Frankland reaction.

$$R-X + 2Zn +RX \longrightarrow R_2Zn + ZnX_2$$

Frankland reagent

$$R_2Zn + R-X \longrightarrow R-R + RZnX$$
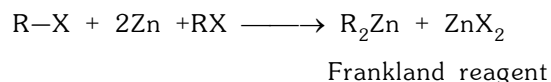
6. From Carboxylic Acid (By decarboxylation) : Saturated monocarboxylic acid salt of sodium or potassium on dry distillation with soda lime give alkane.

$$RCOONa + NaOH \xrightarrow[\text{Cao}]{\Delta} R-H + Na_2CO_3$$
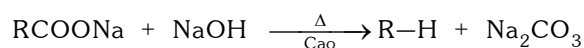
Soda Lime

(a) The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.
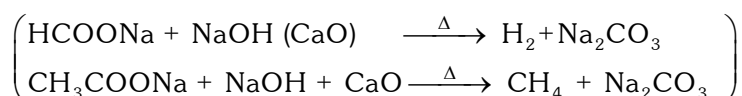
(b) Replacement of -COOH by hydrogen is known as decarboxylation.

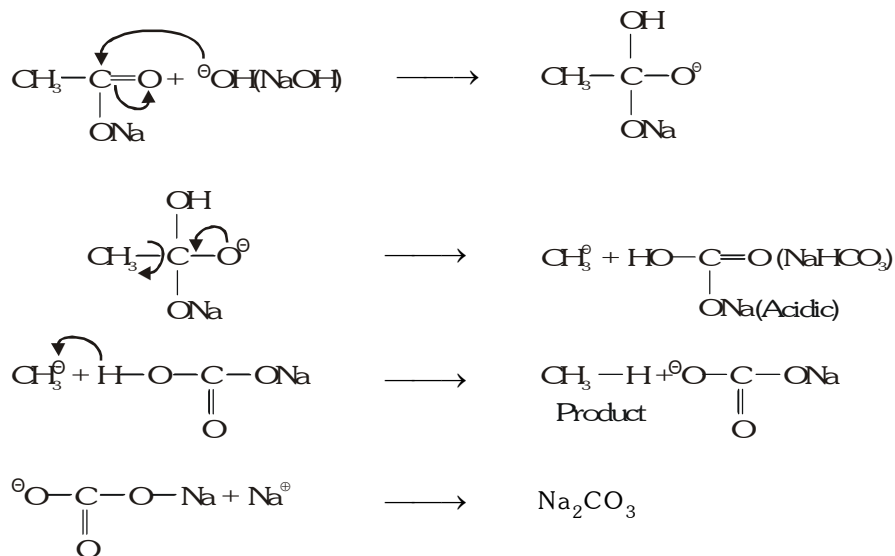The alkane formed always contains one carbon atom less than the original acid.

(c) This reaction is employed for stepping down a homologous series.

(d) Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the products.

(e) Decarboxylation of sodium formate gives H_2

$$\left(\begin{array}{l} HCOONa + NaOH\,(CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3 \\ CH_3COONa + NaOH + CaO \xrightarrow{\Delta} CH_4 + Na_2CO_3 \end{array}\right)$$

◆ **Mechanisim :** Decarboxylation proceeds via. the formation of carbanion intermediate as follows.

$$CH_3-\underset{\underset{ONa}{|}}{C}=O + {}^{\ominus}OH(NaOH) \longrightarrow CH_3-\underset{\underset{ONa}{|}}{\overset{\overset{OH}{|}}{C}}-O^{\ominus}$$

$$CH_3\overset{\overset{OH}{|}}{-}\underset{\underset{ONa}{|}}{C}-O^{\ominus} \longrightarrow CH_3^{\ominus} + HO-\underset{\underset{ONa(Acidic)}{|}}{C}=O \,(NaHCO_3)$$

$$CH_3^{\ominus} + H-O-\underset{\underset{O}{||}}{C}-ONa \longrightarrow CH_3-H + {}^{\ominus}O-\underset{\underset{O}{||}}{C}-ONa$$
$$\text{Product}$$

$${}^{\ominus}O-\underset{\underset{O}{||}}{C}-O-Na + Na^{\oplus} \longrightarrow Na_2CO_3$$

(a) If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating.
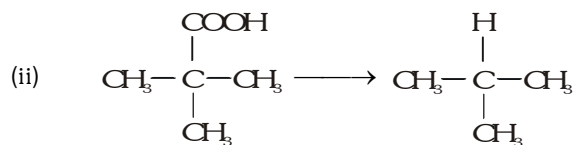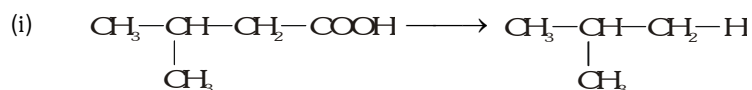
$$CH_2\underset{COOH}{\overset{COOH}{\Big\langle}} \xrightarrow{\Delta} CH_3COOH + CO_2$$
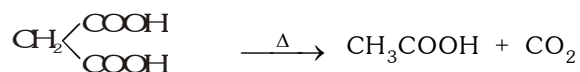
(b) CH_4 can be prepared by CH_3COOH.
(c) C_2H_6 can be prepared by CH_3CH_2COOH.
(d) $CH_3-CH_2-CH_3$ can be prepared by Butanoic acid and 2–Methyl propanoic acid.

Ex. How many acids can be taken to obtain isobutane from decarboxylation ?
(A) 4   (B) 3   (C) 2   (D) 5
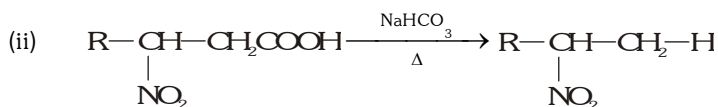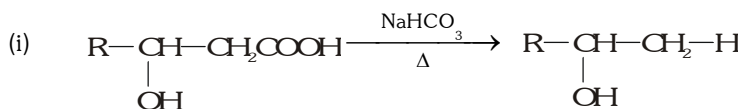
Sol. (C) To obtain isobutane the acids are

(i) $$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-H$$

(ii) $$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$$

So two acids can be taken.

> Reactivity of acid $\propto$ stability of carbanion

Presence of electron attracting group (–I) in the hydrocarbon part of the fatty acid increases the decarboxylation.
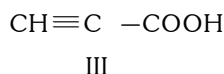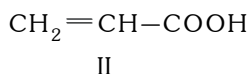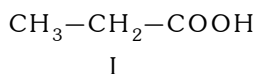If – I is more effective group then weak base may be taken.
Example :

(i) $$R-\underset{\underset{OH}{|}}{CH}-CH_2COOH \xrightarrow[\Delta]{NaHCO_3} R-\underset{\underset{OH}{|}}{CH}-CH_2-H$$

(ii) $$R-\underset{\underset{NO_2}{|}}{CH}-CH_2COOH \xrightarrow[\Delta]{NaHCO_3} R-\underset{\underset{NO_2}{|}}{CH}-CH_2-H$$

(iii) β-Keto acids are decarboxylated readily simply on heating (soda lime is not required)

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2COOH \xrightarrow{\Delta} R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$
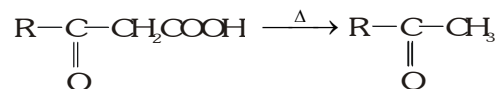
Ex. Give reactivity order for decarboxylation ?

$$CH_3-CH_2-COOH \qquad\qquad CH_2=CH-COOH \qquad\qquad CH\equiv C-COOH$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II} \qquad\qquad\qquad\qquad \text{III}$$
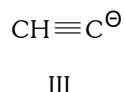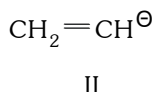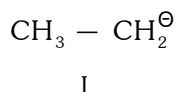
(A) I > II > III (B) III > II > I (C) III > I > II (D) None is correct

Sol. (B) In decarboxylation intermediates are,

$$CH_3-CH_2^{\ominus} \qquad\qquad CH_2=CH^{\ominus} \qquad\qquad CH\equiv C^{\ominus}$$
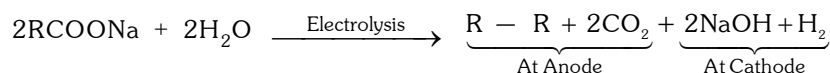$$\text{I} \qquad\qquad\qquad\qquad \text{II} \qquad\qquad\qquad\qquad \text{III}$$
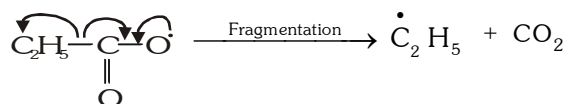
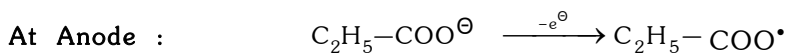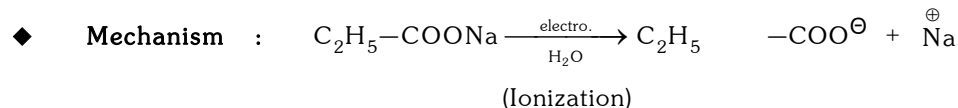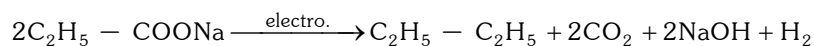The stability order of carbanion – III > II > I

So reactivity order for acid is – III > II > I
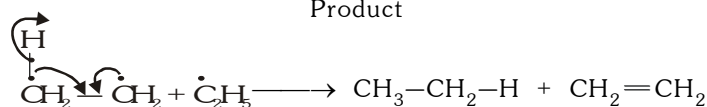
7. From carboxylic acid (By Kolbe's process) :

Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{R-R+2CO_2}_{\text{At Anode}} + \underbrace{2NaOH+H_2}_{\text{At Cathode}}$$

Electrolysis of Sodium propionate solution give n-butane, ethylene, ethane and ethyl propionate as follows-

$$2C_2H_5-COONa \xrightarrow{\text{electro.}} C_2H_5-C_2H_5 + 2CO_2 + 2NaOH + H_2$$

◆ **Mechanism :** $C_2H_5-COONa \xrightarrow[H_2O]{\text{electro.}} C_2H_5-COO^{\ominus} + \overset{\oplus}{Na}$

(Ionization)

At Anode : $C_2H_5-COO^{\ominus} \xrightarrow{-e^{\ominus}} C_2H_5-COO^{\bullet}$

$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O \xrightarrow{\text{Fragmentation}} \overset{\bullet}{C}_2H_5 + CO_2$$

$$\overset{\bullet}{C}_2H_5 + \overset{\bullet}{C}_2H_5 \longrightarrow C_2H_5-C_2H_5$$

Product

$$CH_2=CH_2 + \overset{\bullet}{C}_2H_5 \longrightarrow CH_3-CH_2-H + CH_2=CH_2$$
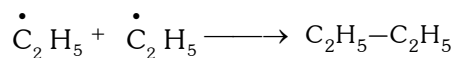
(minor products)

An ester is also formed.

$$C_2H_5-CO\overset{\bullet}{O} + \overset{\bullet}{C}_2H_5 \longrightarrow C_2H_5-COOC_2H_5$$

(minor products)

At cathode : $Na^{\oplus} + e^{\ominus} \longrightarrow Na$
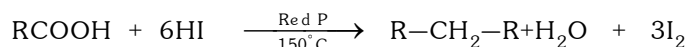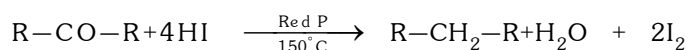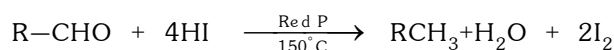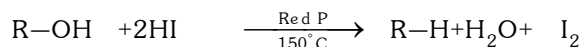
$Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$
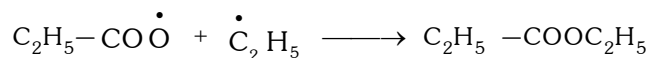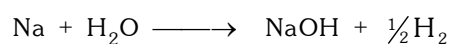
(a) Methane can not be prepared by this method.

(b) Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.

$$R'COOK + R''COOK \xrightarrow{\text{Electrolysis}} (R'-R'' + R'-R' + R''-R'') + 2CO_2 + H_2 + 2NaOH$$
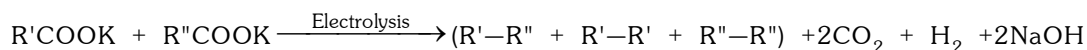
(c) Presence of alkyl groups in α - position decrease the yield of alkanes.

(d) True aromatic acids do not undergo Kolbe's electrolytic reaction.

(e) Free radical mechanism has been suggested for Kolbe reaction.

(f) At anode alkane (major) and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.

(g) The concentration of NaOH in solution is increased with time so pH of solution is also increased.

8. **From alkanol, alkanals, Alkanone and alkanoic acid (By reduction) :**

The reduction of either of the above in presence of red P and HI gives corresponding alkane.

$$R-OH + 2HI \xrightarrow[150°C]{\text{Red P}} R-H + H_2O + I_2$$

$$R-CHO + 4HI \xrightarrow[150°C]{\text{Red P}} RCH_3 + H_2O + 2I_2$$

$$R-CO-R + 4HI \xrightarrow[150°C]{\text{Red P}} R-CH_2-R + H_2O + 2I_2$$

$$RCOOH + 6HI \xrightarrow[150°C]{\text{Red P}} R-CH_2-R + H_2O + 3I_2$$

In the above reaction I_2 is formed which acts as reducing agent and may reduce alkane and form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.

$$R-CH_3 + I_2 \rightleftharpoons R-CH_2-I + HI$$
$$2P + 3I_2 \longrightarrow 2PI_3$$
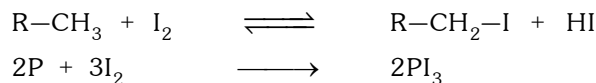
9. **From alkanones (By Clemmensen's method) :**

Carbonyl compound (Preferably ketones) may also be reduced with Zinc amalgam and concentrated HCl (Zn–Hg/HCl), this reaction is called Clemmensen reduction.

$$R-CO-R' + 4H \xrightarrow[\text{con. HCl}]{\text{Zn / Hg}} R-CH_2-R' + H_2O$$
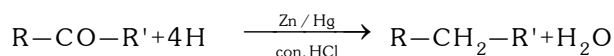
CH_4, CH_3-CH_3, isobutane and neopentane are not obtained from Ketones because these alkane do not contain $>CH_2$ group.

10. **From alkanals and alkanones (By Wolf Kishner reaction) :**

$$>C=O + NH_2NH_2 \longrightarrow >C=N.NH_2 \xrightarrow[\Delta]{\text{Glycol / KOH}} >CH_2 + N_2$$
Hydrazine   Hydrazone
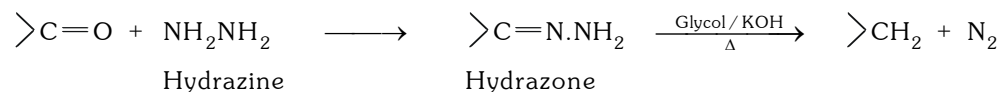
❑ **From G.R. :**

(a) **Formation of alkanes with same number of C atoms :** With same number of C-atoms as G.R. react with compound containing active hydrogen alkanes is obtained.

$$R-Mg-X + H-O-H \longrightarrow R-H + Mg(OH)X$$
$$+ R-O-H \longrightarrow R-H + Mg(OR)X$$
$$+ R-NH-H \longrightarrow R-H + Mg(NHR)X$$
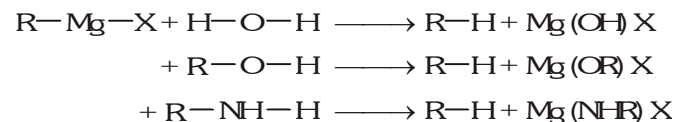
This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

(b) **G.R. react with alkyl halide to give higher alkanes :**
$$RMgX + R'-X \longrightarrow R-R' + MgX_2$$
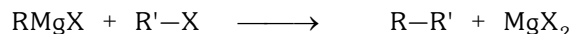
Ex. Which of the following does not give alkane with R—Mg—X.

(A) Ph—OH   **(B) Cl —NH$_2$**   (C) CH$_3$COOH   (D) HCl

Sol. (B)

[**Hint** : Except Cl—NH$_2$ all have active hydrogen, but Cl—NH$_2$ when reacts with R—Mg—X the product is R—NH$_2$.]
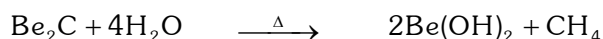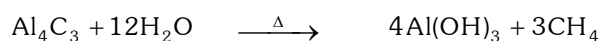
❑ **From metal carbide (By hydrolysis) :**

Only CH$_4$ can be obtained by the hydrolysis of Be or Al carbides

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta} 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \xrightarrow{\Delta} 2Be(OH)_2 + CH_4$$

11. Physical Properties :

(i)   C$_1$ to C$_4$ gases, Neopentane also gas but n-pentane and isopentane are low B.P. liquids.

(ii)   Next members C$_5$ to C$_{17}$ are Colourless liquids and above C$_{17}$ are Waxy solids.

(iii)   **Density** : The density of alkanes increases with increase in molecular weight and becomes constant at 0.8 g/mL. Thus all alkanes are lighter than water.

(iv)   **Solubility** : Alkanes being non polar and thus insoluble in water but soluble in non-polar solvents

      Example : C$_6$H$_6$, CCl$_4$,ether etc.

      ◆   The solubility of alkanes decreases with increase in molecular weight

      ◆   Liquid alkanes are themselves good non-polar solvents.

(v)   **Boiling point** - ∝ molecular weight (for n-alkanes)

∵ | Vanderwaals force of attraction ∝ molecular weight ∝ surface area of molecule. |

i.e.   boiling point   Pentane < hexane < heptane

      Also boiling point $\propto \dfrac{1}{\text{number of side chain}}$

because the shape approaches to spherical which results in decrease in Vanderwaals forces (as surface area decreases)

Thus boiling point n–Pentane > Isopentane > neopentane

(vi)   **Melting Point** : M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their alkanes of odd number of carbon atoms.

      The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.
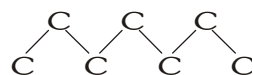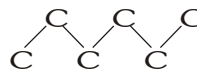
Odd number of carbon   <   Even number of carbon

Ex. Alkanes are inert is nature, why ?

Sol. Alkanes are quite inert substances with highly stable nature. Their inactiveness has been explained as:

(i)   Alkanes have all the C—C and C—H bonds being stronger σ bonds and are not influenced by acid, oxidants under ordinary conditions.

(ii)   The C—C bond is completely non polar and C—H is weak polar. Thus polar species i.e. electrophiles or nucleophiles are unable to attack these bonds under ordinary conditions.
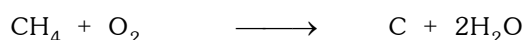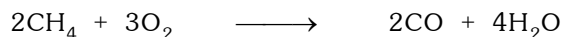
12. Chemical Properties :

❑ **Oxidation :**

◆ **Complete oxidation or combustion :** Burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.
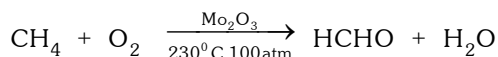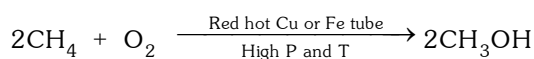
$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)\ H_2O + Q;\ (\Delta H = -ve)$$
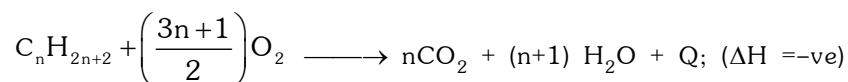
◆ **Incomplete oxidation :** In limited supply of air gives carbon black and CO.

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$
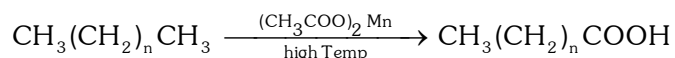$$CH_4 + O_2 \longrightarrow C + 2H_2O$$
$$\text{C–black (used in printing)}$$

◆ **Catalytic oxidation :**

(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

$$2CH_4 + O_2 \xrightarrow[\text{High P and T}]{\text{Red hot Cu or Fe tube}} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[230^0C, 100atm]{Mo_2O_3} HCHO + H_2O$$

(ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

$$CH_3(CH_2)_nCH_3 \xrightarrow[\text{high Temp}]{(CH_3COO)_2\ Mn} CH_3(CH_2)_nCOOH$$

(iii) Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.
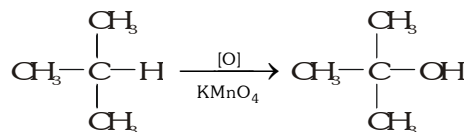
Ex. How many litre of Oxygen required for complete conbustion of 6.0 g ethane at NTP ?

Sol. $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$
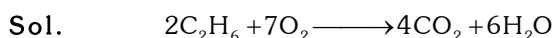
60 g ethane required O_2 (at NTP) = 7 × 22.4 litre

1 g ethane required O_2 (at NTP) = $\dfrac{7 \times 22.4}{2 \times 30}$ litre

6 g ethane required O_2 (at NTP) = $\dfrac{7 \times 22.4}{2 \times 30} \times 6 = 15.68$ litre

❑ **Substitution Reactions :** Substitution reaction in alkanes shows free radical mechanism. They give following substitution reaction.

(a) Halogenation : Replacement of H-atom by halogen atom

$$R-H + X_2 \longrightarrow R-X + HX$$
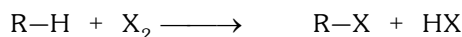
Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temp.

The reactivity order for halogens shows the order. $\boxed{F_2 > Cl_2 > Br_2 > I_2}$

Reactivity order of hydrogen atom in alkane is $\boxed{\text{Tertiary C – H > Sec. C – H > primary C – H}}$

(i) **Fluorination :** Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F_2 diluted with an inert gas (like N_2)

By the action of HgF_2 on bromo or iodo derivatives.

$$C_2H_5I + HgF_2 \longrightarrow C_2H_5F + HgI_2$$

(ii)   **Chlorination** :

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$
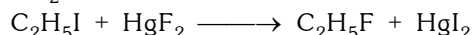
The monochloro derivative of alkane is obtained by taking alkane in large excess.

When chlorine is in excess, a mixture of mono, di, tri, tetra and perchloro derivatives is obtained.

$$\boxed{\text{Explosively } CH_4 + Cl_2 \longrightarrow C + HCl}$$

◆   **Mechanism** for $CH_4 + Cl_2 \xrightarrow{U V}$ $CH_3Cl + HCl$

Step I   **Chain initiation step** : $Cl:Cl \xrightarrow[\text{or } \Delta]{U V} Cl^{\bullet} + Cl^{\bullet}$

Step II   **Chain propagation step** : $Cl^{\bullet} + H:CH_3 \longrightarrow H:Cl + {}^{\bullet}CH_3$

                                                Methane   Methyl radical

$$\dot{C}H_3 + Cl:Cl \longrightarrow CH_3Cl + \dot{C}l$$

Step III   **Chain termination step** : $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$, $CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow CH_3Cl$,

$$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$$

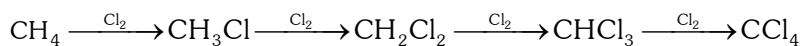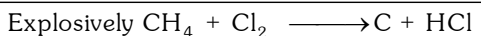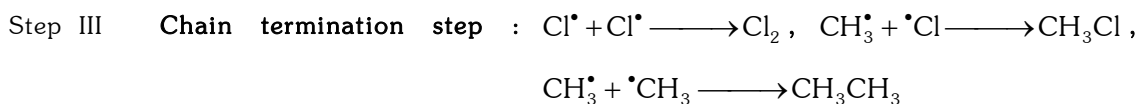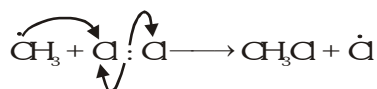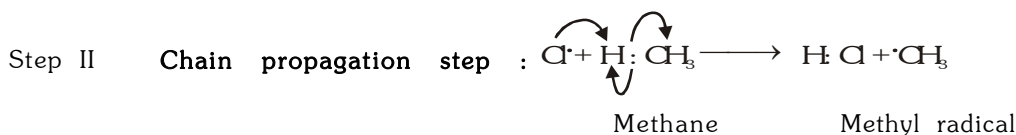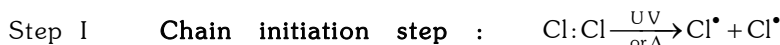A ${}^{\bullet}Cl$ can also attack CH_3Cl to form chloromethyl ($\dot{C}H_2Cl$) free radical. This free radical participates further in the chain reaction to yield methylene chloride (dichloromethane).

$$Cl^{\bullet} + H\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}{-}Cl \qquad \text{and} \qquad Cl{-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{\dot{C}}} + Cl:Cl$$
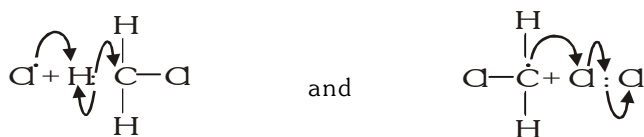
Similarly, chloroform and CCl_4 are obtained by further chain reaction.

(iii) **Bromination** : Br_2 reacts with alkanes in a similar manner but less vigorously.

(iv) **Iodination** : Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the CH_3I to CH_4.

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HIO_4, HNO_3, HgO etc. Which destroy HI,

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$
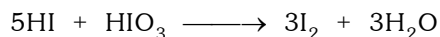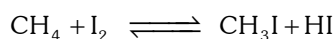
Iodination is very slow because energy of activation of the reaction is very large

$$CH_4 + I^{\bullet} \longrightarrow HI + \dot{C}H_3$$
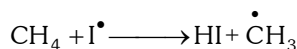
Note :

Halogenation is inhibited in presence of oxygen because oxygen reacts with alkyl free radicals to form less reactive peroxy alkyl radical $R–O–O^{\bullet}$ which can not propagate the chain.

◆   **Reactivity selectivity Principle :**

(i)   Probability factor : The factor is based on the number of each kind of H atom in the molecule.

    For example is $CH_3–CH_2–CH_2–CH_3$ there are six equivalent 1 H's and four equivalent 2 H's.

    The probability of abstracting 1 H's to 2 H's is 6 to 4. i.e., 3 to 2.

(ii) Reactivity of halogen free radical : the more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br radical is more selective and less influenced by the probability factor (Reactivity selectivity principle).

(iii) Reactivity of alkanes (ease of abstration of 'H' atoms) : Since the rate determining step in halogenations is abstraction of hydrogen by a halogen atom be the formation of alkyl radical, halogenation of alkanes follows order of stability of free radical is $3 > 2 > 1 > CH_3$.

Reactivity ratio of H atom for Chlorination   (1 : 2 : 3 H)
                                          1 : 3.8 : 5
Reactivity ratio of H atom for bromination   (1 : 82 : 1600)

The above order of stability of radicals is due to the ease of their formation from the corresponding alkane which in turn is due to difference in the value of ΔH.

$$CH_3-H \longrightarrow \dot{C}H_3 + H^\cdot \qquad\qquad \Delta H_1$$

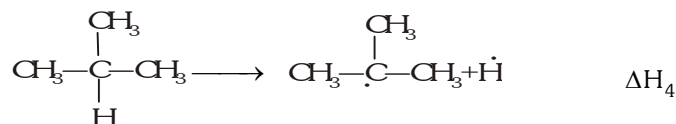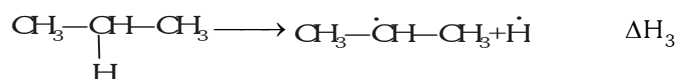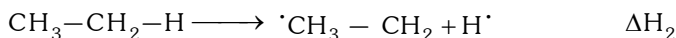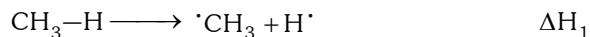$$CH_3-CH_2-H \longrightarrow \dot{C}H_3 - CH_2 + H^\cdot \qquad\qquad \Delta H_2$$

$$CH_3-\overset{|}{\underset{H}{C}}H-CH_3 \longrightarrow CH_3-\dot{C}H-CH_3 + \dot{H} \qquad\qquad \Delta H_3$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\cdot}{C}}-CH_3 + \dot{H} \qquad\qquad \Delta H_4$$

Reactivity of any H-atom $\propto$ number of H atoms of that kind   reactivity of that H.

Thus the amount of energy required to form the various classes of radicals decreases in the order $CH_3 > 1 > 2 > 3$ ($\Delta H_1 > \Delta H_2 > \Delta H_3 > \Delta H_4$). Therefore, it easiest to form 3 radical and it is most difficult to form CH_3. We can also interpret this in an alternative way the case of abstraction of H atoms from hydrocarbon fallows the sequence $3 > 2 > 1$ CH_4 which should also be the case of formation of free radicals.

The above order of stability is in accordance with the stability of free radicals on the basis of delocalization of odd electron. Order of stability of free radical is :

Allyl, benzyl $> 3 > 2 > 1 >$ methyl, vinyl.

Ex. What is the percentage of products obtained from monobromination of isobutane ?

Sol.

$$CH_3-\overset{|}{\underset{CH_3}{C}}H-CH_3 + Br_2 \longrightarrow CH_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 + CH_3-\overset{|}{\underset{CH_3}{C}}H-CH_2-Br$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (I) \qquad\qquad\qquad (II)$$
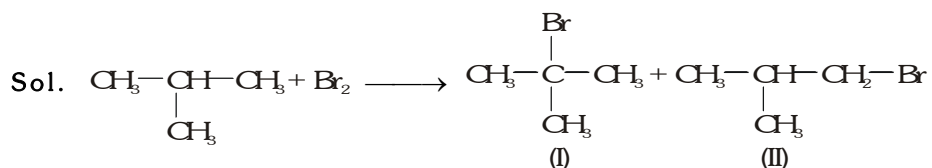
$$\frac{Product\,(I)}{Product\,(II)} = \frac{No.\,of\,primary\,H}{No.\,of\,tertiary\,H} \cdot \frac{reactivity\,of\,primary\,H}{reactivity\,of\,tertiary\,H} = \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600}$$

% of product (I) = $\dfrac{9}{1600+9} \times 100 = 0.56\%$

% of product (II) = $\dfrac{1600}{1600+9} \times 100 = 99.44\%$

(b) **Nitration :** (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with $-NO_2$ group.

At ordinary temperature, alkanes do not react with HNO_3. But reacts with vapours of Conc. HNO_3 at 450 C.

$$R - H + HO - NO_2 \xrightarrow{400-500^0C} R - NO_2 + H_2O$$

Since the reaction is carried at high temp. the C—C bonds of alkanes break during the reaction and a mixture of nitroalkanes is formed.

Example : $CH_3-CH_3 + HNO_3 \xrightarrow{450^0C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

$$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450\ C}$$

|	
1–Nitro propane	25%
2–Nitro propane	40%
Nitro ethane	10%
Nitromethane	25%

◆ **Mechanism** : (Free Radical substitution)

Step – I $\qquad HO - NO_2 \xrightarrow{\Delta} \overset{\bullet}{O}H + \overset{\bullet}{N}O_2$

$\qquad\qquad R \mid H + \overset{\bullet}{O}H \longrightarrow \overset{\bullet}{R} + H_2O$

Step – II $\qquad \overset{\bullet}{R} + HO - NO_2 \longrightarrow R - NO_2 + \overset{\bullet}{O}H$
$\qquad\qquad\qquad\qquad\qquad\qquad$ (Product)

Step – III $\qquad \overset{\bullet}{R} + \overset{\bullet}{N}O_2 \longrightarrow R - NO_2$

$\qquad\qquad \overset{\bullet}{R} + \overset{\bullet}{O}H \longrightarrow R - OH$ (minor)

$\qquad\qquad \overset{\bullet}{O}H + \overset{\bullet}{N}O_2 \longrightarrow HONO_2$

(c) Sulphonation : Replacement of H atom of alkane by $-SO_3H$ is known sulphonation. Alkane react with fuming H_2SO_4 or oleum $(H_2S_2O_7)$.

The branched lower alkanes and higher alkanes react to give alkane sulphonic acid.

Example :

$\qquad$ 2–Methyl propane $\qquad\qquad\qquad\qquad$ 2–methyl propane–2–sulphonic acid

The reactivity order for sulphonation is $\quad$ tert. H > Sec. H > prim. H

◆ **Mechanism** : (Free Radical substitution)

$\qquad HOSO_3H \xrightarrow{400^\circ C} HO^{\bullet} + \overset{\bullet}{S}O_3H$

$\qquad C_6H_{13}H + \overset{\bullet}{O}H \longrightarrow \overset{\bullet}{C}_6H_{13} + H_2O$

$\qquad \overset{\bullet}{C}_6H_{13} + \overset{\bullet}{S}O_3H \longrightarrow C_6H_{13}SO_3H$

Lower members such as propane, butane, pentane etc. react with SO_3 in vapourphase to form sulphonic acids.

$$C_3H_8 + SO_3 \longrightarrow C_3H_7 - SO_3H$$
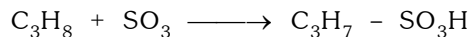
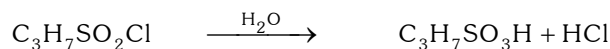**(d)** **Chlorosulphonation (Reed reaction) :** Reaction with a mixture of SO_2 and Cl_2 at ordinary temp. in the presence of UV light is called chlorosulphonation.

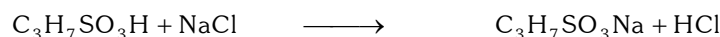$$C_3H_8 + SO_2 + Cl_2 \xrightarrow{\quad UV \quad} C_3H_7SO_2Cl + HCl$$
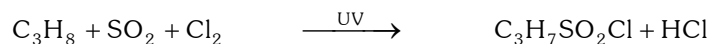
Propane sulphonyl Chloride

Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.

$$C_3H_7SO_2Cl \xrightarrow{\quad H_2O \quad} C_3H_7SO_3H + HCl$$

propane sulphonic acid

$$C_3H_7SO_3H + NaCl \longrightarrow C_3H_7SO_3Na + HCl$$
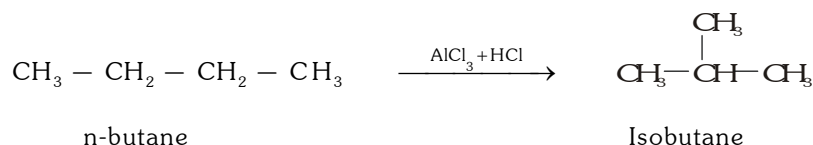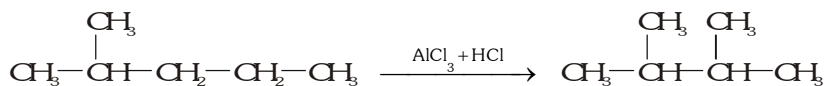
Sodium salt of sulphonic acid (used as detergent)

❑ **Isomerization :**

Unbranched chain alkanes on heating with $AlCl_3$ + HCl / 200^0C are converted in to branched chain alkanes

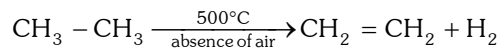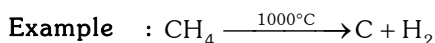$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{\quad AlCl_3 + HCl \quad} \underset{\underset{CH_3}{|}}{CH_3 - CH - CH_3}$$

n-butane   Isobutane

Branched chain alkanes converted to more branched alkane.

$$\underset{\underset{CH_3}{|}}{CH_3 - CH} - CH_2 - CH_2 - CH_3 \xrightarrow{\quad AlCl_3 + HCl \quad} CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3$$

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).
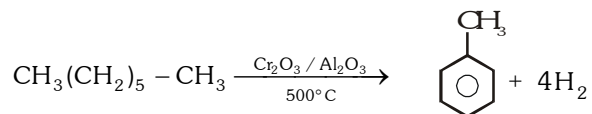
❑ **Pyrolysis or Cracking or thermal decomposition :**

When alkanes are heated to 500-700^{0}C they are decomposed in to lower hydrocarbon. This decomposition is called pyrolysis. In petroleum industry it is also termed as cracking.Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

Example : $CH_4 \xrightarrow{\quad 1000°C \quad} C + H_2$

$$CH_3 - CH_3 \xrightarrow[\text{absence of air}]{\quad 500°C \quad} CH_2 = CH_2 + H_2$$

$$CH_3CH_2CH_3 \longrightarrow \begin{cases} CH_2 = CH_2 + CH_4 \\ CH_3 - CH = CH_2 + H_2 \end{cases}$$

n-Butane $\xrightarrow{\quad Cracking \quad}$ 1-Butene + 2–Butene + Ethane + Ethene + Propene + CH_4+ H_2

The mechanism of pyrolysis occurs via free radicals.

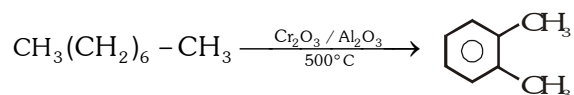❑ **Hydroforming or dehydrogenation or cyclisation or catalytic reforming or aromatization :**

Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on Al_2O_3 support at 500^0 C aromatic hydrocarbons are formed.

$$n-hexane \xrightarrow[500°C]{Cr_2O_3 / Al_2O_3} \text{[benzene]} + 4H_2$$

$$CH_3(CH_2)_5 - CH_3 \xrightarrow[500°C]{Cr_2O_3 / Al_2O_3} \text{[toluene]} + 4H_2$$

n-heptane   Toluene
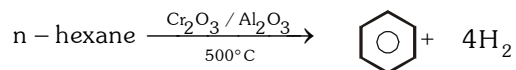
$$CH_3(CH_2)_6 - CH_3 \xrightarrow[500°C]{Cr_2O_3 / Al_2O_3} \text{[o-xylene]}$$

n-octane   o-xylene

It provides an excellent method of passing from aliphatic to aromatic series.

❑ **Chlorinolysis** : $CH_3 - CH_2 - CH_3 + Cl_2 \xrightarrow[Pressure]{300-400^0 C} \underset{(s)}{C_2Cl_6} + \underset{(\ell)}{CCl_4} + \underset{(g)}{HCl}$
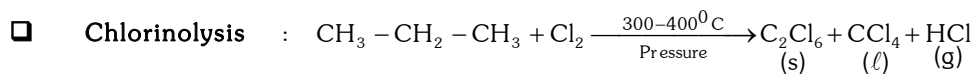
SOLVED EXAMPLES

Ex.1 Which of the following reactions can be employed for getting unsymmetrical alkanes in good yield ?

(A) Wurtz reaction   (B) Corey–House reaction

(C) Both   (D) None of these   **Ans.(B)**

Sol. Wurtz reaction is suitable for symmetrical alkanes

Ex.2 Sodium propionate on decarboxylation with sodalime gives

(A) Propane   (B) Ethane   (C) Butane   (D) Pentane   **Ans.(B)**

Sol. Decarboxylation with soda lime results in the formation of alkane with one carbon less than the starting compounds

Ex.3 Which of the following alkanes cannot be produced by Kolbe electrolysis of sodium or potassium salts of carboxylic acids ?

(A) Methane   (B) Ethane   (C) Butane   (D) Hexane   **Ans.(A)**

Sol. In Kolbe electrolysis, the alkane is formed by union of two alkyl groups. The alkane formed has, thus, two or more carbon atoms.

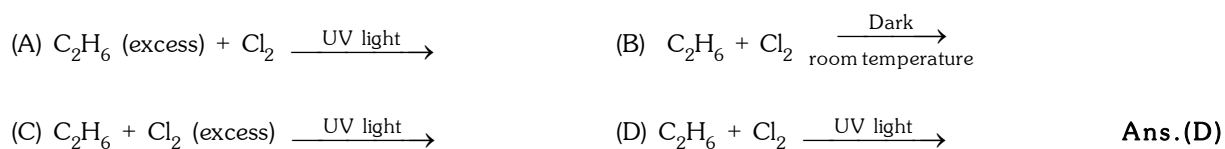**Ex.4** The homolytic fission of hydrocarbon results in the formation of -

(A) Free radicals   (B)   Carbocations

(C)   Carbanions   (D) Carbenes.   **Ans.(A)**

Sol. Homolytic fission results in the formation of free radicals.

Ex.5 n-Heptane when heated to a temperature of about 800 K under high pressure in the presence of Cr_2O_3/Al_2O_3 catalyst gives -

(A) 1-heptene   (B)   2-Methylhexane   (C)   Toluene   (D) Xylene.   **Ans.(C)**

Sol. $$CH_3-(CH_2)_5-CH_3 \xrightarrow{\;-4H_2\;} \underset{\text{Toluene}}{\langle\bigcirc\rangle-CH_3}$$
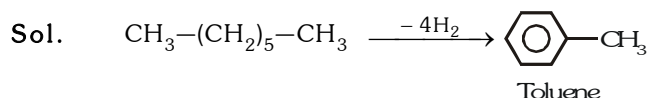
Ex.6 The reaction conditions leading to the best yield of C_2H_5Cl are -

(A) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{UV light}}$ (B) C_2H_6 + $Cl_2 \xrightarrow[\text{room temperature}]{\text{Dark}}$

(C) C_2H_6 + Cl_2 (excess) $\xrightarrow{\text{UV light}}$ (D) C_2H_6 + $Cl_2 \xrightarrow{\text{UV light}}$ **Ans.(D)**

Sol. C_2H_6 should be used in excess, otherwise polychlorination will take place
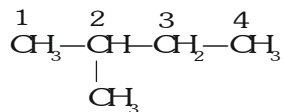
Ex.7 Number of isomer which can be theoretically obtained on monochlorination of 2-methylbutane is -

(A) 1   (B)   2   (C)   3   (D) 4   **Ans.(D)**

Sol.
$$\overset{1}{C}H_3-\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_3$$
$$|$$
$$\overset{1}{C}H_3$$
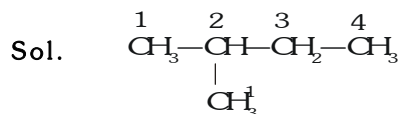
Ex.8 Complete oxidation of ethane yields -

(A) Ethanol   (B)   Ethanoic acid   (C)   Ethanal   (D) CO_2 and H_2O

                                                                                       Ans.(D)

Sol. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Ex. 9 In iso-pentane, the H atom that can be most easily substituted is on -

$$\overset{1}{C}H_3-\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_3$$
$$|$$
$$CH_3$$

    (A) C—1   (B) C—2   (C) C—3   (D) C—4   **Ans.(B)**

Sol. Ease of substitution of various types of H atoms is $3^0 > 2^0 > 1^0$.

Ex.10 8 c.c. of gaseous hydrocarbon requires 40 c.c. of O_2 for complete combustion. Identify hydrocarbon.

Sol. Volume of hydrocarbon = 8 c.c. ;   Volume of O_2 = 40 c.c.

Formula No. 1, $\dfrac{8}{40} = \dfrac{2}{3n+1}$ (For alkane)

$\dfrac{1}{5} = \dfrac{2}{3n+1}$ or   3n + 1 = 10   or   3n = 10 - 1 = 9   ,   n = 3

The value of n comes in whole number from 1st formula it means hydrocarbon is Alkane and it is of 3C atom.

∴   Hydrocarbon is C_3H_8 (Propane)

Ex.11 10 mL of a mixture of CH_4 and C_3H_8 requires 41 mL of oxygen for complete combustion. What is the volume of CH_4 and C_3H_8 in the mixture.

Sol. Suppose the volume of CH_4 in (CH_4 + C_3H_8) mix = x c.c.

= Volume of C_3H_8 will be = 10 – x c.c.

For CH_4 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
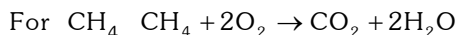
∵   1 Vol. of CH_4 requires 2 vol. of O_2 for complete combustion

∴   x c.c. of CH_4 , 2x c.c. of O_2

For C_3H_8 $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

∵   1 volume of C_3H_8 requires 5 ml of O_2 for complete combustion

∴   (10 – x) c.c. of C_3H_8 requires 5(10 – x) c.c. of O_2

Total Volume of O_2 = 2x + 5 (10 – x) it is equivalent to 41

(according to question)

∵   2x + 5 (10 – x) = 41

∴   x = 3 c.c.

Volume of CH_4 is 3 c.c. and volume of C_3H_8 is 7 c.c.

Ex.12 If 5 g C_2H_5I reacts with Na (Metallic) in presence of ether, and the yield is 60% then how many grams of n-butane will you get.

Sol. $2C_2H_5I + 2Na \rightarrow C_4H_{10} + 2NaI$

Molecular weight of $2C_2H_5I$ = 24 + 5 + 127 = 156

Molecular weight of C_4H_{10} = 48 + 10 = 58

Two molecule of C_2H_5I are taking part in above reaction.

∴   We get 58 g of C_4H_{10} from 2 x 156 g of C_2H_5I

∴   We get $\dfrac{58}{2 \times 156}$ g C_4H_{10} from 1 g of C_2H_5I

∴   We get $\dfrac{58 \times 5}{2 \times 156}$ g C_4H_{10} from 5 g of C_2H_5I

yield is 60%

So the quantity of C_4H_{10} will be $\dfrac{58 \times 5}{2 \times 156} \times \dfrac{60}{100}$ g = 0.55 g

Ex.13 The density of one hydrocarbon at N.T.P. is 1.964 g/litre. Identify the hydrocarbon.

Sol. Molecular weight of Hydrocarbon

= density of 1 lit. x 22.4 = 1.964 x 22.4 = 44

So Molecular weight of hydrocarbon = 44

So the hydrocarbon is C_3H_8 (Propane).