-: Hydrocarbon :-

Alkane (saturated hydrocarbon) :-

General formula C_nH_{2n+2} $n=1$ CH_4 (Marsh gas)

$n=2$ C_2H_6

$C-C = 1.54\,Å$ or 154 Pm.

$C=C = 1.34\,Å$ or 134 Pm.

$C\equiv C = 1.20\,Å$ or 120 Pm.

* SP^3 hybridisation.

Alkane also known as Paraffin

less ↙ ↘ effection (attraction)

Alkane show chain, position + conformational isomerism

General prepration of alkane :→

① From alkene and Alkyne (Hydrogenation or Reduction) :-

$$CH_2=CH_2+H_2 \xrightarrow{Pt/Pd} CH_3-CH_3$$

$$CH=CH+2H_2 \xrightarrow{Pt/Pd} CH_3-CH_3$$

* Sabatier - Senderens Rxn :→

$$CH_2=CH_2+H_2 \xrightarrow[200^\circ C-300^\circ C]{Ni} RCH_2-CH_2R$$

If above rxn is carried out in presence of Ni at 200°C - 300°C.

NOTE → by this method we cannot prepare methane

Form alkyl halide :-

a) Wurtz rxn →

$$R-X+2Na+X-R \xrightarrow[-2NaX]{dry\ ether} R-R \text{ alkane}$$

$$CH_3-Cl+2Na+Cl-CH_3 \xrightarrow{dry\ ether} CH_3-CH_3+2NaCl$$

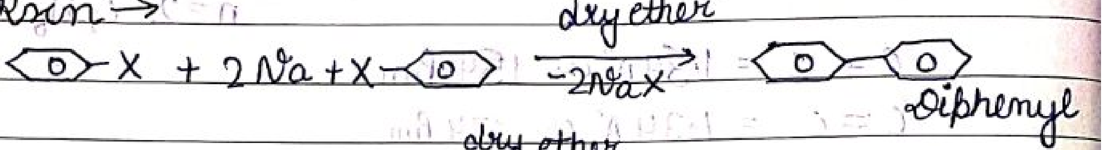
only symmetrical alkane should be prepared.

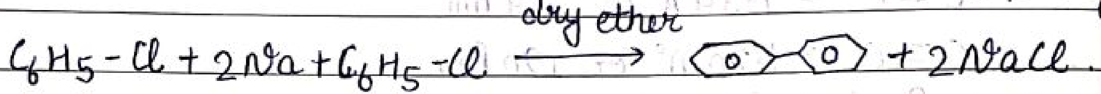
Free Radical Mechanism

Na is react vigrousoly with moisture so dry ether is used as catlyst which is inert i.e less reactive.

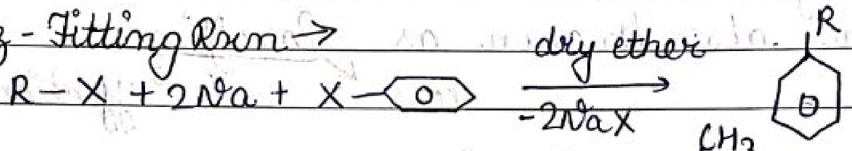
NOTE →

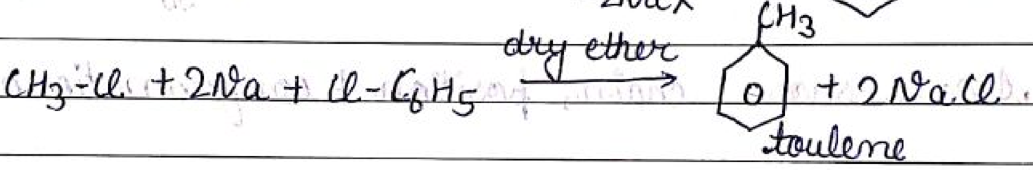
Fitting Rxn →





Wurtz - Fitting Rxn →





B) Corey House Synthesis :- (orgno metallic compound)

$2R-X + 2Li \longrightarrow R-Li + LiX$

$2R-Li + CuX \longrightarrow R_2CuLi + LiX$ → Gilman reagent.

(lithium dialkyl cuprate)

$R_2CuLi + R'-X \longrightarrow R-R' + RCu + LiX.$

All type of alkane can be prepared.

3) From Alcohol, aldehyde, Ketone + carboxylic acid :-

$R-OH + 2HI \xrightarrow{\text{Red P}} R-H + I_2 + H_2O.$

$R-CHO + 4HI \longrightarrow R-CH_3 + 2I_2 + H_2O.$

$R-CO-R + 4HI \longrightarrow R-CH_2-R + 2I_2 + H_2O.$

$R-COOH + 6HI \longrightarrow R-CH_3 + 3I_2 + H_2O.$

HI is act as Reducing agent.

Red phosphorous remove I_2 from rxn

$RCH_3 + I_2 \longrightarrow RCH_2I,$

NOTE →

Here Red phosphorous is used to remove Iodine

$2P + 3I_2 \longrightarrow 2PI_3$

If In above rxn, Iodine does not remove than it further react with alkane.

$$RCH_3 + I_2 \longrightarrow RCH_2I + HI$$

Imp. From carboxylic acid (Decarboxylation) :-

ⓐ From Soda Lime :-

$$RCOOH + Na \longrightarrow RCOONa \text{ [strong electrolyte]}$$

$$RCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + R-H$$

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_3-H + Na_2CO_3$$

Here, from parent acid, less carbon alkane should be form.

ⓑ Kolbe's electrolysis :-

$$2CH_3COONa + 2H_2O \longrightarrow CH_3-CH_3 + 2CO_2 + 2NaOH + H_2$$

at Anode $\quad CH_3COONa \longrightarrow CH_3COO^- + Na^+$

$$CH_3COO^- \longrightarrow CH_3CO\dot{O} + e^-$$

$$CH_3 \mid \underset{\underset{\dot{O}}{|}}{\dot{C}}=O \longrightarrow \dot{C}H_3 + CO_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

Free Radical Mechanism

at cathode :-

$$H_2O + e^- \longrightarrow \dot{H} + OH^-$$

$$\dot{H} + \dot{H} \longrightarrow H_2$$

$$Na^+ + OH^- \longrightarrow NaOH$$

$$\begin{matrix} CH_3COONa \\ + \\ CH_3CH_2COONa \end{matrix} + H_2O \xrightarrow{\text{electrolysis}} \left[\begin{matrix} CH_3-CH_3 \\ CH_3CH_2CH_2CH_3 \\ CH_3CH_2CH_3 \end{matrix}\right.$$

From Grignard Reagent $(R-Mg\cdot X)$ → alkyl magnesium halid

$$R-X + Mg \xrightarrow{\text{Dry ether}} \overset{+\delta}{R}-\overset{+\delta}{Mg}-\overset{-\delta}{X} \text{ (organo metallic salt)}$$

ionic

50% ionic

50% covalent.

$$\overset{-}{R}-\overset{+}{Mg}\overset{-}{X} + C_2H_5\overset{-}{O}H^{+} \longrightarrow \underset{\text{alkane}}{R-\overset{H}{\cancel{C_2H_5}}} + Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$

$$CH_3-MgBr + H-OH \longrightarrow CH_4 + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

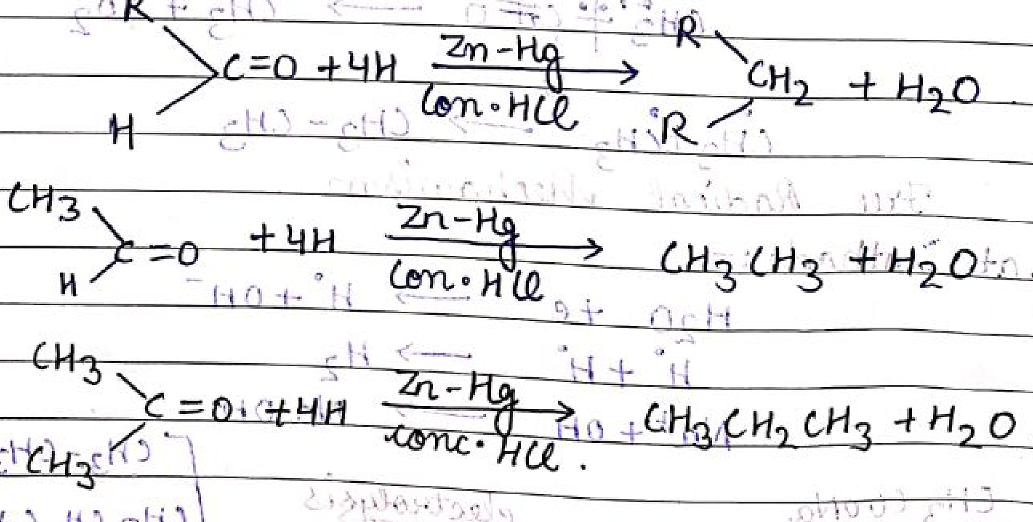
$$CH_3MgBr + CH\equiv CH \longrightarrow CH_4 + Mg\begin{smallmatrix}Br\\C\equiv CH\end{smallmatrix}$$

$$\overset{-}{R}-\overset{+}{Mg}\overset{-}{X} + NH_3 \longrightarrow R-H + Mg\begin{smallmatrix}X\\NH_2\end{smallmatrix}$$

$$CH_3MgBr + R-NH-H \longrightarrow R-H + Mg\begin{smallmatrix}Br\\NHR\end{smallmatrix}$$

Acidic Hydrogen and active Hydrogen gives an alkane, when it treated with grignard reagent.

Clemmensen Reduction :-

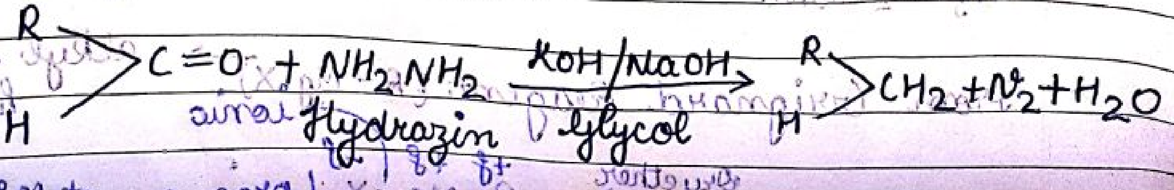


$$\begin{smallmatrix}R\\H\end{smallmatrix}C=O + 4H \xrightarrow[Con.HCl]{Zn-Hg} \begin{smallmatrix}R\\R\end{smallmatrix}CH_2 + H_2O$$

$$\begin{smallmatrix}CH_3\\H\end{smallmatrix}C=O + 4H \xrightarrow[Con.HCl]{Zn-Hg} CH_3CH_3 + H_2O$$

$$\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}C=O + 4H \xrightarrow[conc.HCl]{Zn-Hg} CH_3CH_2CH_3 + H_2O$$

Wolff Kishner Reduction :-

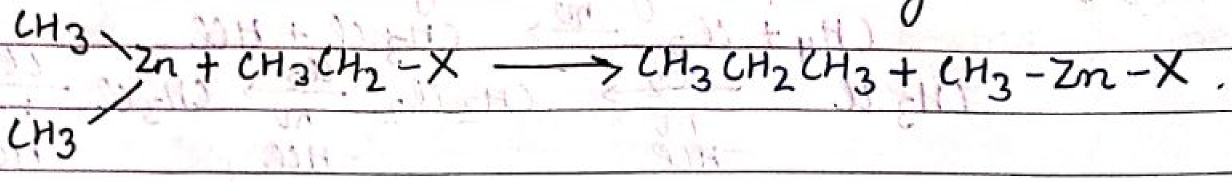


$$\begin{smallmatrix}R\\H\end{smallmatrix}C=O + \underset{\text{Hydrazin}}{NH_2NH_2} \xrightarrow[\text{glycol}]{KOH/NaOH} \begin{smallmatrix}R\\H\end{smallmatrix}CH_2 + N_2 + H_2O$$

From Franland reagent :- (orgnometallic compound)

(di alkyl Zinc) $R_2Zn + R'-X \longrightarrow R-R' + R-Zn-X$.

Alkyl Zinc Halide



$$CH_3 - Zn(CH_3) + CH_3CH_2-X \longrightarrow CH_3CH_2CH_3 + CH_3-Zn-X.$$

All type of Alkane should be prepared.

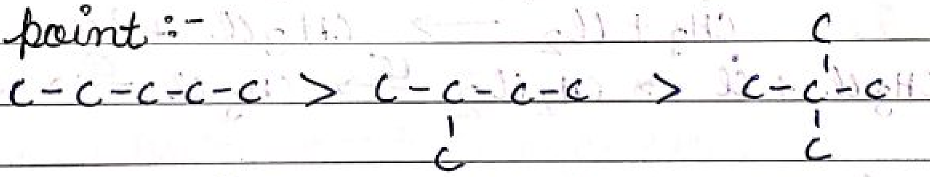
Physical Properties

i) Note soluble in water; soluble in organic solvent

→ $C_1 - C_4$ → gases. more than C_{17} → solid

$C_5 - C_{17}$ → liquid

* Boiling point :-



$$C-C-C-C-C > C-\underset{C}{\underset{|}{C}}-C-C > C-\overset{C}{\underset{C}{C}}-C$$

B.P ∝ surface area (in case of isomer)

$CH_4 < C_2H_6 < C_3H_8$

B.P. ∝ M. wt.

Melting point is depend on size & shape of molecule (compound)

but in case of different alkane M.P. ↑ order as

(5C) n pentane <<< n Hexane ≃ n heptane.

unsymmetrical symmetrical (6C) unsymmetrical (7C)

⇒ n-hexane melting point is slightly lower as compared to n-heptane due to stable symmetrical geometry of n-hexane.

* chemical properties :→

1) A) substitution / Halogenation of alkane :-

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow[h\nu\ -HCl]{Cl_2} CH_2Cl_2 \xrightarrow[h\nu\ -HCl]{Cl_2} CH_3Cl \xrightarrow[h\nu\ -HCl]{Cl_2} CCl_4$$

Mechanism →

Free radical mechanism

This reaction is completed in following 3 steps

a) chain Initiation

$$Cl_2 \text{ or } Cl-Cl \xrightarrow{h\nu} \dot{Cl} + \dot{Cl}$$

b) chain Propagation

$$\dot{Cl} + CH_4 \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{Cl}$$

$$CH_3Cl + \dot{Cl} \rightarrow CH_2Cl_2 \xrightarrow{\dot{Cl}} CH_3Cl \xrightarrow{\dot{Cl}} CCl_4$$

c) chain termination

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow CH_3CH_3$$

$$\dot{C}H_3 + \dot{Cl} \rightarrow CH_3Cl$$

$$\dot{Cl} + \dot{Cl} \rightarrow Cl_2$$

→ Reactivity order of different Halogen

$$F_2 > Cl_2 > Br_2 > I_2$$

$CH_4 + F_2 \xrightarrow{h\nu} CH_3F + HF$ X (Due to highly exothermic rxn)

☆ If we require florro alkane then it can be obtained by Halide exchange of chloro alkane or Bromo alkane /

$$CH_3Cl \xrightarrow{\text{Halide exchange}} CH_3F$$

(I) Swart Rxn (AgF, H_2F)

(II) Finkelstein Rxn

☆ Iodisation of alkane :→

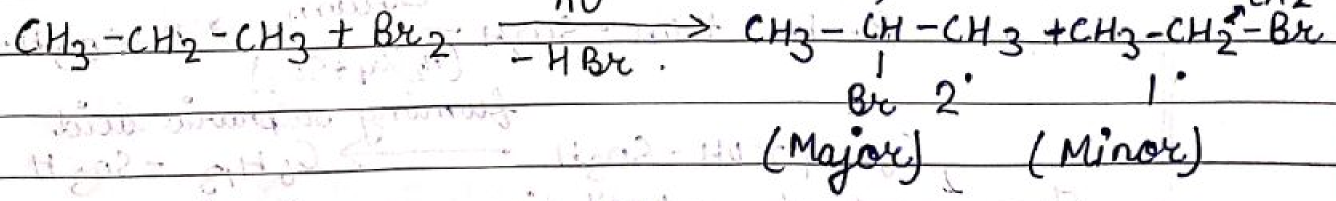
$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$ (highly reducing age)

due to formation of HI this rxn should be reversible. So, decomposition of HI use oxidising agent (HNO_3 or HIO_3) → iodic acid ,

$$HI + HIO_3 \longrightarrow I_2 + H_2O$$
$$HI + HNO_3 \longrightarrow I_2 + NO_2 + H_2O$$

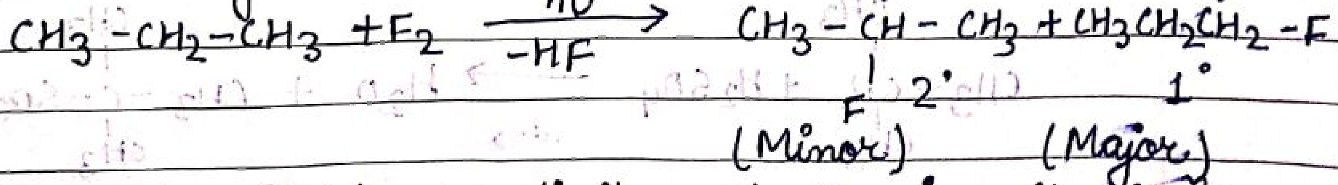
☆ stability order of different alkane in Halogenation :→

3° > 2° > 1°   1° > 2 > 3° (applicable only for in case of florisation)



$$CH_3-CH_2-CH_3 + Br_2 \xrightarrow[-HBr]{h\nu} \underset{\underset{(Major)}{2°}}{CH_3-\underset{Br}{\overset{\bullet}{C}H}-CH_3} + \underset{\underset{(Minor)}{1°}}{CH_3-\overset{CH_2}{CH_2}-Br}$$

In case of Florination :→



$$CH_3-CH_2-CH_3 + F_2 \xrightarrow[-HF]{h\nu} \underset{\underset{(Minor)}{2°}}{CH_3-\underset{F}{\overset{\bullet}{C}H}-CH_3} + \underset{\underset{(Major)}{1°}}{CH_3CH_2CH_2-F}$$

due to highly reactivity of fluorine it is less selective

☆ Nitration (vapour phase nitration) :→

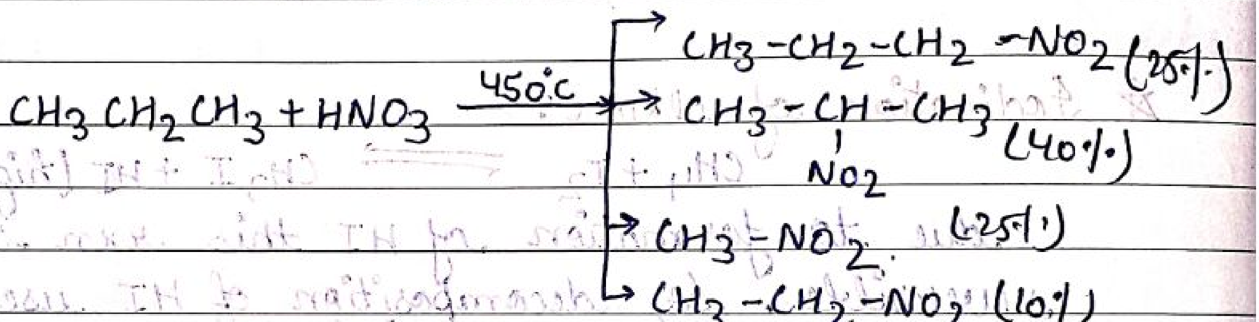
$$R-H + Conc.\ HNO_3 \xrightarrow{R.\ Temp} X$$

$$R-H + HO-NO_2 \xrightarrow[-H_2O]{450^\circ C-500^\circ C} R-NO_2$$

(nitro alkane)

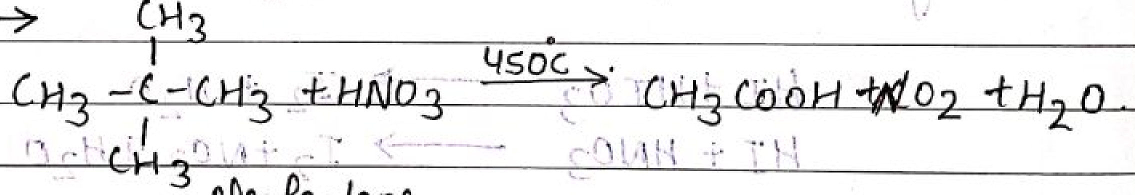
Free radical substitution Rxn (Mechanism)

$$CH_4 + HNO_3 \xrightarrow{450^\circ C} CH_3NO_2 + H_2O.$$



$$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450^\circ C} \begin{cases} CH_3-CH_2-CH_2-NO_2\ (25\%) \\ CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_3\ (40\%) \\ CH_3-NO_2\ (25\%) \\ CH_3-CH_2-NO_2\ (10\%) \end{cases}$$

NOTE :→



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 + HNO_3 \xrightarrow{450^\circ C} CH_3COOH + NO_2 + H_2O.$$

Neopentane.

Sulphonation :→

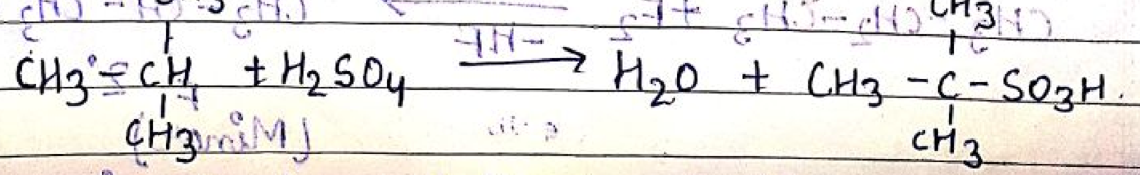
Higher alkane (more than 6 carbon) give sulphonation.

$$R-H + OH-SO_3H \xrightarrow[(H_2SO_4+SO_3)]{Oleum} R-SO_3H + H_2O.$$

$$C_6H_{14} + OH-SO_3H \xrightarrow{\text{fuming sulphuric acid}} C_6H_{13}-SO_3H.$$

Free radical substitution mechanism

$3^\circ > 2^\circ > 1^\circ$



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{CH}}}} + H_2SO_4 \longrightarrow H_2O + CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-SO_3H.$$

* Pyrolysis :→

$CH_3-CH_3 \xrightarrow{600^\circ C} CH_2=CH_2+H_2$

$CH_3-CH_2-CH_3 \xrightarrow{600^\circ C} CH_4+CH_2=CH_2$

$\qquad \rightarrow CH_2=CH-CH_3+H_2$

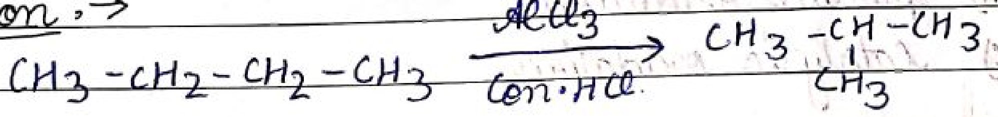
$CH_3-CH_2-CH_2-CH_3 \xrightarrow{\Delta} CH_4+CH_2=CH-CH_3$

$\qquad \rightarrow CH_3-CH_3+CH_2=CH_2$

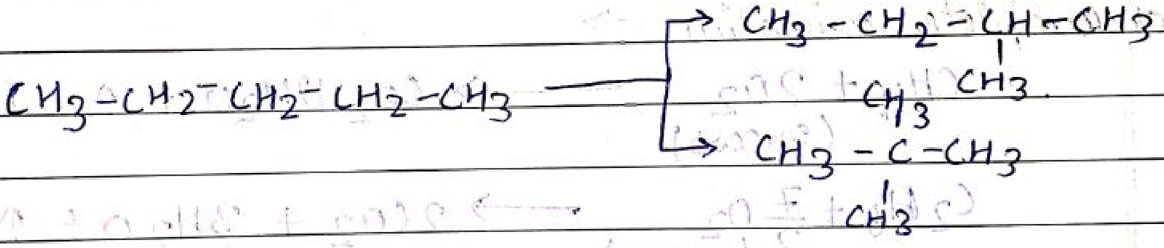
$\qquad \rightarrow CH_3-CH_2-CH=CH_2+H_2$

$\qquad \rightarrow CH_3-CH=CH-CH_3+H_2$

* Isomerisation :→



$CH_3-CH_2-CH_2-CH_3 \xrightarrow[Con.\,HCl]{AlCl_3} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$

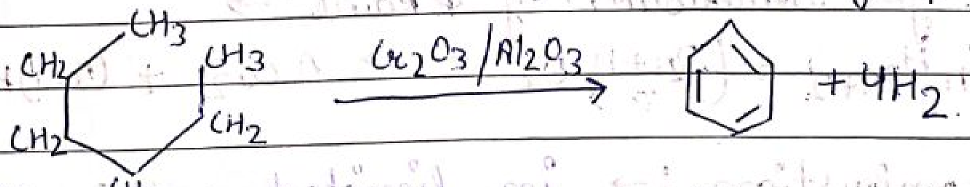


$CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

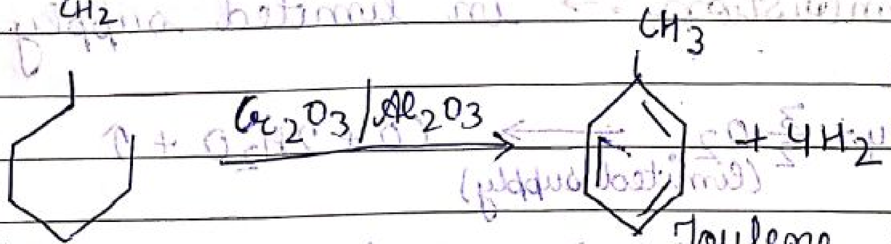
$\qquad \rightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

* Aromatization :→

$C_6H_{14} \xrightarrow[\text{chromium (III) oxide } 600K, \text{ high pressure}]{Cr_2O_3/Al_2O_3} C_6H_6+4H_2$

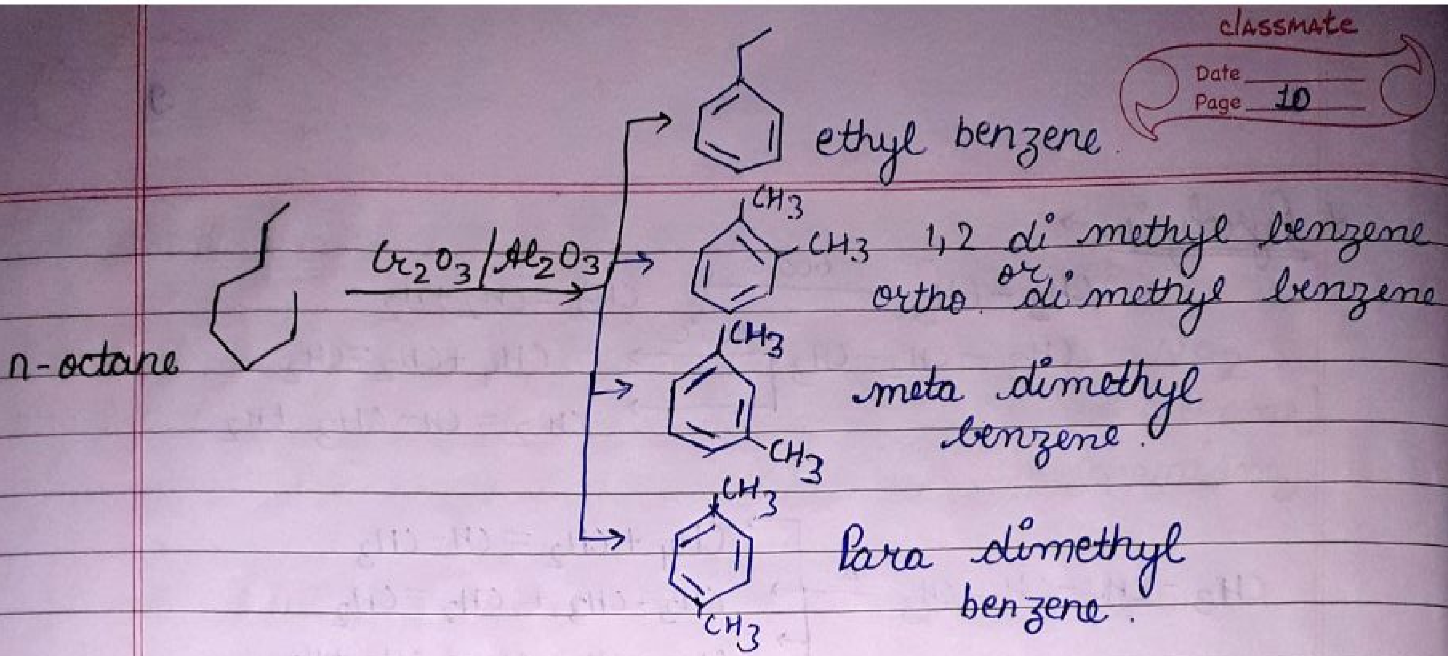


n-hexane



Toulene

n-heptane



* Oxidation of Alkane :→

a) complete oxidation
b) partial oxidation
c) catalytic oxidation

a) complete oxidation :→

$$CH_4 + \underset{(excess)}{2O_2} \longrightarrow CO_2 + 2H_2O + \uparrow$$

$$C_2H_6 + \underset{(excess)}{\tfrac{7}{2}O_2} \longrightarrow 2CO_2 + 3H_2O + \uparrow$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + \uparrow$$

General formula for combustion of Alkane :→

$$C_nH_{2n+2} + \left(\frac{2n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

b) Partial combustion :→ in limited supply of oxygen.

$$CH_4 + \underset{(limited\ supply)}{\tfrac{3}{2}O_2} \longrightarrow CO + 2H_2O + \uparrow$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O + \uparrow$$

$$C_2H_6 + \underset{(limited)}{\tfrac{5}{2}O_2} \longrightarrow 2CO + 3H_2O + \uparrow$$

$$\Rightarrow \underset{(very\ low\ supply\ of\ air)}{CH_4 + O_2} \longrightarrow \underset{black\ carbon}{C} + 2H_2O + \uparrow$$

$$C_2H_6 + \frac{3}{2}O_2 \xrightarrow{\text{(low supply)}} 2C + 3H_2O + \text{Energy}$$

In control oxidation in presence of suitable catalyst we obtained alcohol or Aldehyde or Ketone or Carboxylic acid.

$$CH_4 + O_2 \xrightarrow{Cu/Cu\ tube} CH_3OH \text{ (Alcohol)}$$

Alkane → Alcohol → Aldehyde / Ketone → carboxylic acid

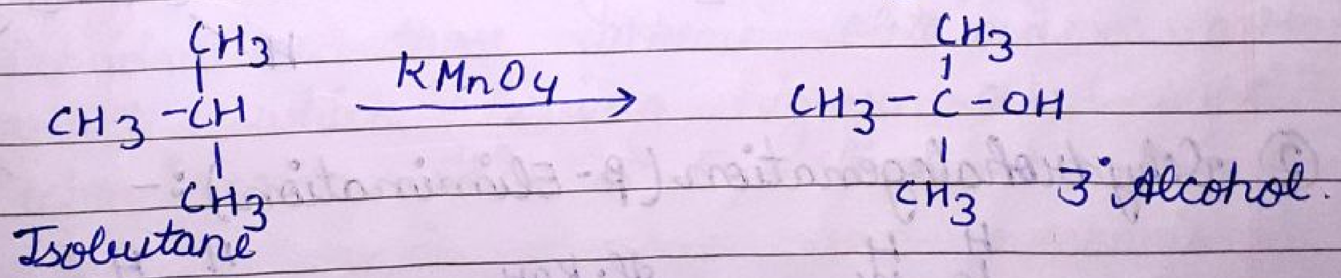
$$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O \text{ (aldehyde)}$$

$$CH_4 + \frac{3}{2}O_2 \xrightarrow[Ag_2O]{(CH_3COO)_2Mn \text{ or}} HCOOH + H_2O \text{ (carboxylic acid)}$$

$$C_2H_6 + O_2 \xrightarrow{Cu/cu\ tube} C_2H_5OH +$$

$$C_2H_6 + O_2 \xrightarrow{Mo_2O_3} CH_3CHO + H_2O$$

$$C_2H_6 + O_2 \xrightarrow[Ag_2O]{(CH_3COO)_2Mn} \cancel{CH_3-\underset{CH_3}{\overset{CH_3}{CH}}}\ CH_3COOH + H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow{KMnO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

Isobutane

3° Alcohol.