Alkanes

→ General name – paraffines

Formula – C_nH_{2n+2}, sp^3-C, tetrahedral (109°28')

C–C bond length – 1.54 Å (or) 154 pm   C–C bond energy – 83 kcal/mol

C–H bond length – 1.09 Å (or) 109 pm   C–H bond energy 99 kcal/mol

⇒ **Preparation:**

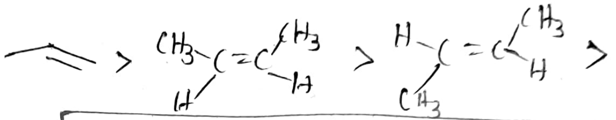
① Catalytic hydrogenation – (or) Sabatier-Senderen's rxn –

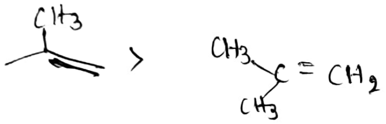
$$R\text{–}CH{=}CH\text{–}R' \xrightarrow[Pt/Pd/Ni]{H_2\ 25^\circ C} R\text{–}CH_2\text{–}CH_2\text{–}R'$$

(syn addition)

$$R\text{–}C{\equiv}C\text{–}R \xrightarrow[Pt/Pd/Ni]{H_2\ 25^\circ C} R\text{–}CH_2\text{–}CH_2\text{–}R'$$

Reactivity order –



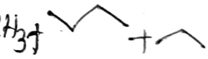


R–X, R–OH, R–CHO, R–COOH, R–CO–R, R–C(=O)–OR, R–C(=O)–Cl
↓ HI/Red P
Alkane

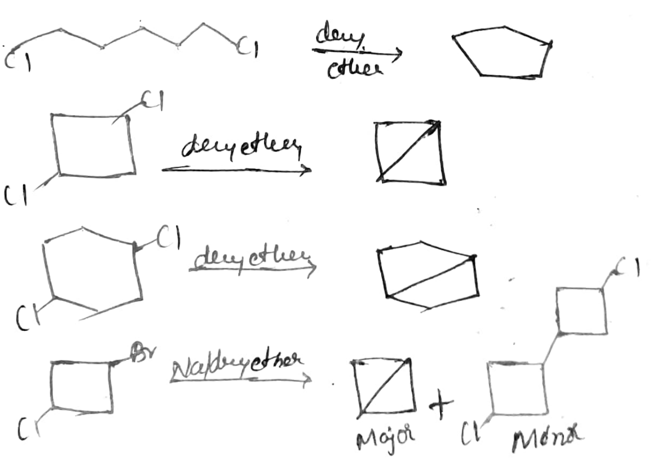
② **Wurtz reaction:**

(disproportionation reaction mech.)

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

Crossed – $CH_3I + 2Na + CH_3\text{–}CH_2\text{–}I \xrightarrow[ether]{dry} CH_3\text{–}CH_3 +$ 

Intramolecular –



Reactivity – R–I > R–Br > R–Cl > R–F

③ **Frankland reaction:**

$$2R\text{–}X + Zn \xrightarrow{\Delta} R\text{–}R + ZnX_2$$

even no. of alkanes

④ Decarboxylation: Mix. of NaOH & CaO used for decarboxylating agent

$$R-\overset{O}{\overset{\|}{C}}-ONa + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

$C^{\oplus}$ is intermediate. stability of $C^{\oplus}$ α rate of rxn

Kolbe: $R-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow{\text{electrolysis}} R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Na^{+}$ (anode)

Dumas method: $R-COONa + NaOH \xrightarrow[CaO]{\text{heat}} R-H + Na_2CO_3$

NaOH : CaO = 3:1

$$2\,R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na + H_2O \xrightarrow{\text{electrolysis}} R-R + 2CO_2 + 2\,NaOH + H_2$$

⑤ Corey house synthesis:

R_2CuLi – Gilman's reagent

$$R_2CuLi + R-X \longrightarrow 2R-R' + CuX + LiX$$

for odd no of alkanes

⑥ From alkyl halide:

$$R-X + H_2 \xrightarrow[Pt/Pd]{Zn/HCl(\text{or})} RH + HX$$

⑦ From RMgX:

$$RMgX + HOH \longrightarrow RH + MgX(OH)$$
$$R-X' + RMgX \longrightarrow R-R + MgXX'$$

$$\Rightarrow 2R-COOH + 6HI \longrightarrow R-R + 2H_2O + 3I_2$$

$$R-OH\,/\,R-CHO\,/\,R_2CO\,/\,R(OCl)\,/\,R-CONH_2 + HI \xrightarrow[\Delta(150-200^{\circ}C)]{Red\ P} RH + H_2O + I_2$$

⑧ Clemmenson reduction

$$R-CHO\,/\,R-COR + 4H \xrightarrow[HCl]{Zn-Hg} R-R + H_2O$$

⑨ Wolffkishner reduction

$$R_2CO \xrightarrow[-H_2O]{NH_2-NH_2} R_2C=NNH_2 \xrightarrow[180^{\circ}C,\ -N_2]{C_2H_5ONa} R-CH_2-R$$

⇒ Physical Properties

(i) Physical state – alkanes are colourless, odourless & tasteless.

Alkanes	State
C_1-C_4	Gaseous
C_5-C_{17}	liquid except (except neopentane – g)
$C_{18} < C_n$	solids (waxes)

(ii) Alkanes are lighter than water.

(iii) Insoluble in water, soluble in organic solvents.

Solubility $\propto \frac{1}{\text{molecular mass}}$

(iv) B.P's & M.P's $\propto$ Molecular $\propto \frac{1}{\text{No. of branches}}$

M.P of even alkanes > M.P of odd no of C alkanes due to symmetry.

⇒ Chemical Properties:

(i) Sub. rxn's ⇒ $R-H + X-X \longrightarrow R-X + HX$

$F_2 > Cl_2 > Br_2 > I_2$, Cl_2, Br_2 in dark

$CH_4 + 2X_2 \xrightarrow[-HCl]{UV} CH_2Cl_2 \xrightarrow[-HCl]{UV} CHCl_3 \xrightarrow[Cl_2]{-HCl} CCl_4$

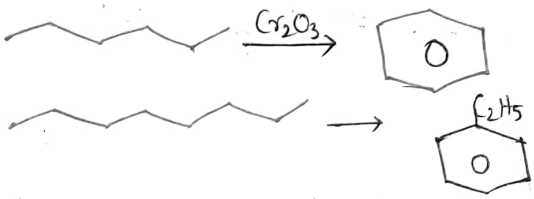
(ii) Free radical mech. ⇒ $R-H + HONO_2 \xrightarrow{\text{high temp.}} R-NO_2 + H_2O$

(Con. H_2SO_4 + Con. HNO_3) at 250°C

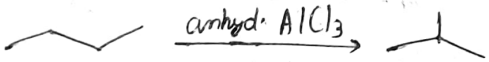
$R-H + H_2SO_4 \xrightarrow[\Delta]{SO_3} R-SO_3H + H_2O$

(iii) Aromatisation: presence of Cr_2O_3 (or) Pt/600°C (or) V_2O_5 (or) Mo_2O_3

Min. no of C = 6



(iv) Isomerisation:



Min. no of C = 4

(v) Pyrolysis (or) cracking: $CH_3-CH_3 \xrightarrow[Al_2O_3]{700K} CH_2=CH_2 + H_2\uparrow$

C–C bond cleavage low energy than C–H bond.

(vi) Oxidation: $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

Controlled $CH_4 + O_2 \xrightarrow{Cu\ tube} CH_3OH$

$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2$

$R-CH_3 + O_2 \xrightarrow[Al_2O_3]{(CH_3COO)_2Mn} R-COOH$

Degree of unsaturation (D.U) $= \frac{2(C+1) - (H+X-N)}{2}$

N - no of nitrogen atoms