B.Sc. I Yr

Unit IV

Hydrocarbons

- Saturated
  - Alkanes
  - Cycloalkanes
- Unsaturated
  - Alkenes
  - Dienes
  - Alkynes

Saturated = Single C–C bond / Paraffin / less reactive

Unsaturated = C=C, C≡C

Alkanes C_nH_{2n+2}

n = no. of carbon atoms

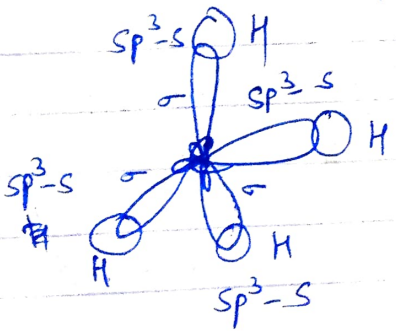
sp^3 hybridized

C–C Bond length 1.54 A°

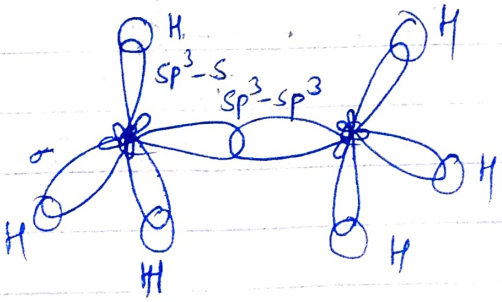
C–H " " 1.14 A°

C–C bond energy = 80 Kcal/mol

Shape = Tetrahedral



CH_4

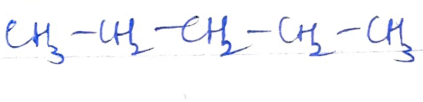


Suffix = ane

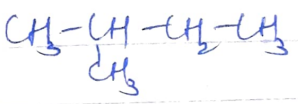
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
	is obutane

C_5H_{12}	Pentane, isopentane neopentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane
C_9H_{20}	Nonane
$C_{10}H_{22}$	Decane
$C_{11}H_{24}$	undecane
$C_{12}H_{26}$	dodecane

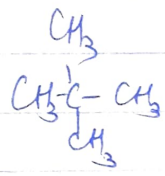
$C_{20}H_{42}$	icosane
$C_{30}H_{62}$	~~Triocto~~ Triacontane



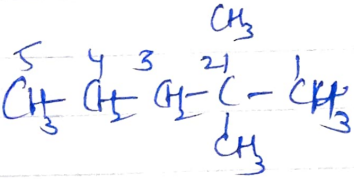
Pentane



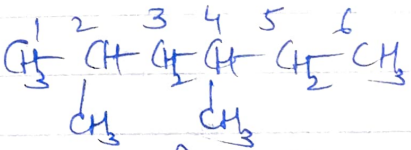
isopentane



Neopentane



2,2-Dimethyl pentane



2,4-Dimethyl hexane.

Sources:-

→ Crude petroleum, natural gases

→ marshy areas

→ coal mines in form of explosive gases

Methods of preparation :-

Decarboxylation (Lab. Method)

1) $RCOONa + NaOH(CaO) \rightarrow RH + Na_2CO_3 + CaO$

Sodium salt of fatty acid

$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$

2) Lab. Method :-

$R-X + 2H \xrightarrow{Zn+HCl} RH + HX$

$CH_3I + 2H \xrightarrow{Zn-Cu\ couple} CH_4 + HI$

$C_2H_5-Br + 2H \longrightarrow C_2H_6 + HBr$

3) Wurtz synthesis :-

$RI + 2Na + IR \xrightarrow{dry\ ether} R-R + 2NaI$

$CH_3I + 2Na + ICH_3 \longrightarrow CH_3-CH_3 + 2NaI$

→ Method used to obtain higher alkanes

4) Kolbe Synthesis :-

$2RCOONa + 2H_2O \xrightarrow{electrolysis} R-R + 2CO_2 + 2NaOH + H_2$

Mechanism :-

$2\,CH_3COONa \rightleftharpoons 2\,CH_3COO^- + 2\,Na^+$

$2\,CH_3COO^- \rightarrow 2\,CH_3COO^{\cdot} + 2e^-$

$2\,CH_3COO^{\cdot} \rightarrow CH_3-CH_3 + 2\,CO_2$ } at anode

$2\,Na^+ + 2e^- \rightarrow 2\,Na$

$2\,Na + 2\,H_2O \rightarrow 2\,NaOH + H_2$] Cathode

5. From Grignard Reagent :-

$$Mg\begin{matrix}-C_2H_5\\-I\end{matrix} + H-OH \longrightarrow C_2H_6 + Mg\begin{matrix}-OH\\-I\end{matrix}$$

$$Mg\begin{matrix}-CH_3\\-I\end{matrix} + H-OH \longrightarrow CH_4 + Mg\begin{matrix}-OEt\\-Br\end{matrix}$$

6. Reduction of aldehydes, ketone, alcohol or fats :-

$$CH_3OH + 2HI \xrightarrow[150^\circ C]{Red\,P} CH_4 + H_2O + I_2$$

$$CH_3CHO + 4HI \xrightarrow{Red\,P,\,150^\circ C} CH_3-CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \longrightarrow CH_3-CH_2-CH_3 + H_2O + 2I_2$$

$$CH_3COOH + 6HI \xrightarrow[150^\circ C]{Red\,P} CH_3-CH_3 + 2H_2O + 3I_2$$

$CH_3CH_2CHO + 2H_2 \xrightarrow{Zn\text{-}Hg/HCl} CH_3-CH_2-CH_3 + H_2O$

$CH_3CH_2COCH_3 + 2H_2 \longrightarrow CH_3-CH_2-CH_2-CH_3 + H_2O$

7. By Frankland Method :-

$RX + Zn + XR \rightarrow R-R + ZnX_2$

$CH_3I + Zn + ICH_3 \rightarrow CH_3-CH_3 + ZnI_2$

8. Sabetiar & Senderson's Reagent :- (Raney Ni)

$CH_2=CH_2 + H_2 \xrightarrow[200^\circ C.]{Ni} CH_3-CH_3$

$CH\equiv CH + 2H_2 \xrightarrow{Ni} CH_3-CH_3$

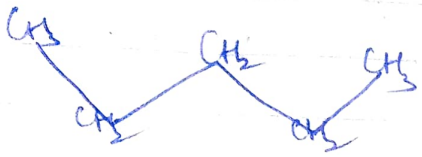
Physical Properties :-

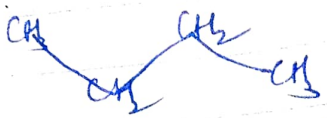
→ First four members → colourless, odourless gases
Higher member (upto C_{15}) liquids.
Remaining " (solid colourless)

→ insoluble in H_2O but soluble in organic solvents (alcohols, ether, benzene).
As mol. wt ↑se, Solubility ↓ses.

→ Specific density → ↑ as mol. wt ↑ses.
& approx stable at 0.78.

→ M.P. & B.P. →
M.P. of even carbon no. high than M.P. of odd carbon no.





In case of even no (2+n), both ends of chain are opp. to each other, and they pack in crystal closely & Tse intermolecular forces

In case of odd, both ends same side, due to which distance Tse b'n atoms in crystals. Thus attraction forces reduce & M.P. less.

Unbranched alkanes → M.P. & B.P. high
branched " → less because surface area ↓ses due to branching, thus mutual attraction forces ↓ses, thus less M.P. & B.P.

Chemical Reactivity :-

→ Alkanes, highly stable compounds.
→ No effects of acids, bases & oxidants in normal state.
→ At high temp, react ē O_2, H_2 & Br_2 easily
→ Reason for less chemical reactivity →
B.E of C-C & C-H bond 83 & 99 KCal/mol

Under special conditions, they give following reactions:

1. Substitution: Halogenation, Nitration, Chlorosulfonation etc.

a) Halogenation:

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

$$F_2 > Cl_2 > Br_2 > I_2$$

$3^\circ > 2^\circ > 1^\circ > CH_3-H$ (Order of sub. of H atom from alkanes)

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3 \xrightarrow[300^\circ C]{Cl_2} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_2Cl + CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_3$$

Minor (1°) Major (3°)

Bromination takes place similarly.

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

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

{ HI is a reducing agent that again converts RX into alkane }

∴ Rx ~~was~~ is done in presence of oxidizing agents like HIO_3, HNO_3, HgO etc which (oxidizes) ~~converts~~ HI.

Fluorination: (explosive)

$$2C_2H_5Br/I + HgF_2 \xrightarrow{} 2C_2H_5F + HgBr_2$$

HgF

B) Nitration :-

$CH_3-CH_3 + HNO_3 \xrightarrow{450^\circ C} CH_3-CH_2NO_2 + H_2O$

$CH_3-CH_2CH_2CH_3 \xrightarrow[HNO_3]{450^\circ C}$

- Direct → $CH_3-CH_2-CH_2-CH_2NO_2$ (1-Nitro) + $CH_3-\underset{NO_2}{CH}-CH_2-CH_3$ (2-Nitro)
- fission → $CH_3-CH_2CH_2NO_2 + C_2H_5NO_2 + CH_3NO_2$

C) Sulphonation :-

$R-H + HOSO_3H \longrightarrow R-SO_3H + H_2O$

$(CH_3)_3CH + HO-SO_3H \rightarrow (CH_3)_3C-SO_3H + H_2O$

D) Chloro - sulphonation :-

$R-H + HOSO_2Cl \xrightarrow[\text{Pyridine}]{\text{light}} R-SO_2Cl + H_2O$

Chloro sulfonic acid — alkyl sulfonyl chloride

Free radical rxs. while in benzene (Electrophilic Sub. rxn)

2. Pyrolysis, Thermal Decomposition / Cracking :-

→ Complex hydrocarbon convert to simple molecule by the effect of heat → Cracking

$C_8H_{18} \rightarrow C_4H_{10} + C_4H_8$

$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$

$C_8H_{18} \rightarrow C_4H_{10} + CH_4 + C_3H_4 + C$

$C_8H_{18} \rightarrow C_8H_{16} + H_2$

3 Combustion :-

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\ K\,Cal$$

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O + 736.8\ K\,Cal.$$

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow n\,CO_2 + (n+1)\,H_2O$$

$$\text{Value of } n = \frac{\text{Volume of alkane}}{\text{Vol. of } O_2} = \frac{1}{\frac{3n+1}{2}} = \frac{2}{3n+1}$$

Free Radical Mechanism :-

3 Steps :-

1) Chain initiation शुरुआत
2) Chain Propogation (संचरण)
3) Chain ~~de~~ Termination (समापन)

1) $X_2 \xrightarrow[\text{UV light}]{\text{high temp}} 2X^{\cdot}$ $\quad (X = Cl, Br, I, F)$

$F > Cl > Br > I$

2) $X^{\cdot} + R-H \rightarrow R^{\cdot} + X-H$

$R^{\cdot} + X-X \rightarrow R-X + X^{\cdot}$

3) $X^{\cdot} + \dot{X} \rightarrow X_2$

$R^{\cdot} + X^{\cdot} \rightarrow R-X$

$R^{\cdot} + R^{\cdot} \rightarrow R-R$