Alkanes

Chemical Properties

Halogenation of Alkane

(Part 1)

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Alkane Chemical Reaction

Alkanes:-

- Saturated Hydrocarbon
- More Stable than Alkene and alkyne
- Low Chemical Reactivity
  - C-C, σ Bond is stronger then C=C/C≡C π bonds
  - All bond are Non-Polar

- **Main Two reaction occurs in Alkanes**
  - Substitution Reaction- Halogenation, Nitration, Sulfonation
  - Oxidation Reaction

Alkane Chemical Reaction

Substitution Reaction in Alkane

Electrophilic
Nucleophilic

- ❖ Free Radical Substitution Reaction

1. Halogenation Reaction – (X)

$$R\text{-}CH_3 + X_2 \xrightarrow[\Delta]{h\nu} R\text{-}CH_2\text{-}X + HX$$

, alkyl halide / halo-alkane

2. Nitration – ($-NO_2$)

$$R\text{-}CH_3 \xrightarrow[\Delta]{HNO_2 / HNO_3} R\text{-}CH_2\text{-}NO_2$$

nitroalkane

3. Sulfonation – ($-SO_3H$)

$$R\text{-}CH_3 \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} R\text{-}CH_2\text{-}SO_3H$$

, alkane Sulfonic acid

Alkane Chemical Reaction

Halogenation Reaction

$$CH_4 + X_2 \xrightarrow[\rightarrow \text{Heat} \rightarrow \text{Sunlight} \rightarrow \text{peroxide}]{h\nu} CH_3\text{-}X \xrightarrow[HX]{h\nu\ X_2} CH_2\text{-}X_2 \xrightarrow[HX]{h\nu\ X_2} CH\text{-}X_3 \xrightarrow[HX]{h\nu\ X_2} CX_4$$

X : Cl, I, Br, F

$$CH_4 + X_2 \xrightarrow{h\nu} CH_3\text{-}X \text{ Major}$$

excess

$$CH_4 + X_2 \xrightarrow{h\nu} \begin{matrix} CH_3\text{-}X \\ CH_2\text{-}X_2 \\ CH\text{-}X_3 \\ C\text{-}X_4 \end{matrix}$$

excess

all are major

Alkane Chemical Reaction

Chlorination Reaction on Methane

$CH_4 \xrightarrow{Cl_2, h\nu} CH_3Cl \xrightarrow{Cl_2, h\nu} CH_2Cl_2 \xrightarrow{Cl_2, h\nu} CHCl_3 \xrightarrow{Cl_2, h\nu} CCl_4$

methane → Chloro methane (+HCl) → dichloro methane (+HCl) → trichloro methane (+HCl) → tetrachloro methane

"Chloroform" — "Carbon tetrachloride"

Reaction Mechanism → Free Radical Substitution

$CH_4 + Cl_2 \xrightarrow{\Delta} CH_3Cl + HCl$

Step 1.) Chain Initiation → Free Radical formation

Endothermic

$Cl-Cl \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$ → highly Reactive

↓

Homolytic fission

Alkane Chemical Reaction

Chlorination Reaction on Methane

✓ # Exothermic → F_2, Cl_2, Br_2
Endothermic → I_2

Step 2) Chain propogation → production of more Free Radical
→ Exothermic

$H_3C-H + Cl^{\bullet} \longrightarrow CH_3^{\bullet}$ methyl radical → highly Reactive

↓

H–Cl → Cl make strong bond with H so make HCl

$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3-Cl + Cl^{\bullet}$

Alkane Chemical Reaction

Chlorination Reaction on Methane

step 3) Chain termination → Two free Radical – $Cl^{\bullet}$ & $CH_3^{\bullet}$

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3-CH_3$ ethane

$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3-Cl$

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$

methyl Chloride

$+ CH_3-CH_3$

$+ Cl_2$

Alkane Chemical Reaction

Chlorination Reaction on Methane

$CH_3Cl + Cl_2 \xrightarrow{\Delta} CH_2Cl_2 + HCl$

React^n Mech. →

Step 1 → $Cl_2 \longrightarrow Cl^{\bullet} + Cl^{\bullet}$

Step 2 → $H-\underset{H}{\overset{H}{C}}-Cl + Cl^{\bullet} \longrightarrow \dot{C}H_2Cl + HCl$

$\dot{C}H_2Cl + Cl-Cl \longrightarrow CH_2Cl_2 + Cl^{\bullet}$

step 3) $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

$\dot{C}H_2Cl + \dot{C}H_2Cl \longrightarrow ClH_2C-CH_2Cl$

$\dot{C}H_2Cl + Cl^{\bullet} \longrightarrow CH_2Cl_2$

Alkane Chemical Reaction

Chlorination Reaction on Methane

Same in further Reacts

↳ $CH_2Cl_2 \xrightarrow[\Delta]{Cl_2} CHCl_3 + HCl$
$+ Cl_2 + CHCl_2 - CHCl_2$

↳ $CHCl_3 \xrightarrow[\Delta]{Cl_2} CCl_4 + HCl$
$+ Cl_2 + CCl_3 - CCl_3$

Reactivity of halogen

$F_2 > Cl_2 > Br_2 > I_2$

(A) $CH_4 + Cl_2 \longrightarrow CH_3-Cl$

(B) $CH_4 + F_2 \longrightarrow CH_3-F$

B > A

Alkane Chemical Reaction

Bromination Reaction on Methane- Similar as Chlorination

Fluorination Reaction on Methane

$CH_4 + F_2 \xrightarrow{h\nu} CH_3F + HF$

step1 - endothermic
step 2 - "highly Exothermic"
→ produce Bomb like energy

- So cant prepare in laboratory
- Mainly CH_3F is prepared by "Halide Exchange method"

CH_3Cl or CH_3Br or CH_3I + AgF or HgF_2 or SbF_3 ⟶ "CH_3F" + $AgCl$

"Swart's Reaction"

Alkane Chemical Reaction

Iodination Reaction on Methane

$CH_4 + I_2 \xrightleftharpoons{h\nu} CH_3I + HI$

↳ step 1 & step 2 – both Endothermic

Problem to product of CH_3I by this method –

↳ Required continous Energy

↳ Reversible Reaction may occurs due to HI (strong Reducing Agent)

this can be solved by following –

$CH_4 + I_2 \xrightarrow{h\nu} CH_3I + HI$

$HI \xrightarrow{HNO_3 \text{ or } HIO_3} I_2 + H_2O$

Alkane Chemical Reaction

Chlorination Reaction on Ethane

$C_2H_6 + Cl_2 \xrightarrow[\Delta]{} C_2H_5Cl \xrightarrow{} C_2H_4Cl_2 \xrightarrow{} C_2H_3Cl_3 \longrightarrow C_2H_2Cl_4$

$C_2H_6 \xrightarrow{} HCl$

$C_2H_5Cl \xrightarrow{} HCl$

$C_2H_4Cl_2 \xrightarrow{} HCl$

$C_2H_2Cl_4 \xrightarrow{} HCl$, C_2HCl_5

$C_2HCl_5 \xrightarrow{} HCl$, C_2Cl_6

Alkanes

Chemical Properties

Halogenation of Alkane

(Part 2)

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Alkane Chemical Reaction

Reaction mechanism

$CH_4 + Cl_2 \xrightarrow[\Delta]{h\nu} CH_3Cl + HCl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3 \longrightarrow CCl_4$

1) $Cl-Cl \longrightarrow Cl^{\cdot} + Cl^{\cdot}$

2) $H-CH_3 + Cl^{\cdot} \longrightarrow H-Cl + \dot{C}H_3$

$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3Cl + Cl^{\cdot}$

3) terminate

$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$

$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3-CH_3$ ethane

$CH_3^{\cdot} + Cl^{\cdot} \longrightarrow CH_3Cl$

Alkane Chemical Reaction

Chlorination Reaction on Propane

Important for MCQs 3° > 2° > 1° > methyl

$CH_3-CH_2-CH_3 \xrightarrow[\Delta]{Cl_2}$ $CH_3-\underset{Cl}{CH}-CH_3$ – 56%

$CH_3-CH_2-CH_2-Cl$ → 44%

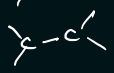
Mechanism →

step 1) $Cl_2 \longrightarrow Cl^{\cdot} + Cl^{\cdot}$

step 2) $CH_3-CH_2-CH_3 \xrightarrow{Cl^{\cdot}}$ $CH_3-CH_2-\dot{C}H_2 \xrightarrow{Cl_2} CH_3-CH_2-CH_2-Cl$

$CH_3-\dot{C}H-CH_3 \xrightarrow{Cl_2} CH_3-\underset{Cl}{CH}-CH_3$

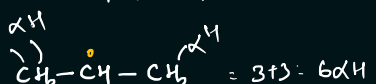
step 3 - terminate Cl^2, Hexane



Alkane Chemical Reaction

Chlorination Reaction on Propane

Stability of Alkyl Free Radical → 3° > 2° > 1°



= 3+3 = 6αH

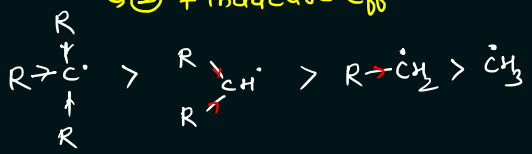
$CH_3-CH_2-\dot{C}H_2$ (1°) = 2αH

↳ ① Hyper Conjugation

↳ no. of α Hydrogen ∝ Stability

↳ αH_2 → Hydrogen at adjuscent C-atom

↳ ② + Inductive Effect • Free Radical – e^- deficient



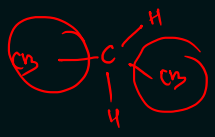
Alkane Chemical Reaction

Fluorination Reaction on Propane

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

$CH_3-CH_2-CH_3 + F_2 \xrightarrow{\Delta} CH_3-CH_2-CH_2-F + CH_3-CH(F)-CH_3$

(1° 2° 1°) — Major — minor



Bromination & Iodination Reaction on Propane

$CH_3-CH_2-CH_3 \xrightarrow{Br_2} CH_3-CH(Br)-CH_3 + CH_3-CH_2-CH_2Br$

major — minor

$CH_3-CH_2-CH_3 \xrightarrow{I_2} CH_3-CH(I)-CH_3 + CH_3-CH_2-CH_2I$

Alkane Chemical Reaction

$F_2 > Cl_2 > Br_2 > I_2$

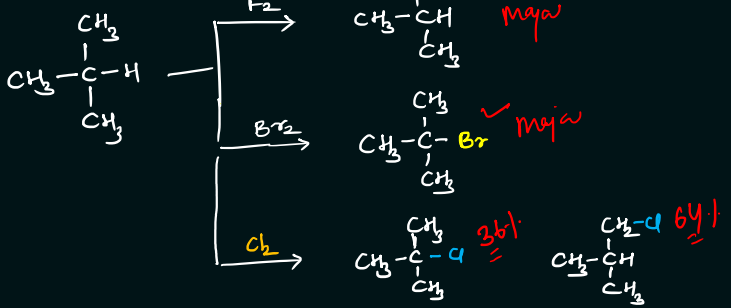
↳ Least Selective & more Reactive

↳ Attack- less steric hinderance

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

↳ Selective and Less Reactive

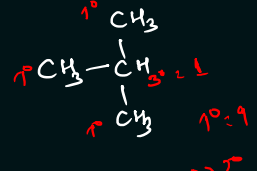
↳ $3^\circ > 2^\circ > 1^\circ$



Alkane Chemical Reaction

Selectivity Ratio of Cl_2 →

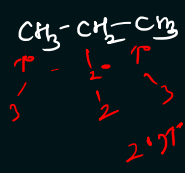
3°	2°	1°
5	3.8	1



proportion of 3° = 1 × 5 = 5 → % of 3° = $\frac{5}{14} \times 100 \simeq 36\%$

" " 1° = 9 × 1 = 9 → % of 1° = $\frac{9}{14} \times 100 = 64\%$

14

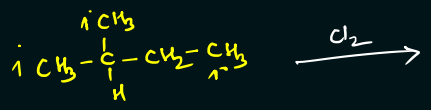


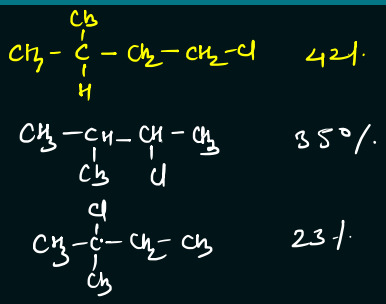
proportion of 2° = 2 × 3.8 = 7.6 → % of 2° = $\frac{7.6}{13.6} \times 100 = 56\%$

" " 1° = 6 × 1 = 6 → % of 1° = $\frac{6}{13.6} \times 100 = 44\%$

13.6

Alkane Chemical Reaction





proportn of 1° = 9 × 1 = 9

" " 2° = 2 × 3.8 = 7.6

" " 3° = 1 × 5 = 5

21.6

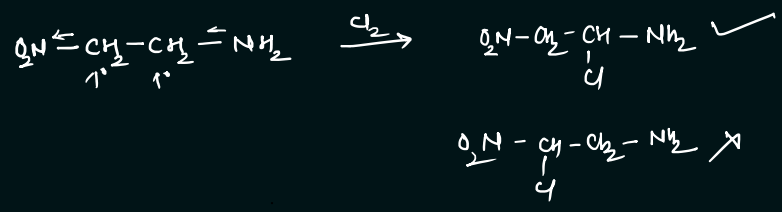
% of 1° = $\frac{9}{21.6} \times 100 = 42\%$

2° = $\frac{7.6}{21.6} \times 100 = 35\%$

3° = $\frac{5}{21.6} \times 100 = 23\%$

1°) 2°) 3°

Alkane Chemical Reaction



Selectivity Ratio

Br_2	3°	2°	1°
	1600	82	1

$2 \times 1 = 2$

$1 \times 100 = 100$

Alkanes

Chemical Properties

- ✓ Nitration
- ✓ Sulfonation
- ✓ Pyrolysis
- ✓ Aromatization
- ✓ Isomerization

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Alkane Chemical Reaction

2. Nitration → formation of nitro alkane from Alkane

$R-H$ (Alkane) + $HO-NO_2$ (Conc.) → (Vapour phase, High temp 450 °C) $R-NO_2$ (Nitro alkane) + H_2O

Conc. HNO_3 | Room temp → No Reaction

Reaction Mechanism → CH_4 (methane) + $HO-NO_2$ → (VP, 450°C) CH_3-NO_2 (Nitromethane) + H_2O

Step 1) Initiation $OH-NO_2 \rightarrow HO^{\cdot} + \dot{N}O_2$ formation of Free Radical

Step 2) Propogation $CH_3-H + HO^{\cdot} \rightarrow H_2O + \dot{C}H_3$

Step 3) Termination - $\dot{C}H_3 + \dot{N}O_2 \rightarrow CH_3-NO_2$ Nitromethane

Alkane Chemical Reaction

2. Nitration

$CH_3-CH_2-CH_3$ (propane) → (Conc HNO_3, Δ)

- $CH_3-\dot{C}H-CH_3 \rightarrow CH_3-CH(NO_2)-CH_3$ 2-nitro propane 40%
- $CH_3-CH_2-\dot{C}H_2 \rightarrow CH_3-CH_2-CH_2-NO_2$ 1-nitro propane 25%

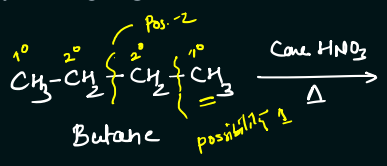
At high temp, higher alkane → Rupture C–C bond

$CH_3-CH_2-CH_3$ →

- $CH_3-\dot{C}H_2 \rightarrow CH_3-CH_2-NO_2$ nitroethane 10%
- $\dot{C}H_3 \rightarrow CH_3-NO_2$ nitromethane 25%

Alkane Chemical Reaction

2. Nitration



① $CH_3-CH_2-\underset{NO_2}{CH}-CH_3$

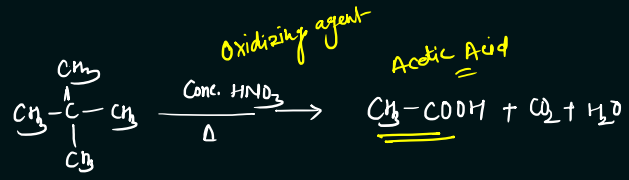
② $CH_3-CH_2-CH_2-CH_2-NO_2$

③ $CH_3-CH_2-NO_2$

④ CH_3-NO_2

⑤ $CH_3-\underset{NO_2}{CH}-CH_3$

⑥ $CH_3-CH_2-CH_2-NO_2$

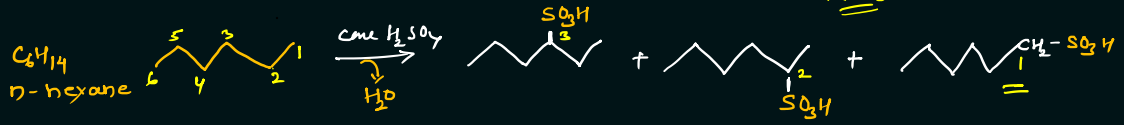


Alkane Chemical Reaction

3. Sulfonation :- In Extreme Conc H_2SO_4 or Fuming ($SO_3 + H_2SO_4$) - $H_2S_2O_7$ Oleum

Sulfonation Reaction occurs in higher alkane > C_6 (n-alkane)

$R > C_6$



Exception - Isobutane $CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow{\text{Conc } H_2SO_4} CH_3-\underset{CH_3}{\overset{SO_3H}{C}}-CH_3$

Alkane Chemical Reaction

3. Sulfonation

- Free Radical mechanism
- No bond Rupture unlike Nitration.

Mechanism

Step 1) Initiation – $HO-SO_3H \longrightarrow \overset{\bullet}{HO} + \overset{\bullet}{SO_3H}$

Step 2) Propogation — $C_6H_{14} + HO^{\bullet} \longrightarrow \overset{\bullet}{C_6H_{13}} + H_2O$

Step 3) Termination – $\overset{\bullet}{C_6H_{13}} + \overset{\bullet}{SO_3H} \longrightarrow C_6H_{13}-SO_3H$

Alkane Chemical Reaction

4. Pyrolysis

- Thermal decomposition Reaction
- > 500°C, 773 K
- Alkane → lower alkane and alkene

$R-C\equiv C \xrightarrow[500^\circ C]{\text{Oxides of Al, Zn, Silica}}$ Lower alkane & Alkene

$R-C\equiv H \xrightarrow{\text{oxides of Cr, V, Mo}}$ Alkene

$CH_3-\overset{2}{C}H_2-\overset{1}{C}H_2-CH_3 \xrightarrow[\Delta]{Al_2O_3}$ Butane

① $CH_3-CH_2-\dot{C}H_2 + \dot{C}H_3 \longrightarrow CH_3-\dot{C}H-CH_2 + CH_4$ methane

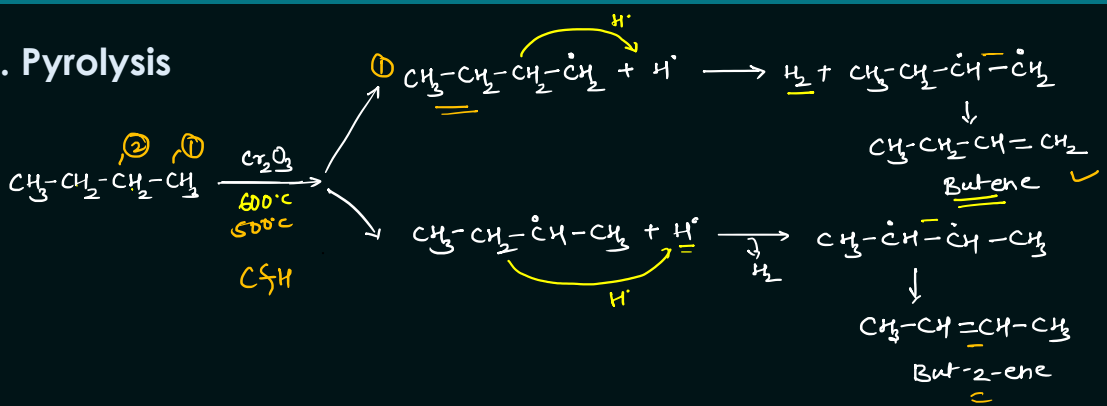
↳ $CH_3-CH=CH_2$ Propene

② $CH_3-\dot{C}H_2 + CH_3-\dot{C}H_2 \longrightarrow \dot{C}H_2-\dot{C}H_2 + CH_3-CH_3$ ethane

↳ $CH_2=CH_2$ ethene

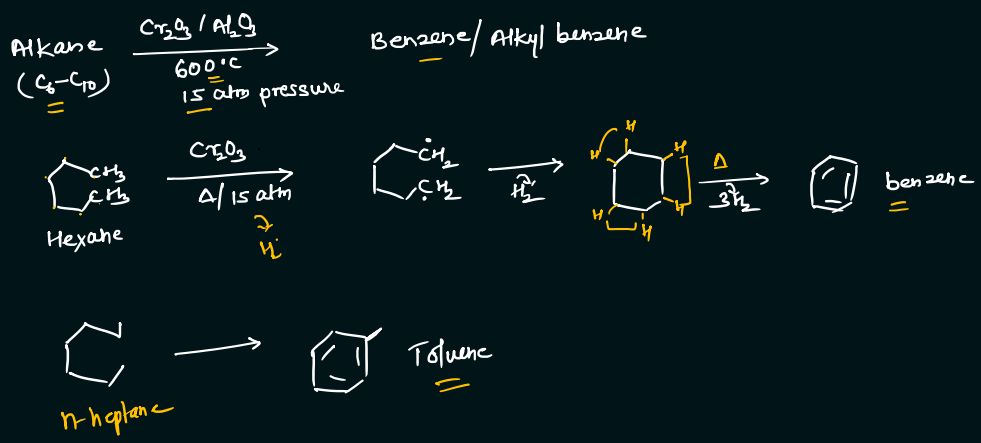
Alkane Chemical Reaction

4. Pyrolysis



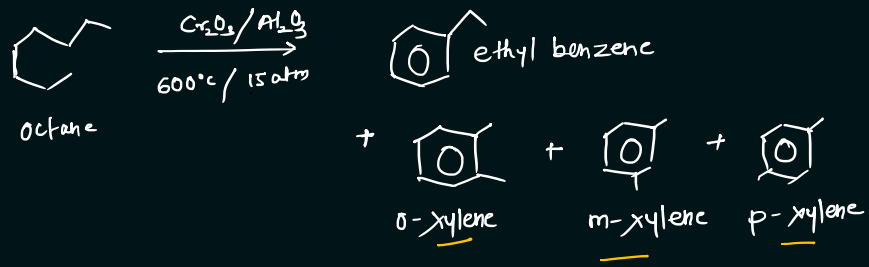
Alkane Chemical Reaction

6. Aromatization



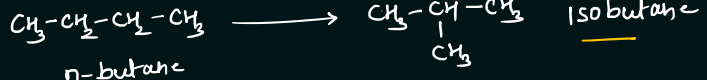
Alkane Chemical Reaction

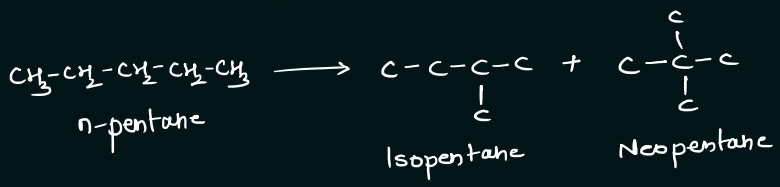
6. Aromatization



Alkane Chemical Reaction

7. Isomerization :- Anh. $AlCl_3$/ Conc HCl, 200°c





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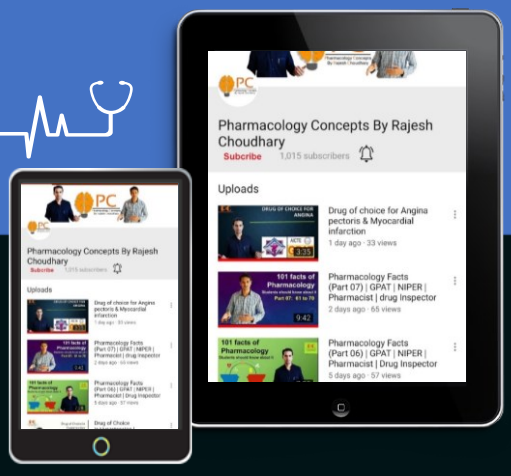

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