Physical Properties

① **Order of Bond length**
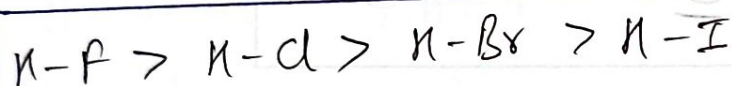
$$C-F < C-Cl < C-Br < C-I$$

② **Order of Bond dissociation Enthalpy:**

$$C-I < C-Br < C-Cl < C-F$$
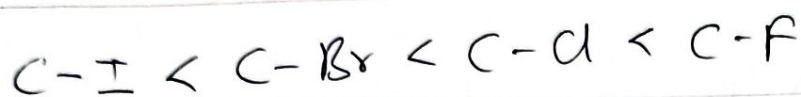
③ **Order of Dipole Moment. (Exception)**

$$C-Cl > C-F > C-Br > C-I$$

In case of $H-X$, the order of Dipole Moment,

$$H-F > H-Cl > H-Br > H-I$$

→ Boiling point of alkyl halide decrease in the order

$$RI > RBr > RCl > RF$$
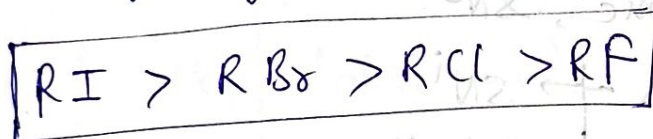
with increasing carbon ↑ ⟹ B.P↑

Eg
CH_3Cl	248·8
CH_3CH_2Cl	285·5

Increasing Branching ↑ ⟹ B.P↓

Eg
$CH_3CH_2CH_2CH_2Br$	375 K
$CH_3-\underset{\underset{Br}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3$	346 K

sec-butyl :

iso-butyl :

$X → Cl, Br, OH$ etc.

$$CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{\underset{5}{C}}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{I}{\mid}}{CH}}-CH_3$$
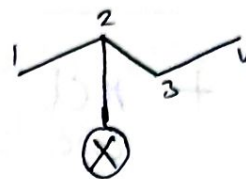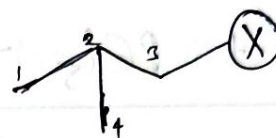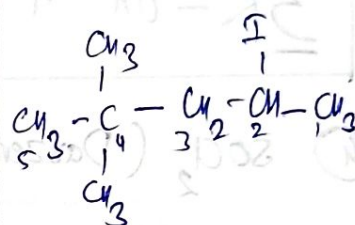
Priority: $I > CH_3$

2-Iodo 4,4-dimethyl pentane

Boiling point:

$$HF > H-Cl > H-Br$$
$$> H-I$$
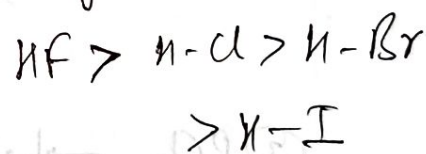
Preparation of Haloalkanes from Alcohols

① conc. HCl + Anhy $ZnCl_2$ $\longrightarrow$ Luca's Reagent

$$R-OH + HCl \xrightarrow[conc.]{ZnCl_2} R-Cl + H_2O$$

② with PCl_5

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$
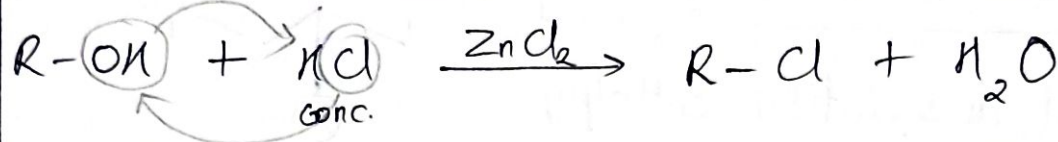
③ with PCl_3
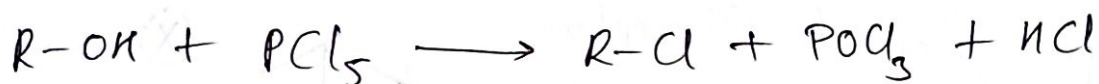
$$\underline{3}R-OH + PCl_3 \longrightarrow \underline{3}R-Cl + H_3PO_3$$

④ $SOCl_2$ (Darzen's Method)

Summary:

① Lucas $\longrightarrow$ Racemic, $SN^①$

② $PCl_5 \rightarrow$ i) gas $\begin{cases} SN^i \\ \rightarrow \text{Retention} \end{cases}$

       ii) solid $\begin{cases} SN^② \\ \rightarrow \text{Inversion} \end{cases}$

③ $PCl_3 \begin{cases} \rightarrow \text{Inversion} \\ \rightarrow SN^② \end{cases}$

④ $SOCl_2 \begin{cases} SN^i \\ \rightarrow \text{Retention} \end{cases}$

⑤

$$R-OH + \underset{48\%}{HBr} \xrightarrow[\Delta]{NaBr, H_2SO_4} R-Br + H_2O$$

$$R-OH + HI \xrightarrow[\substack{H_3PO_4 \\ (95\%)}]{NaI \text{ or } KI} R-I + H_2O$$
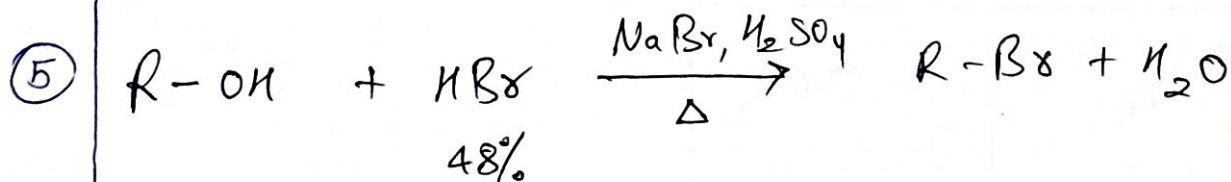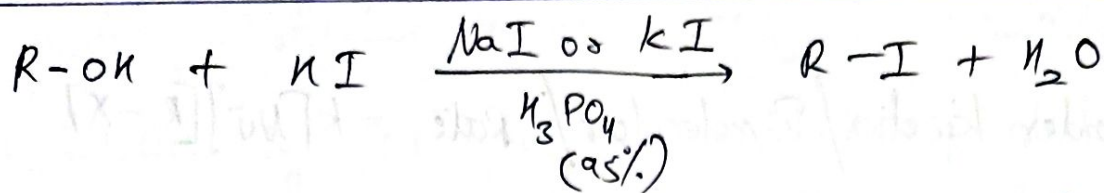
Chemical Properties ① SN^1 & SN^2 ② Elimination Rxn
③ Reaction with metal.

① $\underline{SN^1}$

i) Unimolecular / Rate $\propto [R-X]^1$ / first order kinetics.

ii) Rearrangement of carbocation takes place $\Rightarrow$ more stable Carbocation.

3) Polar Protic solvent : eg $H-OH$, C_2H_5-OH, CH_3COOH, CH_3-OH

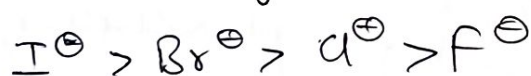4) Exothermic : $\Delta H < 0$

⑤ Stereochemistry : Racemix mixture.

* $\underline{Factors}$ which affect Rate of SN^1

i) Nature of alkyl halide $\rightarrow$ {Most stable carbocation}

$3° > 2° > 1° >$ Methyl

2) Nature of Leaving group

$\quad \hookrightarrow$ easily leave $\Rightarrow$ Rate $\uparrow$

$I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$

② SN₂

i) Second order kinetic/ Bimolecular / $Rate = k[Nu^-][R-X]$

2) No carbocation. → instead forms → Transition state

Jitna stable transition state ↑ ⇒ SN₂ ↑

3) Polar Aprotic : eg. Acetone ⇝ $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$

   eg. DMF (Dimethyl formide) ⇝ $O = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - N - CH_3$...

$O = C - H$ / $CH_3 - N - CH_3$

   eg. DMSO (Dimethyl sulpho oxide) ⇝ $CH_3 - \overset{\overset{O}{\|}}{S} - CH_3$

4) Exothermic → first found by (walden)

5) stereochemistry :→ only Inversion

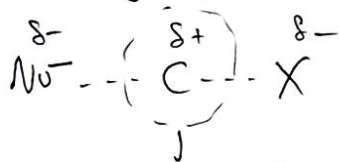Factors affecting Rate of SN₂ rxn.

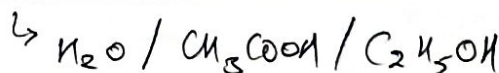1) Nature of Alkyl halide : | $Rate \propto \dfrac{1}{steric\ hinderance}$ |

   $3° < 2° < 1° < methyl$

2) stability of Transition state

   $\overset{\delta^-}{Nu} - - - (\overset{\delta^+}{C}) - - \overset{\delta^-}{X}$

   Jitna adha Electro coi thdrawing → T-S stable ↑   > steric
   group   ⇕   hinderance.
   (-I effect)   Rate of SN₂

3) Nature of Nucleophile : ....

   | Strong Nu⁻ ⟶ SN₂ | | Weak Nu⁻ ⟶ SN₁ |

   eg. $OH^⊖ / CN^⊖ / S-Ph / SH^⊖$ ↳ $H_2O / CH_3COOH / C_2H_5OH$
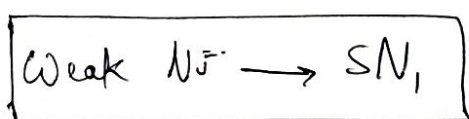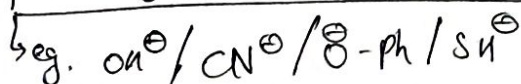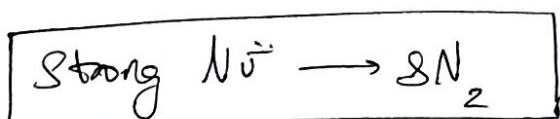
...cleophilic substitution reactions of alkyl halide

① Substitution by $-OH$ group $\Rightarrow$ formation of alcohol
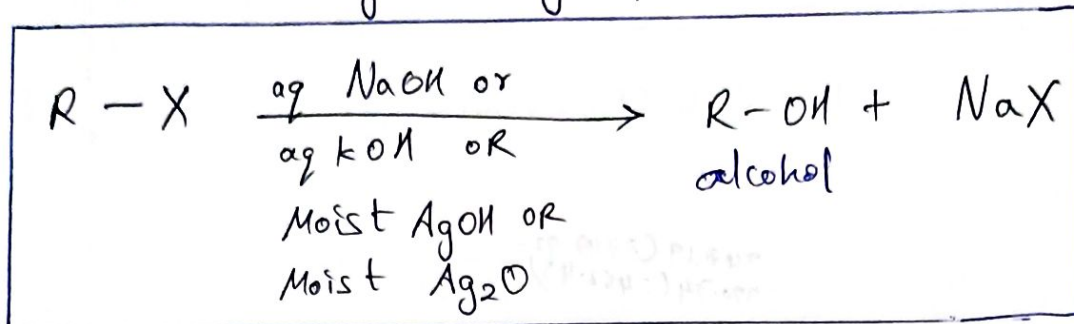
$$R-X \xrightarrow[\substack{aq \; KOH \quad OR \\ Moist \; AgOH \; OR \\ Moist \; Ag_2O}]{aq \; NaOH \; or} R-OH + NaX \quad \text{(alcohol)}$$ $SN^{②}$

② substitution by $-OR$ group $\Rightarrow$ formation of ether

$$R-X + Na^{⊕}\overset{⊖}{O}R \longrightarrow R-O-R + NaX$$ $SN^{②}$
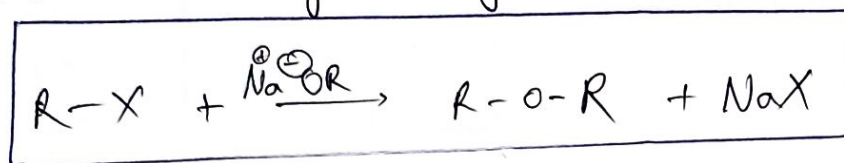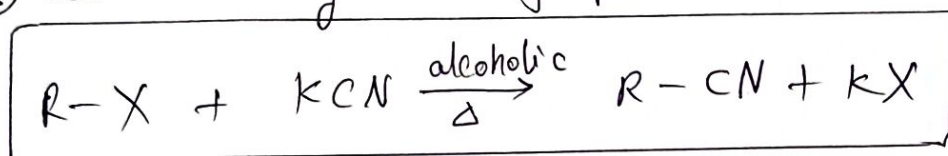
③ substitution by $-CN$ group $\Rightarrow$ formation of alkyl cyanide

$$R-X + KCN \xrightarrow[\Delta]{alcoholic} R-CN + KX$$ $SN^{②}$

④ substitution by $-NC$ group $\Rightarrow$ formation of alkyl isocyanide

$$R-X + AgCN \longrightarrow R-\overset{+}{N}\equiv\overset{-}{C} + AgX$$ $SN^{②}$

⑤ substitution by $-O-N=O$ (Nitrite) $\rightarrow$ alkyl nitrile
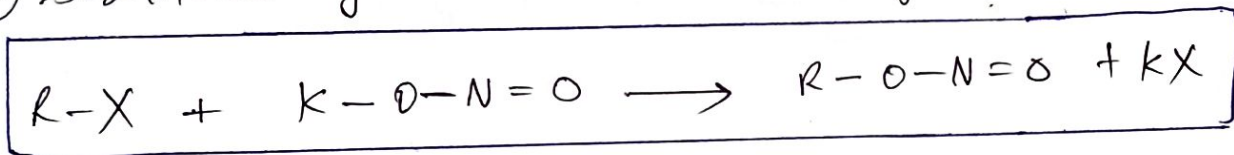
$$R-X + K-O-N=O \longrightarrow R-O-N=O + KX$$ $SN^{②}$

⑥ substitution by $\left(-\overset{+}{N}\overset{O}{\diagdown}_{O^-}\right)$ Nitro group $\Rightarrow$ Nitro alkane (NO_2)
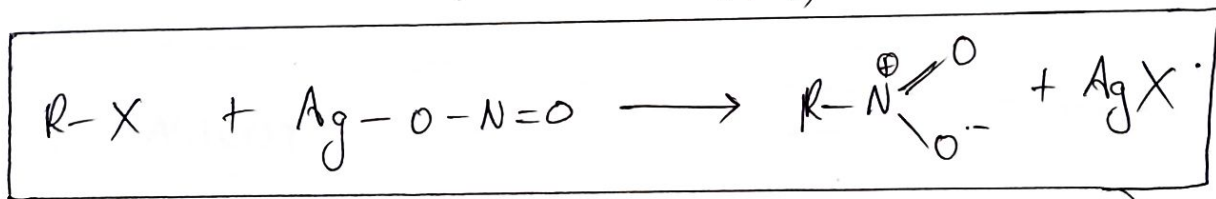
$$R-X + Ag-O-N=O \longrightarrow R-\overset{⊕}{N}\overset{\diagup O}{\diagdown}_{O^-} + AgX$$ $SN^{②}$

⑦ Substitution by $(-NH_2)$ group $\Rightarrow$ Amine ... {amine chp}

⑧ Substitution by carboxylate $\left(-O-\overset{O}{\overset{\|}{C}}-R\right)$

$$R-X + R'-\overset{O}{\overset{\|}{C}}-O-Ag \xrightarrow{\Delta} R-O-\overset{O}{\overset{\|}{C}}-R' + AgX\downarrow$$
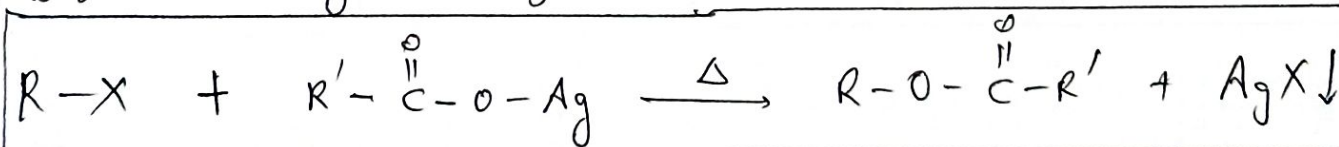
Reaction with active Metals:

① Reaction with Magnesium ② wurtz Rxn ⊘

Reaction of haloarenes:

① wurtz-fittig rxn ② fittig Rxn

③ Nucleophilic substitution S_N of haloarenes:

→ Greater the number of electron withdrawing groups at o/p position, greater is the reactivity.

Electron withdrawing group at meta position has practically no effect on reactivity
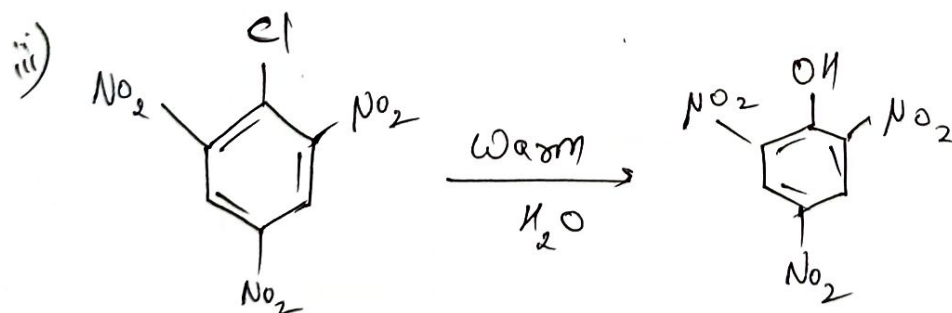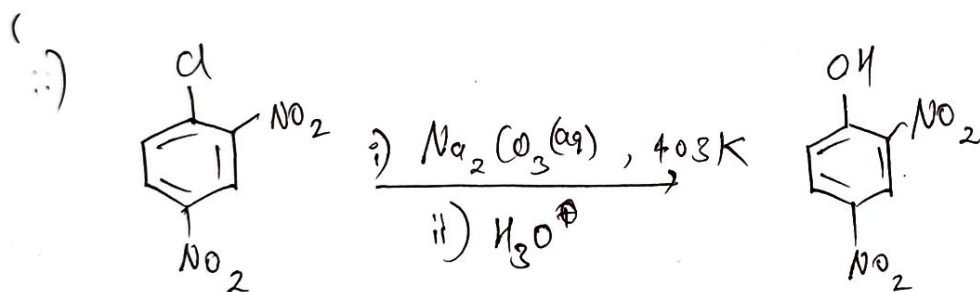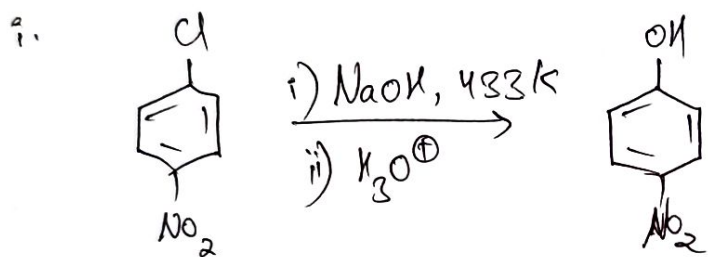
i.

$\xrightarrow[\text{ii) } H_3O^⊕]{\text{i) NaOH, 433k}}$

(ii)

$\xrightarrow[\text{ii) } H_3O^⊕]{\text{i) } Na_2CO_3(aq) \text{ , 408K}}$

iii)

$\xrightarrow[H_2O]{warm}$

① Halogenation.

$$\underset{\text{Cl}}{\bigcirc} + Cl_2 \xrightarrow[Cl_2]{\text{anhy. } FeCl_3} \underset{\text{Cl}}{\bigcirc} + \underset{\text{Cl}}{\bigcirc}^{Cl} + HCl$$

② Nitration

$$\underset{\text{Cl}}{\bigcirc} + HNO_3 \text{ conc.} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{Cl}}{\bigcirc}_{NO_2} + \underset{\text{Cl}}{\bigcirc}^{NO_2}$$
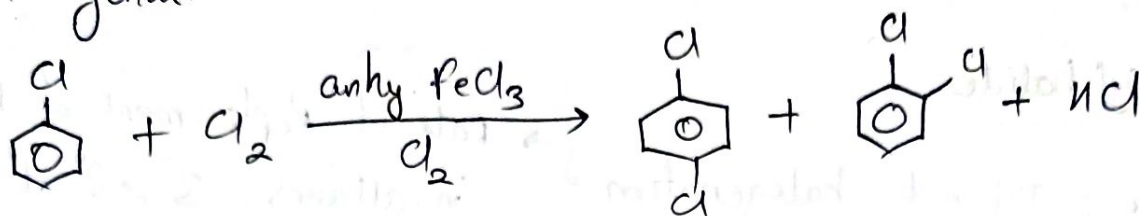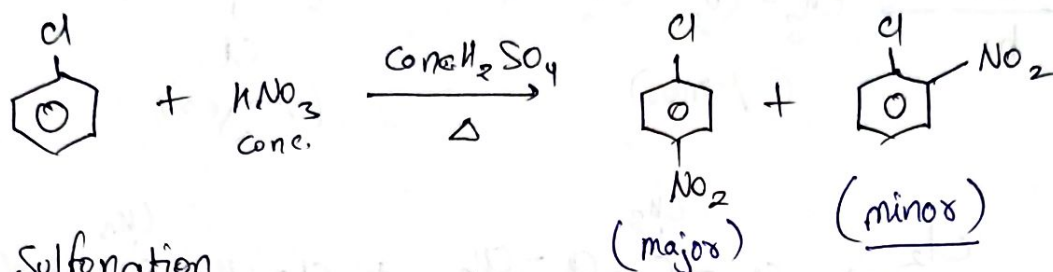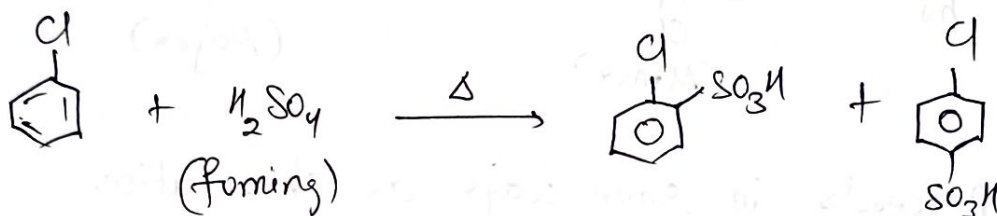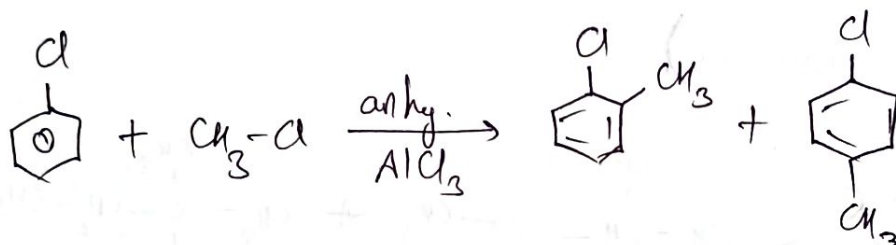
(major)   (minor)

③ Sulfonation

$$\underset{\text{Cl}}{\bigcirc} + H_2SO_4 \text{ (fuming)} \xrightarrow{\Delta} \underset{\text{Cl}}{\bigcirc} SO_3H + \underset{\text{Cl}}{\bigcirc}_{SO_3H}$$

④ Friedel Craft's alkalyation.

$$\underset{\text{Cl}}{\bigcirc} + CH_3-Cl \xrightarrow{\underset{AlCl_3}{\text{anhy.}}} \underset{\text{Cl}}{\bigcirc}^{CH_3} + \underset{\text{Cl}}{\bigcirc}_{CH_3}$$

⑤ Friedel Craft's acyalation

$$\underset{\text{Cl}}{\bigcirc} + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{anhy. } AlCl_3} \underset{\text{Cl}}{\bigcirc}^{\overset{O}{\overset{\|}{C}}-CH_3} + \underset{\text{Cl}}{\bigcirc}_{O=\overset{}{C}-CH_3}$$

$$\underset{\text{Benzene}}{\overset{CH_3}{\bigcirc}} + Br_2 \xrightarrow[dark]{Fe} \underset{\text{}}{\overset{CH_3}{\bigcirc}}^{Br} + \underset{Br}{\overset{CH_3}{\bigcirc}} + HBr$$

$$\bigcirc + I_2 \xrightarrow{HNO_3/KIO_4} \bigcirc^{I}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-O-Ag + Br_2 \xrightarrow{CS_2} CH_3-Br + AgBr + CO_2$$

Silver acetate
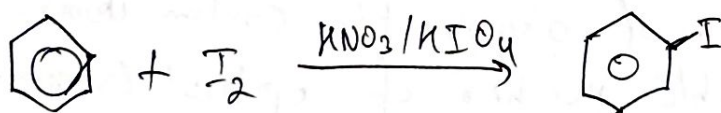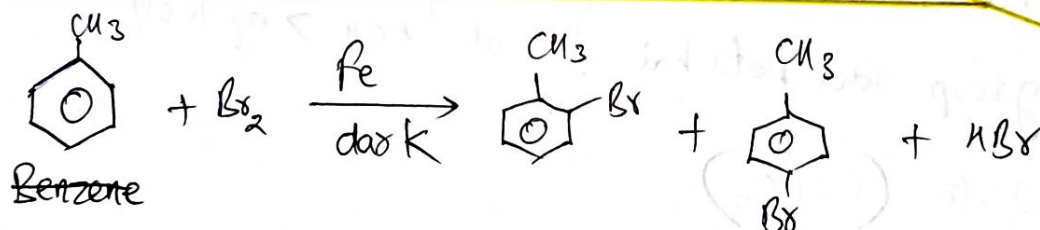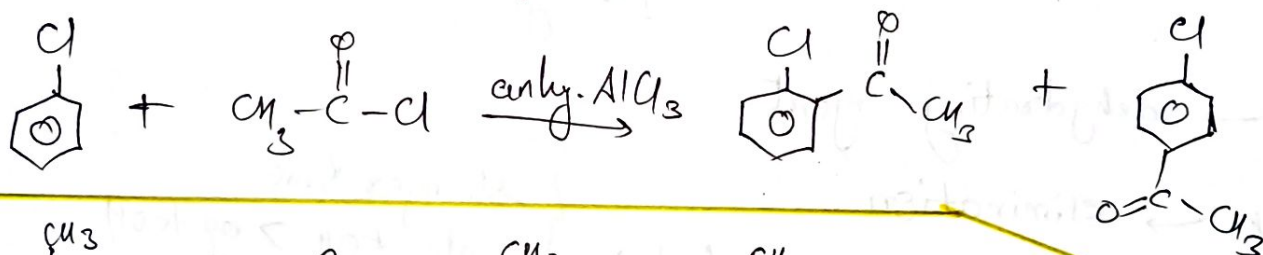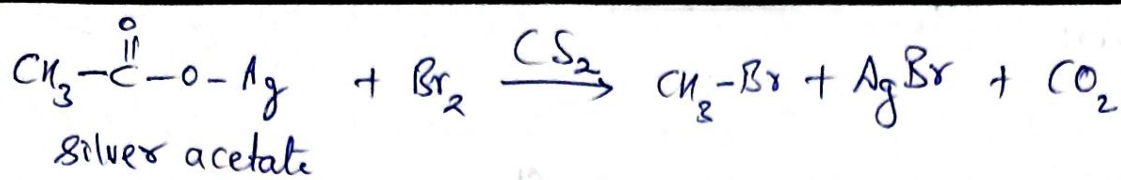
MoP of Alkyl halide :

I from Alkane : Direct halogenation $\to$ | Rate of Replacement of H in alkanes $3° > 2° > 1°$

$$CH_3-CH_2-CH_3 \xrightarrow{\underset{h\nu}{Cl_2}} CH_3-CH_2-CH_2-Cl + CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

(Minor) (Major)

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow{\underset{h\nu}{Cl_2}} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3 + Cl-CH_2-\underset{\underset{}{}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-CH_3$$

(Exception) (Minor) (Major)
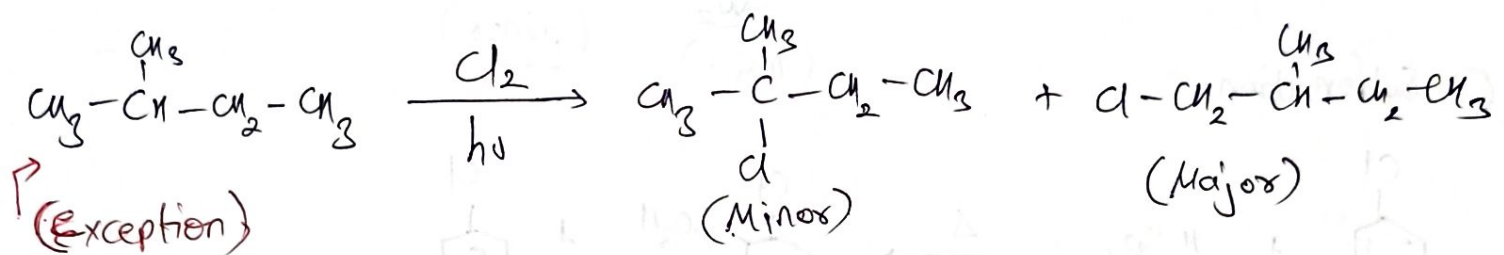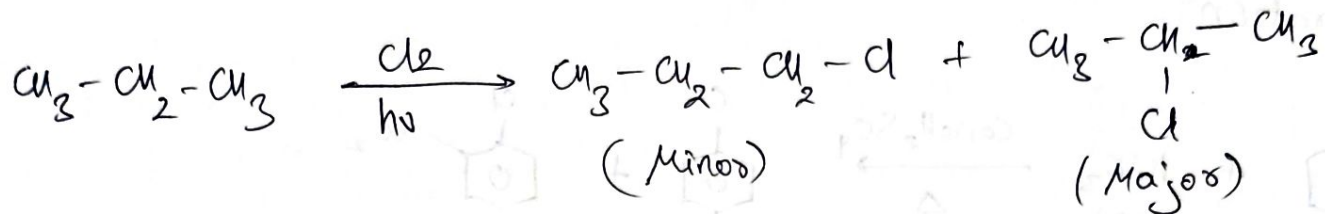
ii) Bromination : $\to$ proceeds in same ways as chlorination.

iii) Iodination   iv) fluorination $\nearrow$

II from Alkene (Electrophilic addition)

(Exception)

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{\underset{HBr}{M.R}} CH_3-\underset{\underset{}{}}{\overset{\overset{CH_3}{|}}{CH}}-\underset{\underset{Br}{|}}{CH}-CH_3 + CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2$$

[wrong]
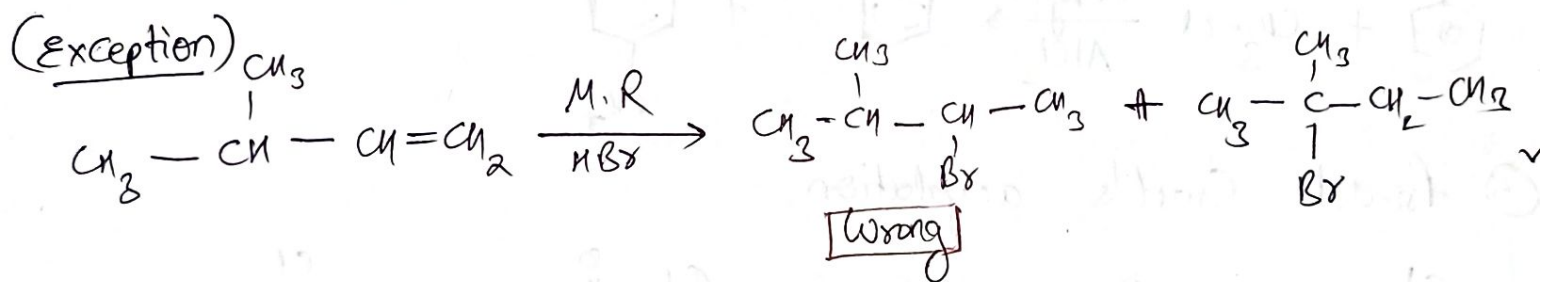
$Al_2O_3 \to$ dehydrating agent

alc. KOH $\to$ Elimination

aq. KOH $\to$ OH group add hota hai

$\left.\begin{array}{l} \text{stronger Base.} \\ \text{alc. KOH} > \text{aq KOH} \end{array}\right\}$

$\to$ Nicol prism $\to$ Calcite $(CaCO_3)$

If 'n' represents total number of asymmetric Carbon atoms in a compound, the possible number of optical isomers of the compound is $\boxed{2^n}$