Haloalkanes and Haloarenes

INTRODUCTION:-

The halogen derivatives of aliphatic and aromatic hydrocarbons are called alkyl halide (Haloalkanes) and aryl halide (Haloarenes)

Haloalkanes contain halogen atom attached to the sp^3 hybridised C-atom of an alkyl group. Whereas Haloarenes contain halogen atom attached to sp^2 hybridised C-atom of an aryl group.

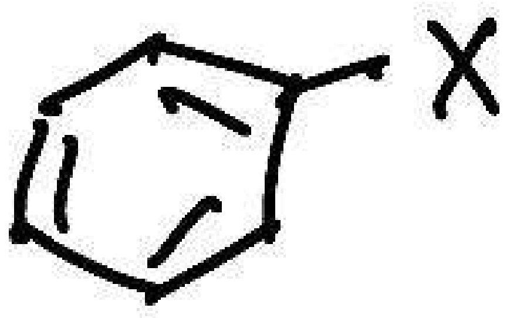
CLASSIFICATION OF HALOALKANES & HALOARENE

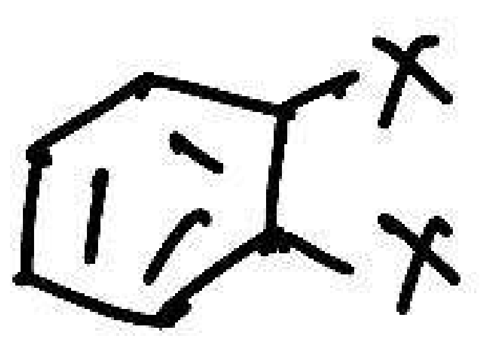
(*) On the basis of no. of halogen atoms

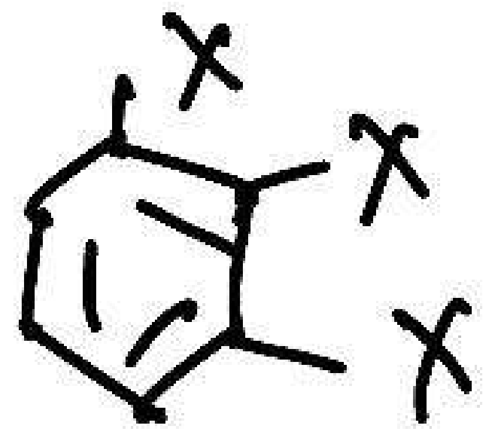
i) C_2H_5-X (Monohaloalkanes)

ii) $\begin{array}{l} CH_2-X \\ | \\ CH_2-X \end{array}$ (Dihaloalkanes)

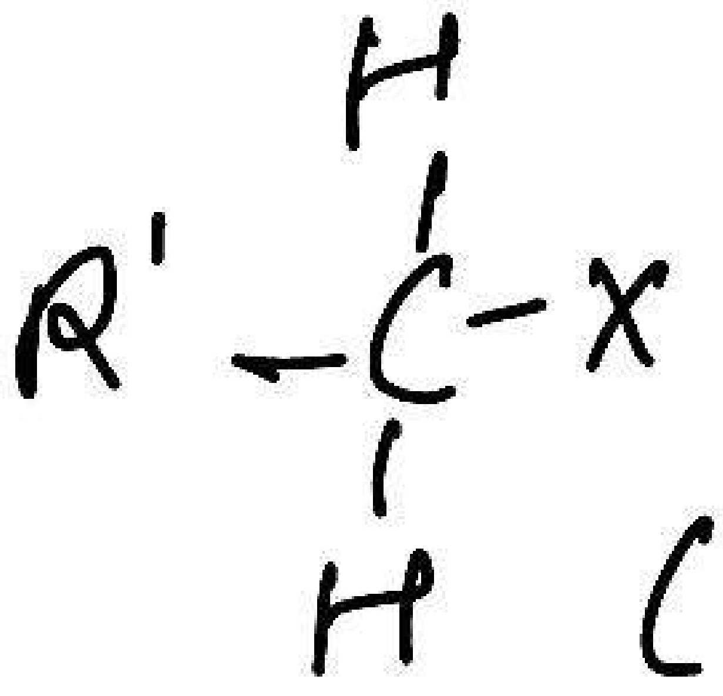
iii) $\begin{array}{l} CH_2-X \\ | \\ CH-X \\ | \\ CH_2-X \end{array}$ (Trihaloalkanes)

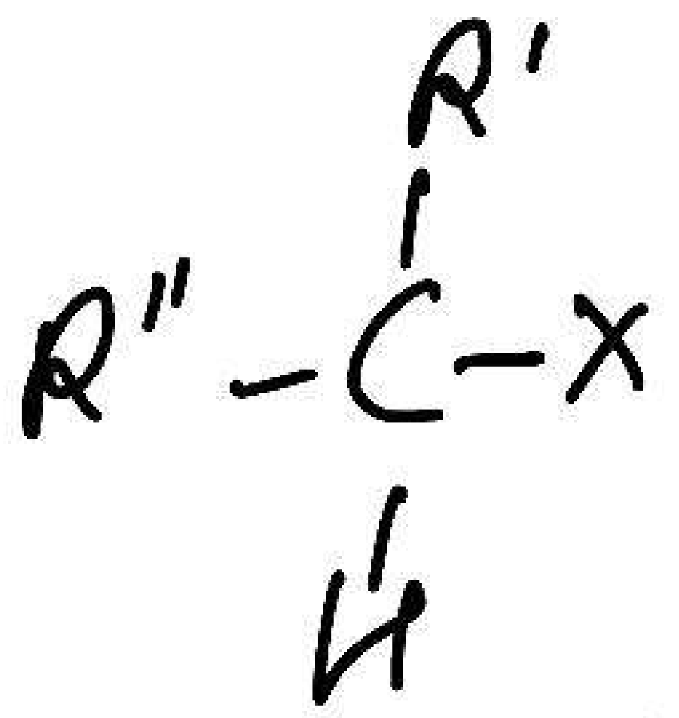

(monohaloarenes)

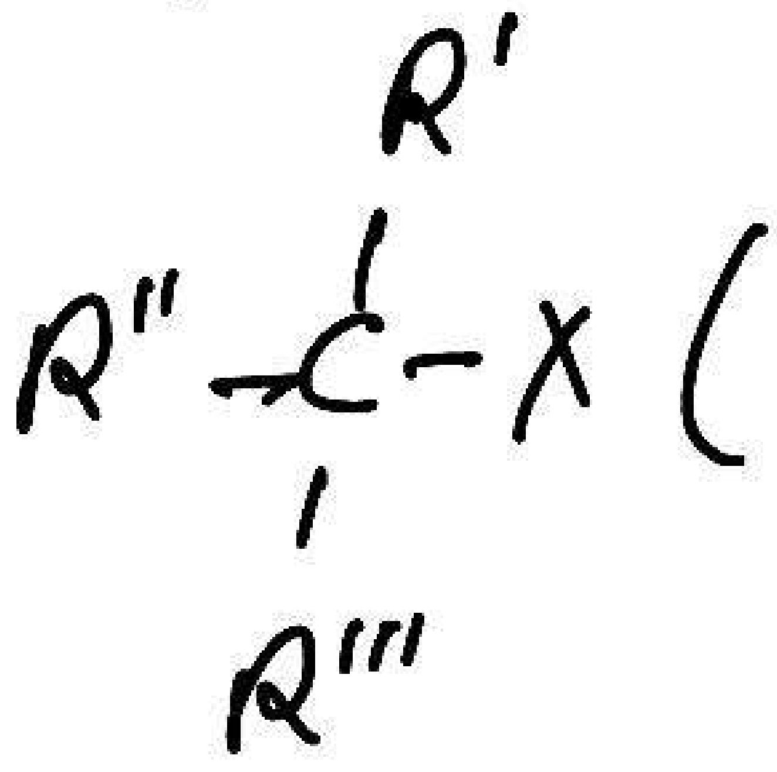

(Dihaloarenes)


(Trihaloarenes)

(*) On the basis of hybridisation state.


$R'-\underset{H}{\overset{H}{C}}-X$ (1°-Primary)


$R''-\underset{H}{\overset{R'}{C}}-X$ (2°-Secondary)


$R''-\underset{R'''}{\overset{R'}{C}}-X$ (3° Tertiary Haloalkane)

$\boxed{X = F, Cl, Br, I}$

ALLYLIC HALIDES :-

the halogen is bonded to an sp^3 C-atom next to the C=C.

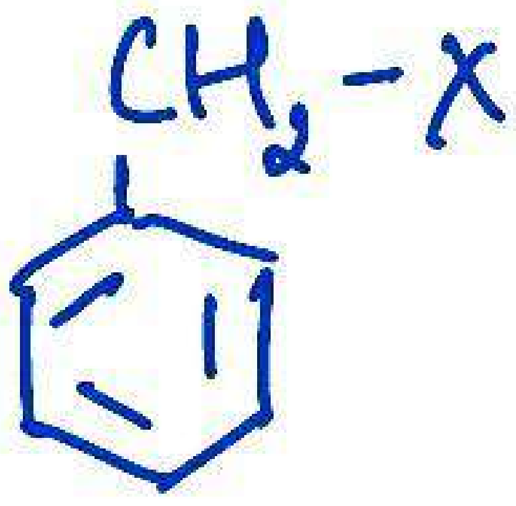
e.g. $R-CH=CH-CH_2-X$

Allylic carbon ↵

BENZYLIC HALIDE :-

the halogen atom is bonded to an sp^3 C-atom next to an aromatic ring

e.g



PROPAGYL HALIDE :-

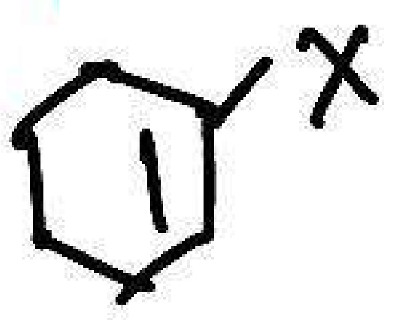
the halogen atom is bonded to an sp^3 C-atom, next to a C≡C bond.

e.g $R-C\equiv C-CH_2-X$

Vinyl Halide:

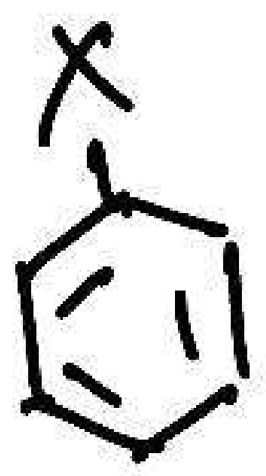
the halogen atom is bonded to an sp^2 C-atom

e.g $R-CH_2=CH-X$,

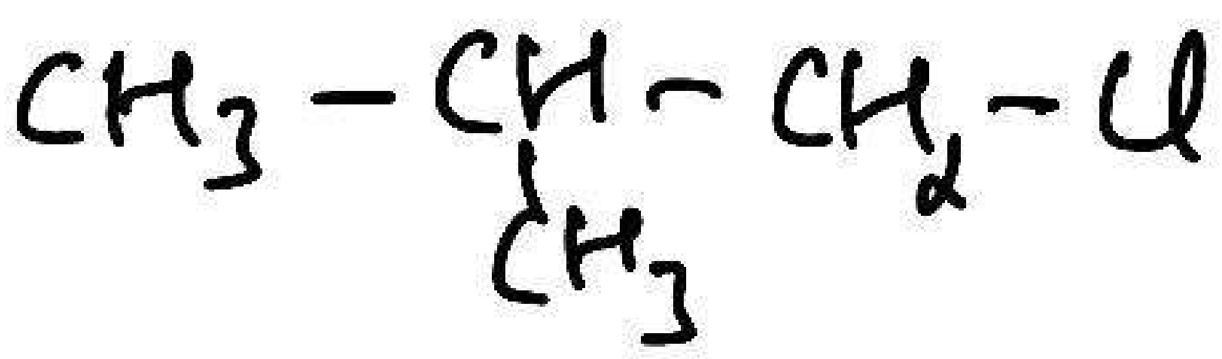
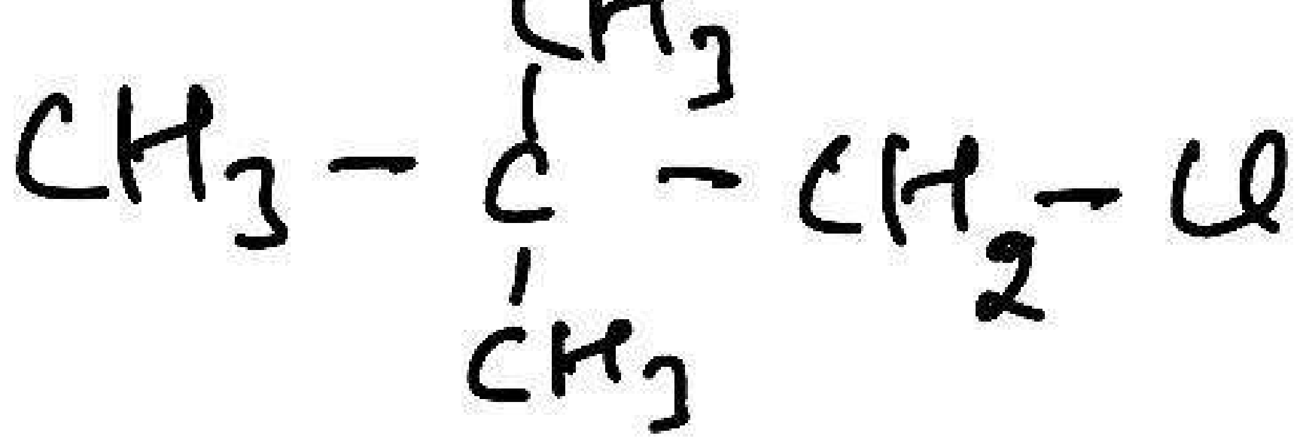


Aryl Halide :

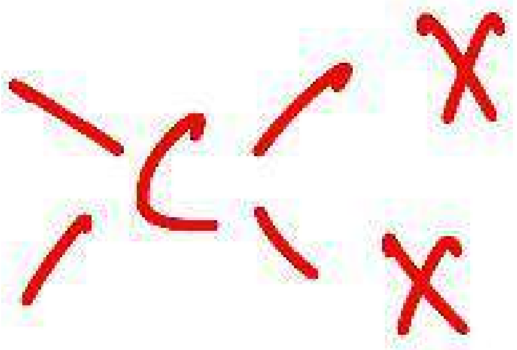
the halogen atom is bonded to sp^2 C-atom of an aromatic ring.

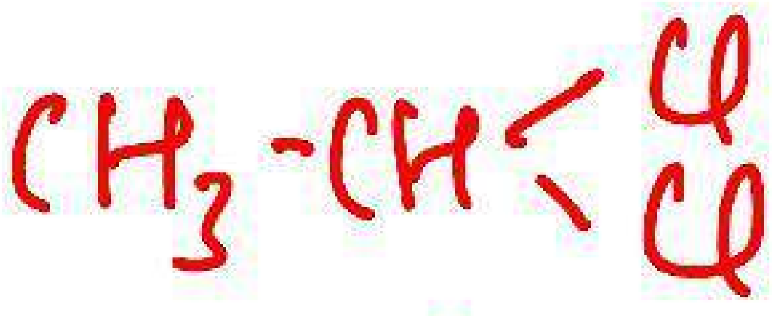


NOMENCLATURE OF HALOALKANES

	Common Name	IUPAC Name
• CH_3-Cl	Methyl Chloride	Chloromethane
• $CH_3CH_2CH_2Br$	n-Propyl Bromide	Bromopropane
•  $CH_3-\underset{CH_3}{CH}-CH_2-Cl$	isobutyl chloride	1-chloro-2-methyl propane
•  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Cl$	neopentyl chloride	1-chloro-2,2-dimethyl propane.

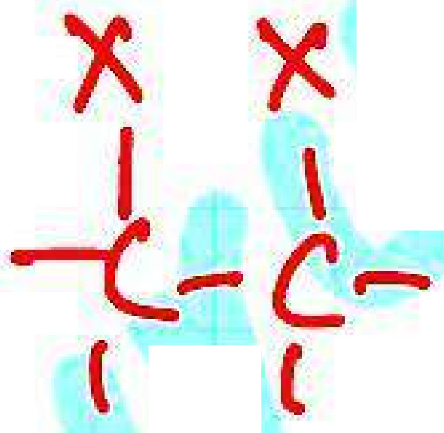
a) when both halogen atoms are attached to the same C-atom, these are called gem-dihalides also called alkylidene dihalide.

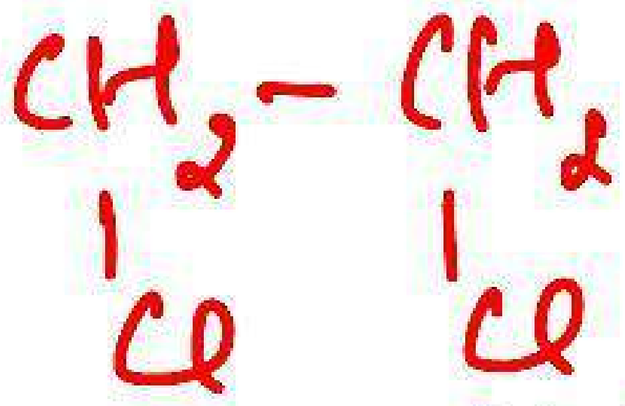

gem-dihalide

e.g

$CH_3-CH\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$

ethylidene dichloride

b) when two halogen atoms are present at adjacent C- then they are called vicinal dihalide also called alkylene dihalide



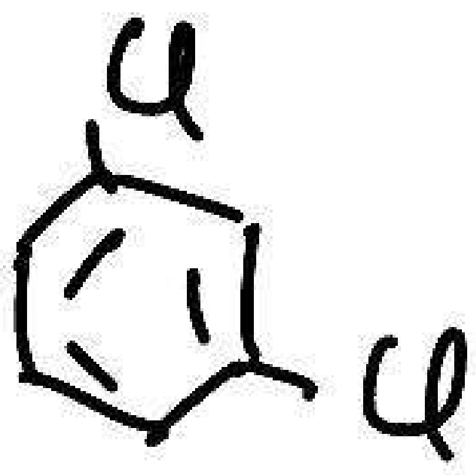

$\underset{Cl}{CH_2}-\underset{Cl}{CH_2}$

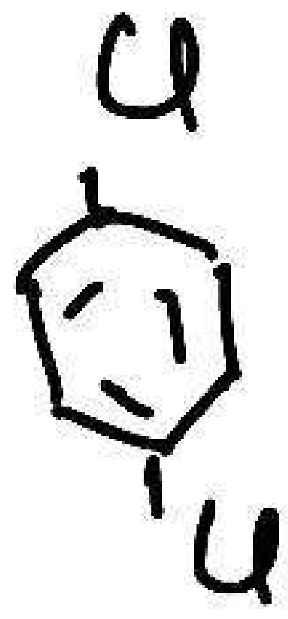
ethylene dichloride

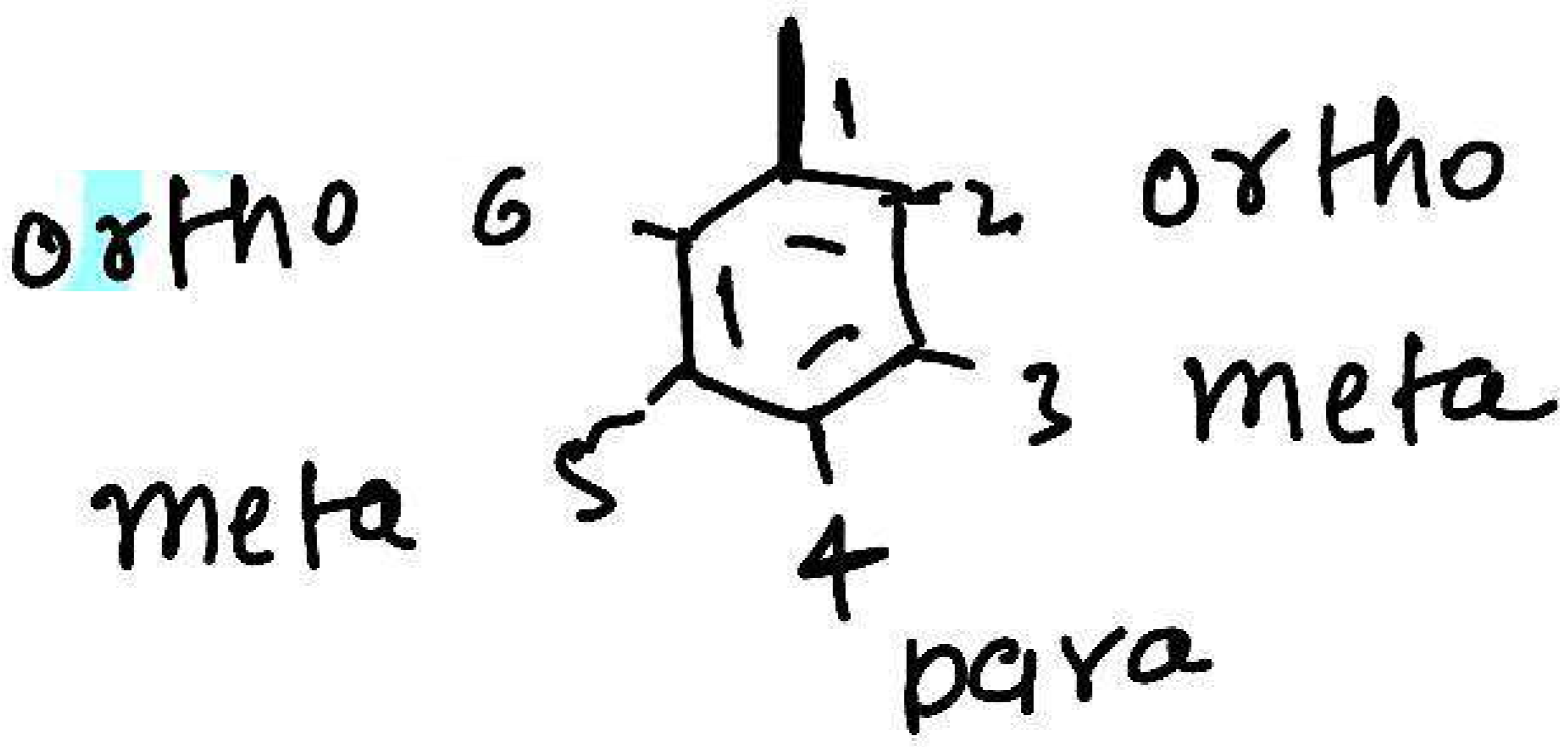
NOMENCLATURE OF HALOARENES


Chloro benzene


1,2-Dichlorobenzene (o-Dichloro benzene)

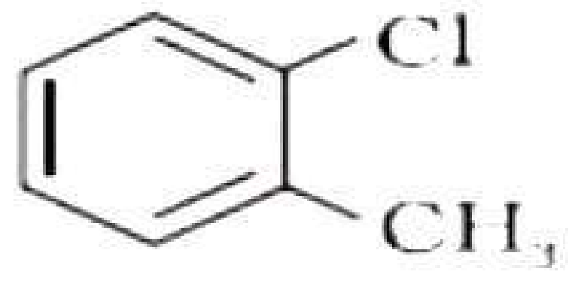
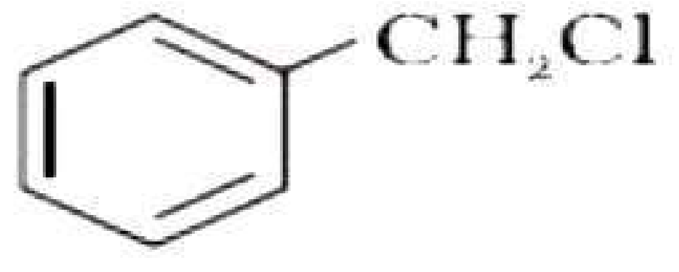

1,3-Dichloro benzene (m-Dichloro benzene)


1,4-Dichloro benzene (p-Dichloro benzene)



ओमपाल

o, m, p

$CH_2=CHCl$	Vinyl chloride	Chloroethene
$CH_2=CHCH_2Br$	Allyl bromide	3-Bromopropene
	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Nature of C-X Bond

the C-X bond is covalent but the electronegativity of halogen atom is more than C, due to which C-X bond is polar

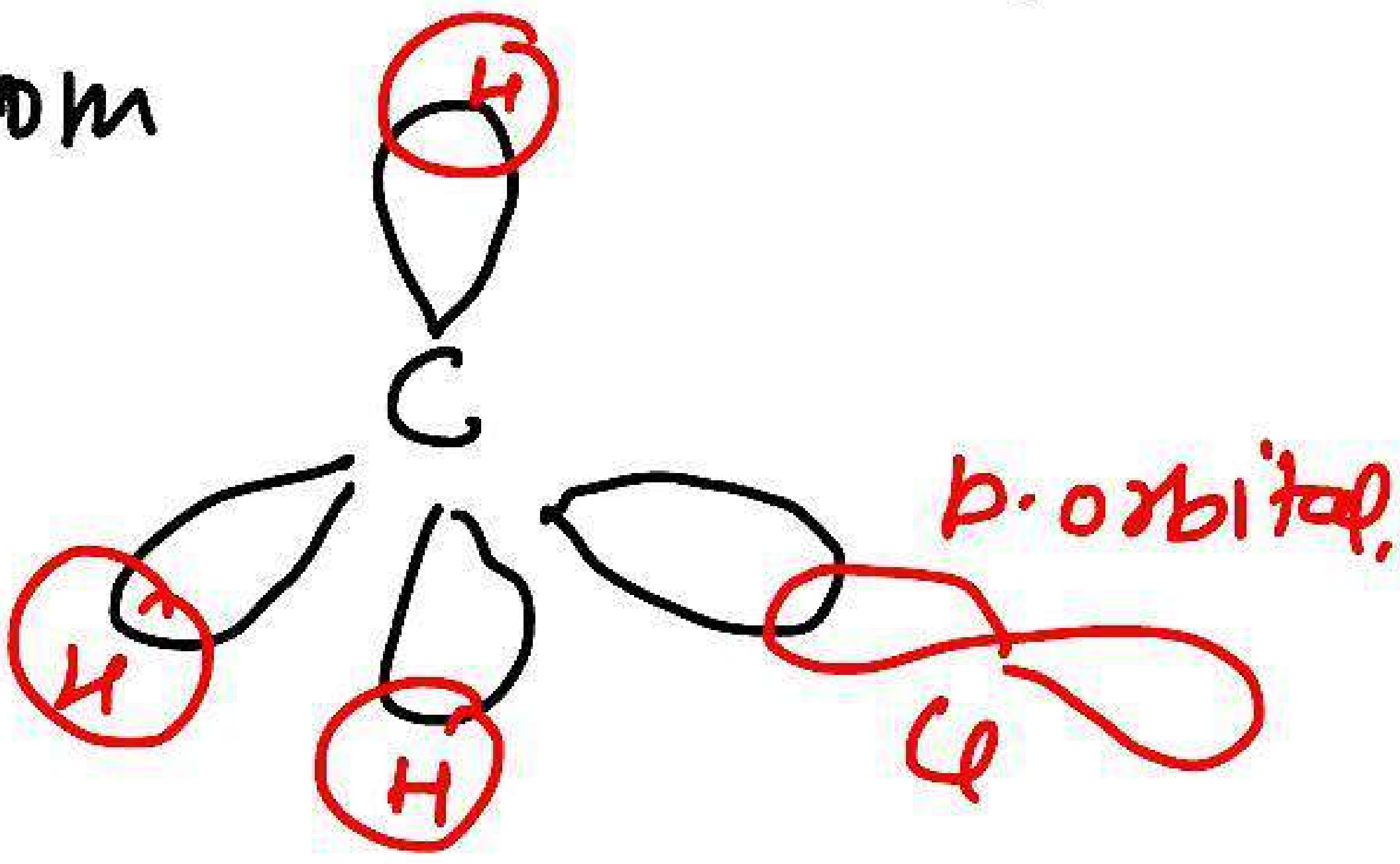
$$-\overset{|}{\underset{|}{C}}-X \longrightarrow -\overset{|}{\underset{|}{C}}^{\delta+}-X^{\delta-}$$ Polar Bond

Table : Carbon-Halogen (C—**X**) Bond Lengths, Bond Enthalpies and Dipole Moments

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol⁻¹	Dipole moment/Debye
CH_3-F	139	452	1.847
CH_3- Cl	178	351	1.860
CH_3-Br	193	293	1.830
CH_3-I	214	234	1.636

• Molecular Structure of CH_3Cl

the C-X bond is formed by the overlaping of sp^3 hybrid orbital of C-atom and p-orbital of Cl-atom



METHODS OF PREPARATION OF HALOALKANES :-

1. From Alcohol

a) By the action of halogen acid

$$R-OH + HX \longrightarrow R-X + H_2O$$

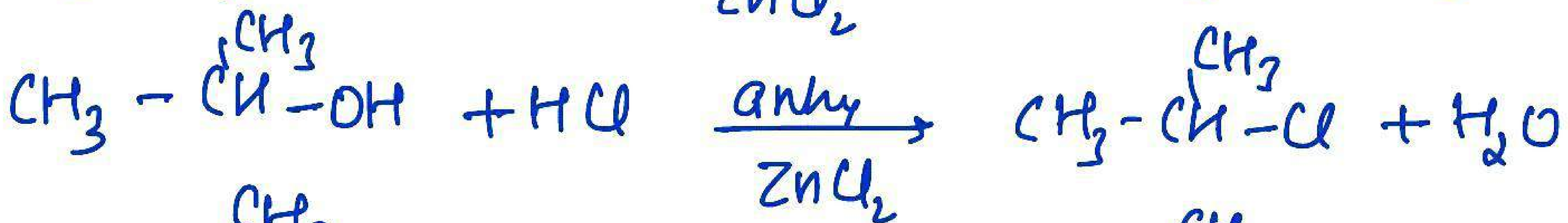
1° & 2° alcohols form chloroalkanes, when hydrochloric acid gas is passed through alcohol in the presence of anhydrous $ZnCl_2$

This is known as "Groove's Process"

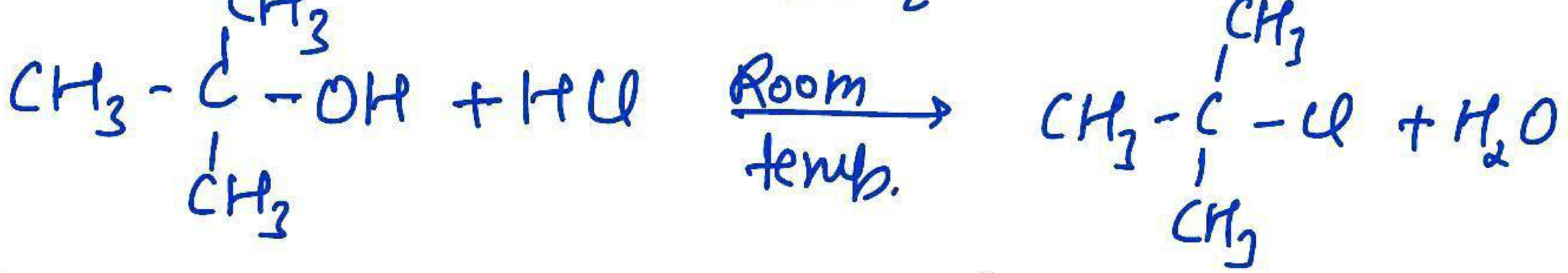
$ZnCl_2$ help in the cleavage of C-O bond.

→ 3° alcohols are very reactive, they react with conc. HCl at room temp. without $ZnCl_2$

- $CH_3-CH_2-OH + HCl \xrightarrow[ZnCl_2]{anhy} CH_3-CH_2-Cl + H_2O$



$$CH_3-\overset{CH_3}{CH}-OH + HCl \xrightarrow[ZnCl_2]{anhy} CH_3-\overset{CH_3}{CH}-Cl + H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HCl \xrightarrow[temp.]{Room} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + H_2O$$

Note 2° & 3° bromides and iodides can not be prepared from the respective alcohols because 2° & 3° alcohols on heating with conc. H_2SO_4 undergo dehydration and form alkene

→ HF is least reactive. So fluoroalkane is not formed.

Order of reactivity of alcohol → 3°>2°>1°
Reactivity of halogens → HI > HBr > HCl

· By the action of Phosphorous Halides:

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$

Note PBr_3 & PI_3 are not stable, so they are prepared on the site of reaction (SITU)

· By the action of thionyl Chloride

$$R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2\uparrow + HCl\uparrow$$

→ This method is preferred than other method because both the side products (SO_2 & HCl) are gaseous and can easily escape.

From Hydrocarbons

a) From Alkanes

Cl_2 & Br_2 reacts with alkanes in the presence of UV light to form haloalkanes This reaction is "Free radical substitution reaction"

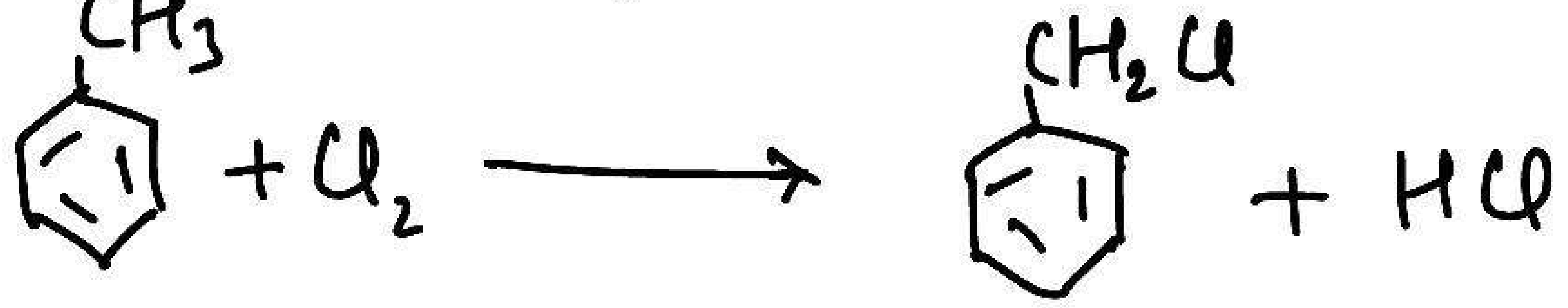
ex. $CH_3CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2} \underset{(45\%)}{CH_3CH_2CH_2Cl} + \underset{(55\%)}{CH_3\underset{Cl}{CH}CH_3}$

Note → The reactivity of different type of hydrogen in halocompound are

{ Benzylic = allylic > Alkyl > Vinyl = aryl }

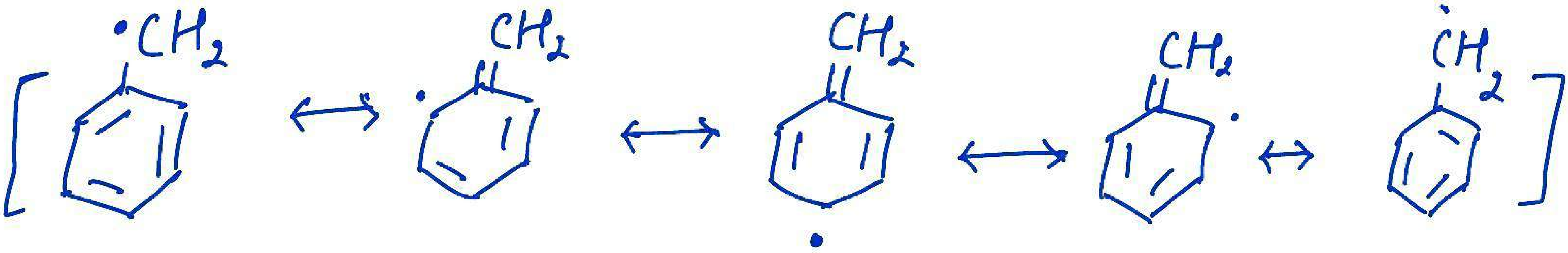
→ Allylic and benzylic halides can be easily prepared

- $CH_2=CH-CH_3 + Cl_2 \xrightarrow{\Delta} CH_2=CH-CH_2Cl + HCl$

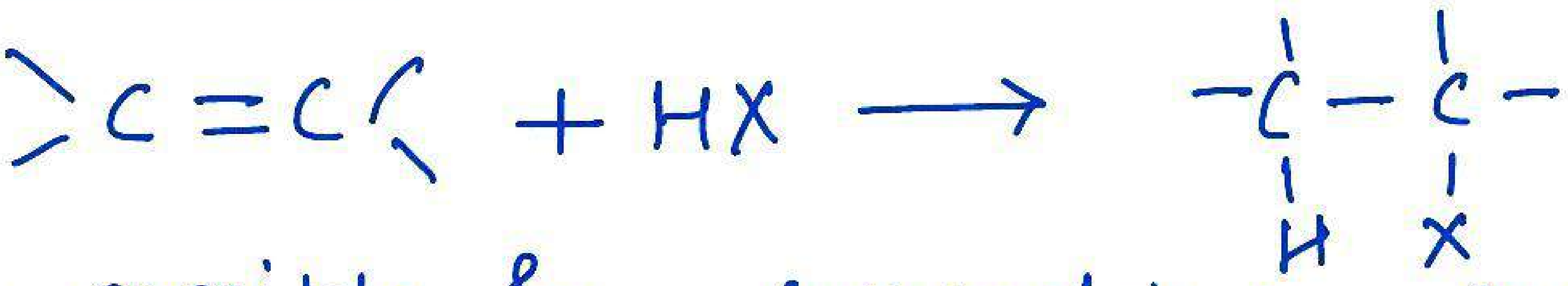


→ Both are highly reactive and this can be explained in terms of stabilisation by resonance

$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$



From Alkenes



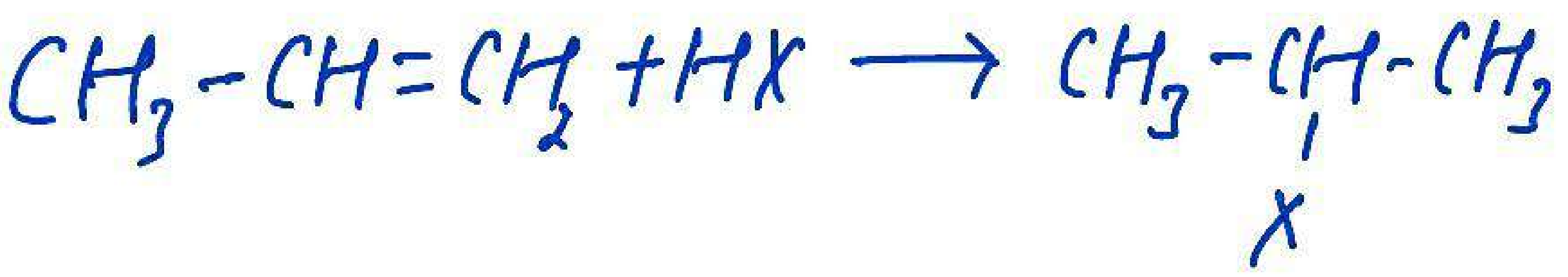
$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

- It is possible in symmetrical alkenes (−CH=CH−)

Markovnikov's Rule:-

In unsymmetrical alkenes, the −ve part of the addendum goes to that carbon having lower no. of hydrogen

नटखट	Negative (⟷)
लाल	lower
हलवाई	Hydrogen

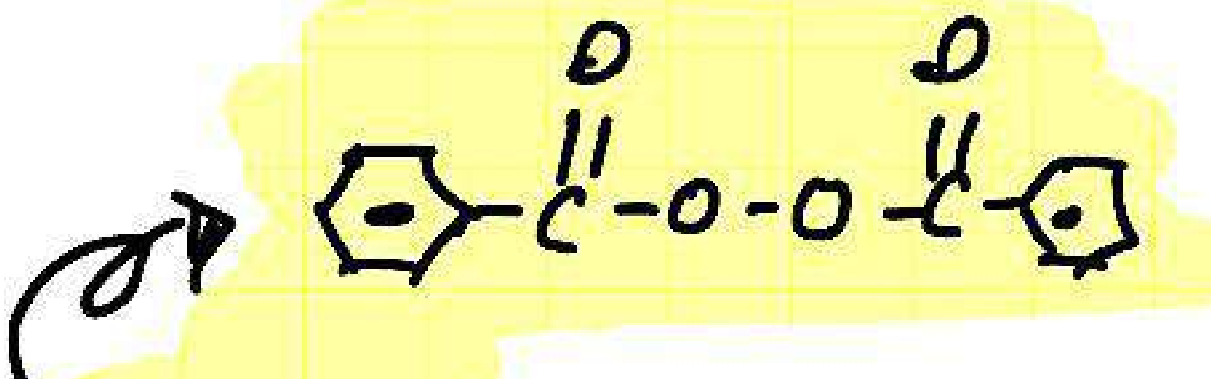


$$CH_3-CH=CH_2 + HX \longrightarrow CH_3-\underset{X}{CH}-CH_3$$

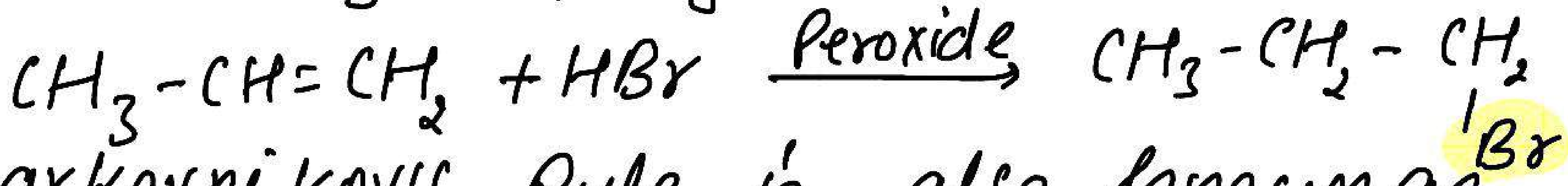
ANTI-MARKONIKOV'S RULE:-

↳ Applicable to HBr

↳ takes place in the presence of organic peroxide



In unsymmetrical alkenes, the negative part of the additive goes to that carbon having higher no. of hydrogen



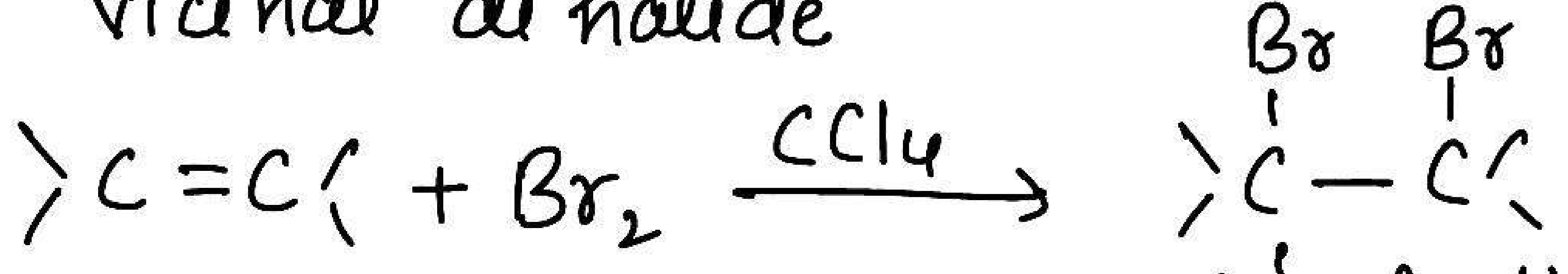
$$CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3-CH_2-\underset{Br}{CH_2}$$

Anti-markovnikov's Rule is also known as peroxide effect or Kharasch effect.

नटखट	Negative (⟷)
हरा	Higher
हलवाई	Hydrogen.

Addition of Halogen:

when Br_2 & Cl_2 is added to alkenes the addition occur at the double bond forming vicinal dihalide



$$>C=C< + Br_2 \xrightarrow{CCl_4} >\overset{Br}{C}-\overset{Br}{C}<$$

(vicinal dihalides)

Note This test is used to check unsaturation because reddish brown colour of Br_2 disappeared when reacts with alkene

• By Halogen Exchange:-

$$R\text{-}X + NaI \xrightarrow[Heat]{Acetone} R\text{-}I + NaX \quad (X = Cl, Br)$$

Finkelstein Reaction

- Fluoroalkanes are difficult to prepare directly these are prepared by treating alkyl chloride and bromide with inorganic fluoride such as (Hg_2F_2, AgF, CoF_3, SbF_3) and this reaction is termed as **swarts reaction**

$$CH_3\text{-}Br + AgF \longrightarrow CH_3\text{-}F + AgBr$$

• From Silver Salt of Acids:-

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr$$

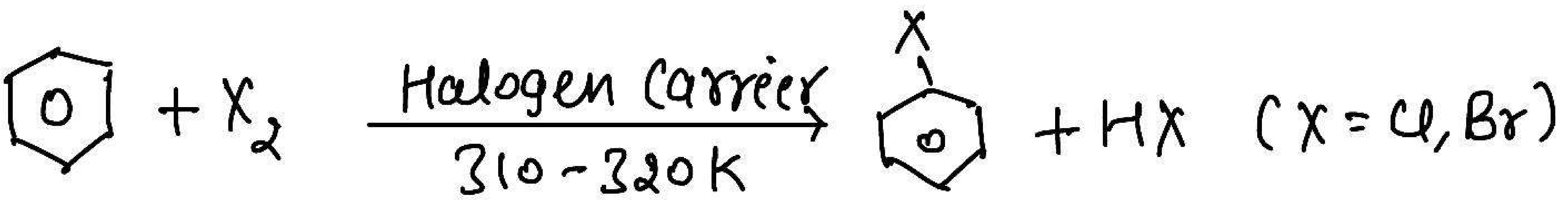
"Borodine Hunsdiecker Reaction"

$$2CH_3COOAg + I_2 \xrightarrow{CCl_4} CH_3COOCH_3 + CO_2 + 2AgI$$

"Birnbaum Simonini Reaction"

Methods of Preparation of Haloarenes

Electrophilic Substitution of Arenes OR Direct Halogenation of aromatic ring:



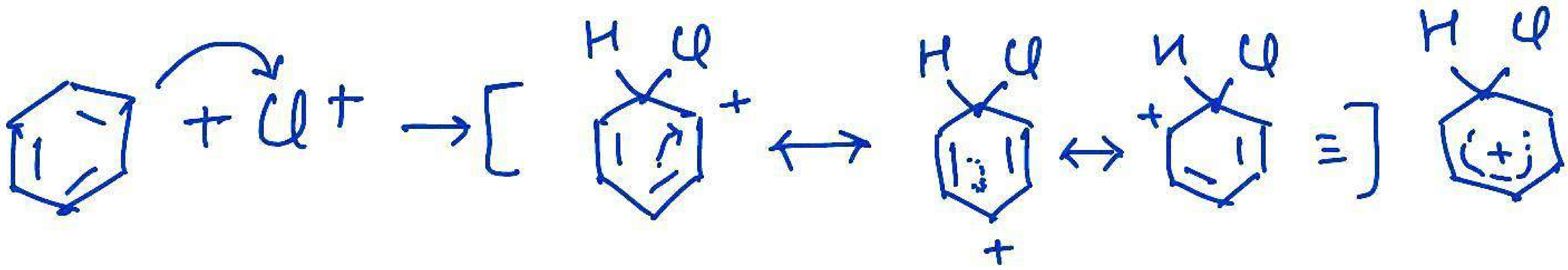
{Here Halogen carrier → $FeCl_3$ / $FeBr_3$ / $AlCl_3$
LEWIS ACID }

Mechanism:-

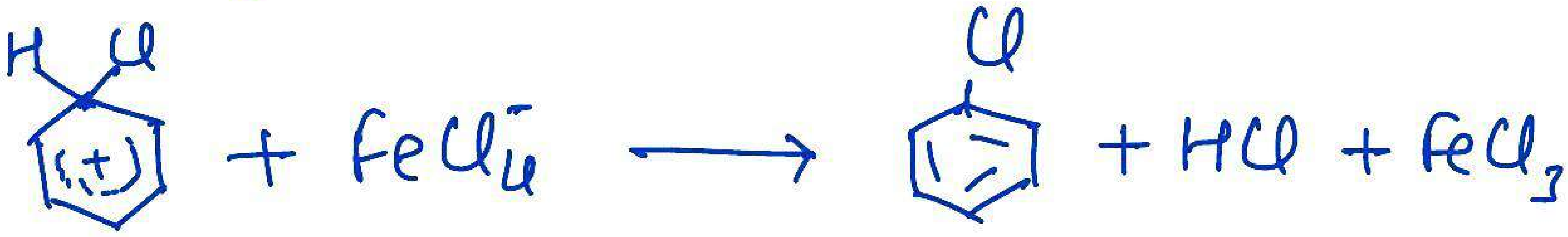
Step-1 Generation of electrophile

$$Cl_2 + FeCl_3 \longrightarrow FeCl_4^- + Cl^+$$

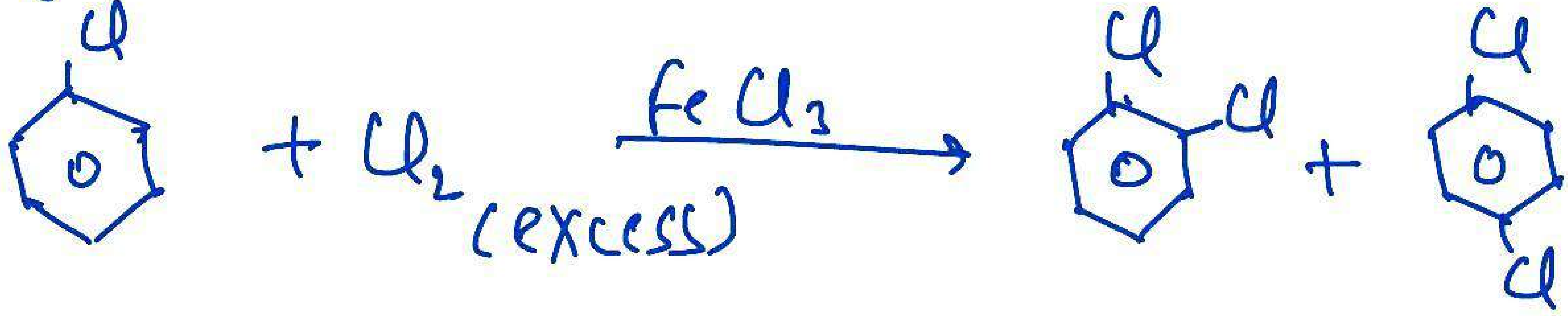
Step-2 Formation of carbocation intermediate



Step-3 loss of proton from the intermediate

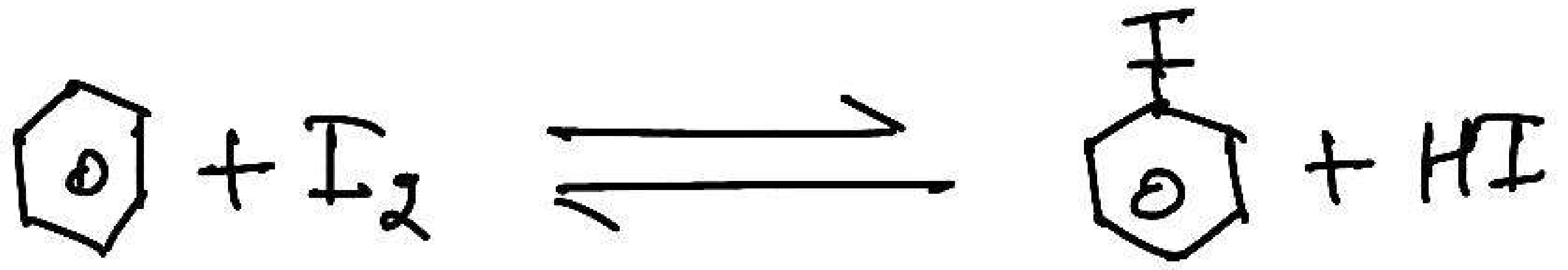


If excess of Halogen is used, the second halogen attached to ortho & para position



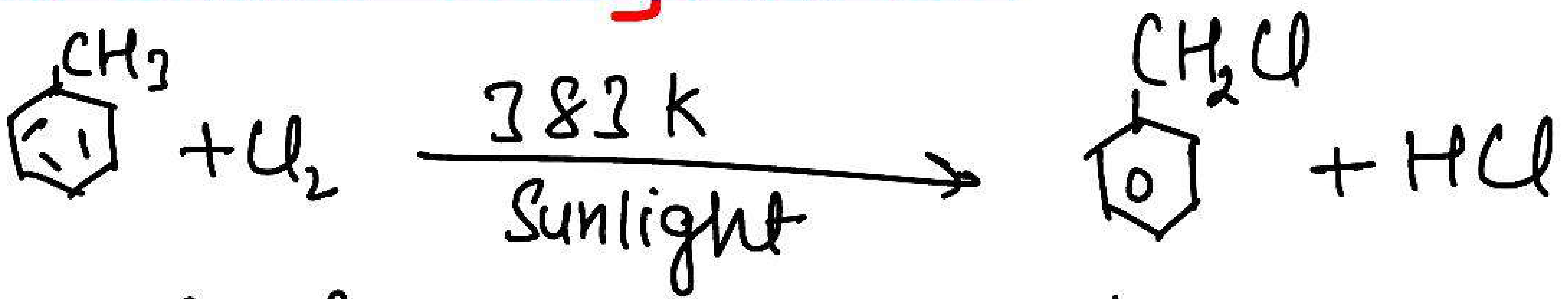
Note → The reaction with fluorine is violent or vigrous and can not be controlled

→ The reaction with I_2 is not possible because when product is formed, HI reduce to back



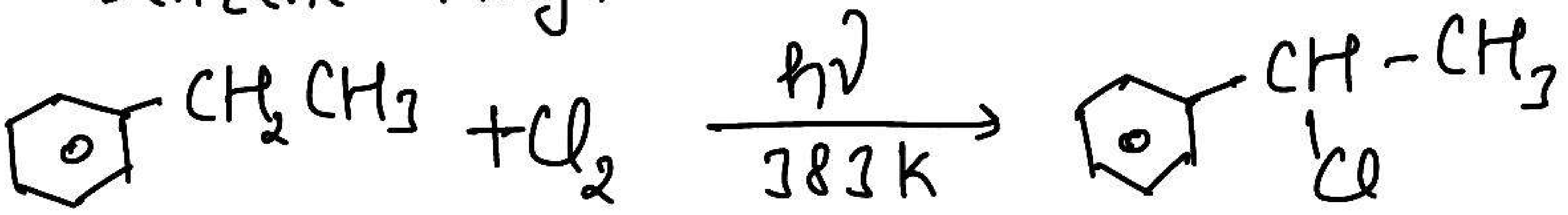
→ So the reaction is carried out in the presence of oxidising agent (HIO_3, HgO) to oxidise HI.

Side Chain Halogenation:



- If Cl_2 is in excess than all "H" are replaced by "Cl"

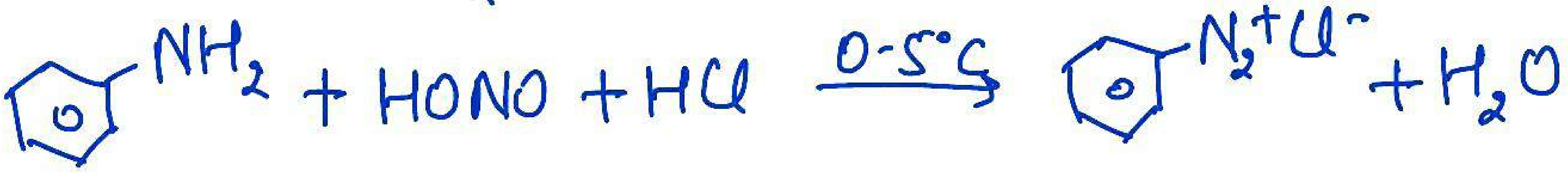
when the side chain is larger than a methyl group, halogenation occur at C-atom next to benzene ring.



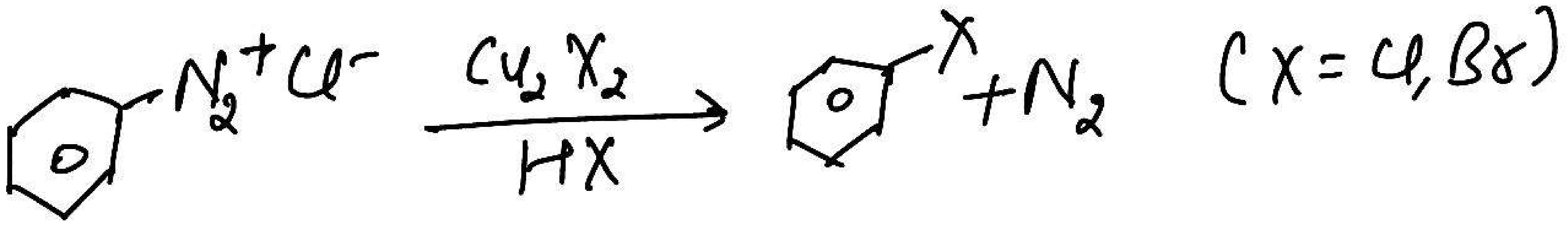
From Diazonium Salt:

- Diazotization Reaction

$$NaNO_2 + HCl \longrightarrow NaCl + HONO$$

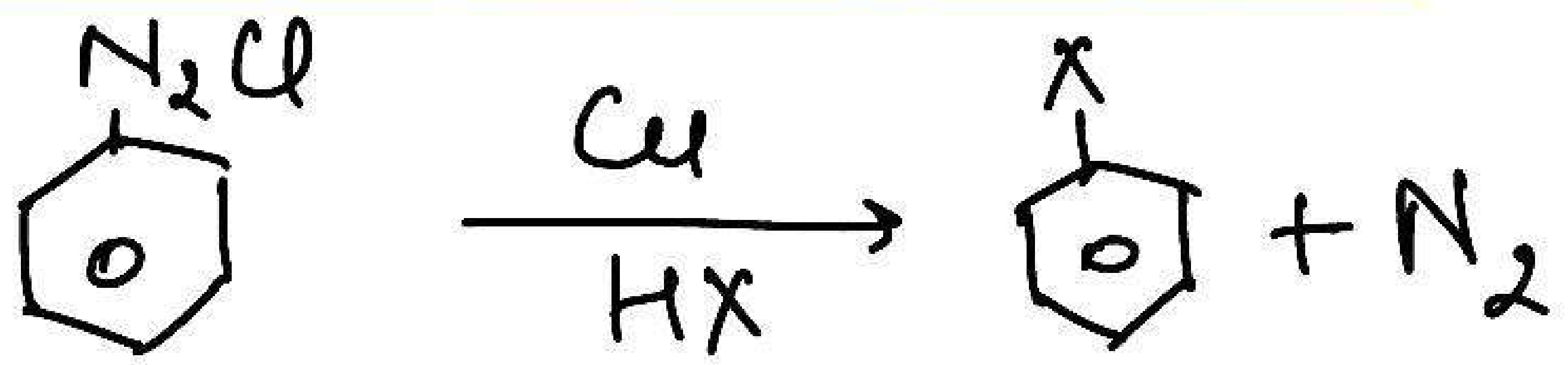


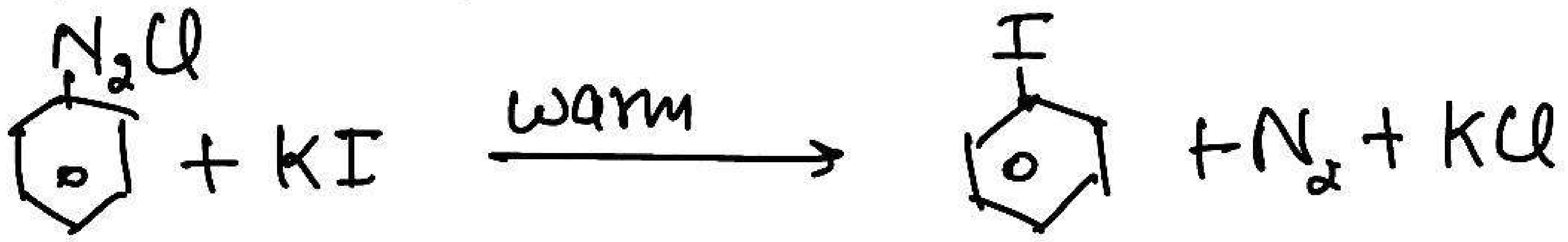
Sandmeyer Reaction



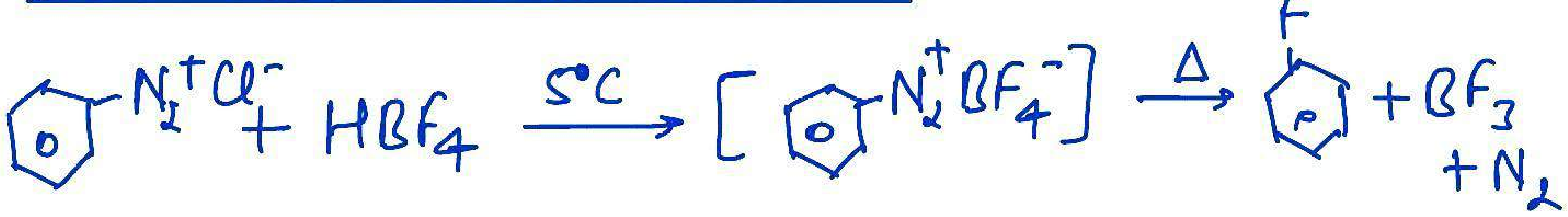
(X = Cl, Br)

Gattermann Reaction

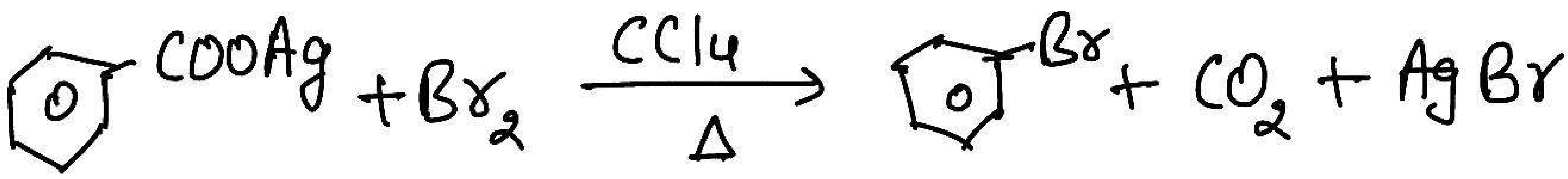




Balz- Schiemann Reaction



from Silver Salt of Aromatic Acid:



Note Haloarenes can't be prepared from phenol because it is difficult to replace −OH group. This is due to resonance in phenol.

Physical Properties of Haloalkanes :-

→ In general haloalkanes are colourless (when pure) sweet smelling liquids.

→ They are slightly soluble in water because of low tendency to form Hydrogen Bond.

→ Density : F < Cl < Br < I

more no. of H-atom, less is density

e.g $CH_2Cl_2 < CHCl_3$

→ Boiling Point

$B.Pt \propto$ Mol. Mass

$B.Pt \propto \frac{1}{\text{Branching}}$

Physical Properties of Haloarenes:

1. These are generally colourless liquid or crystalline solid.
2. The aryl halides are heavy than water. insoluble in water but soluble in organic solvents.
3. The m.pt & b.pt of aryl halides are nearly the same of alkyl halide containing the same no. of carbon atoms.

B.Pt → ortho > Para > meta
M.Pt → Para > ortho > meta

Chemical Properties Of Haloalkanes

*) **Nucleophilic Substitution Reaction** :-

$$-\overset{|}{\underset{|}{C}}-X \longrightarrow -\overset{|}{\underset{|}{C}}{}^{\delta+}-X^{\delta-} + Nu^{\ominus} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^{\ominus}$$

Reactivity order :- R-I > R-Br > R-Cl > R-F

Types
- S_N^1 (Unimolecular Nucleophilic Sub. Rxn)
- S_N^2 (Bimolecular Nucleophilic Sub. Rxn)

S_N1 $R-X + Nu^{\ominus} \longrightarrow R-Nu + X^-$

Rate ∝ [R-X]

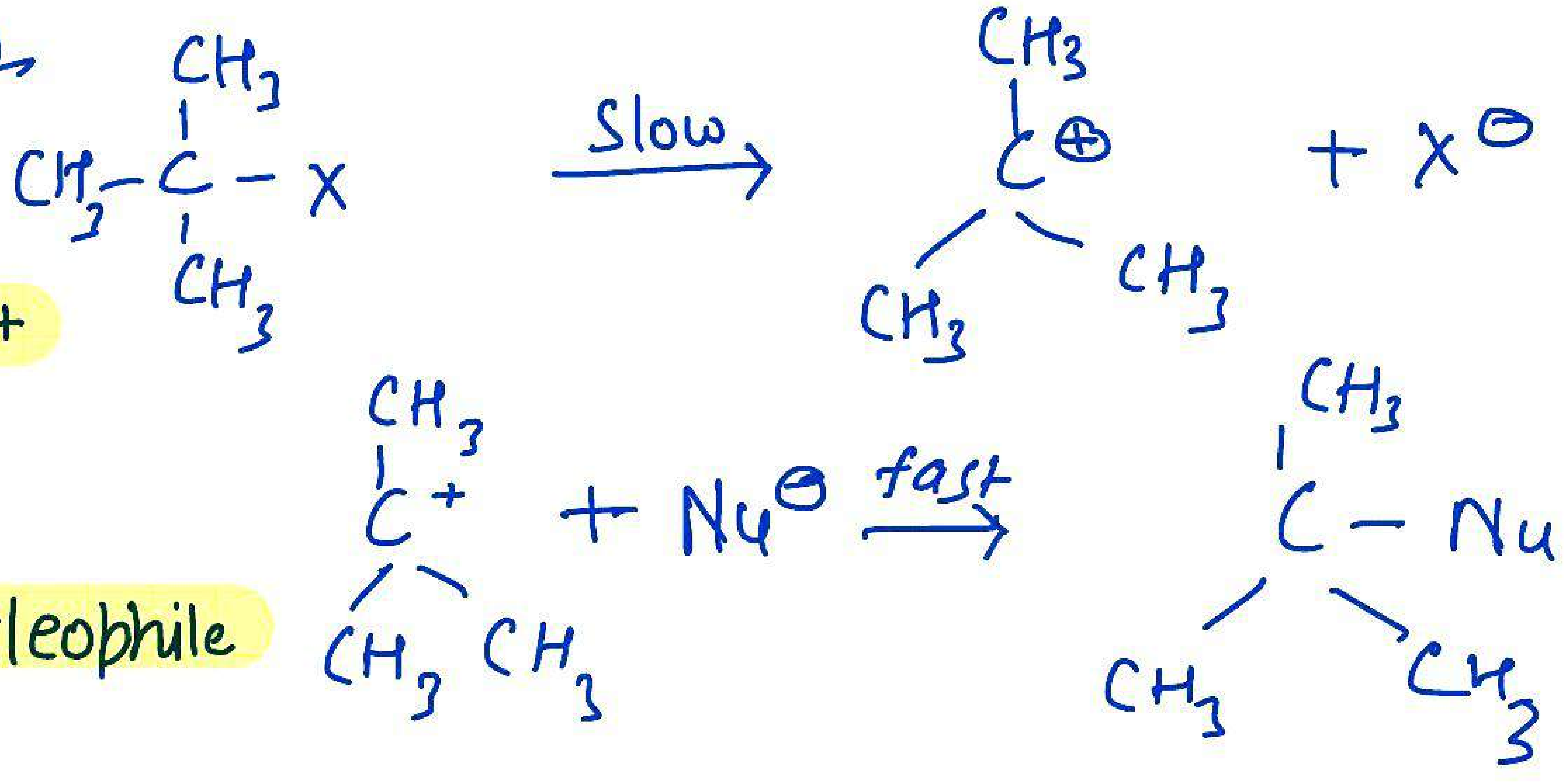
Mechanism

Step-1

Formation of C^+

Step-2

Attack of Nucleophile



- Retention as well as inversion of configuration takes place

Order of SN¹ reaction $(CH_3)_3C-X > (CH_3)_2CH-X > CH_3-CH_2-X > CH_3-X$

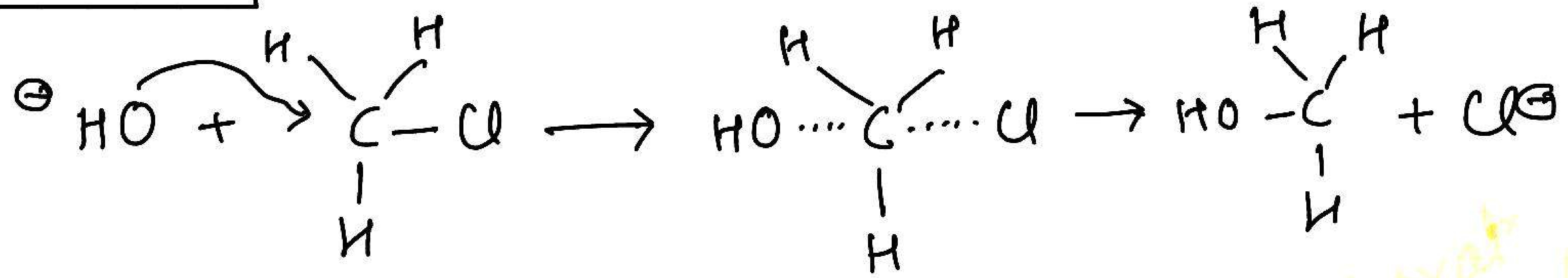
Allylic and benzylic halides show higher reactivity towards the SN¹ reaction. The carbocation thus formed get stabilised through resonance.

SN² (Bimolecular Nucleophilic Substitution Rxn)

$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X^{\ominus}$$

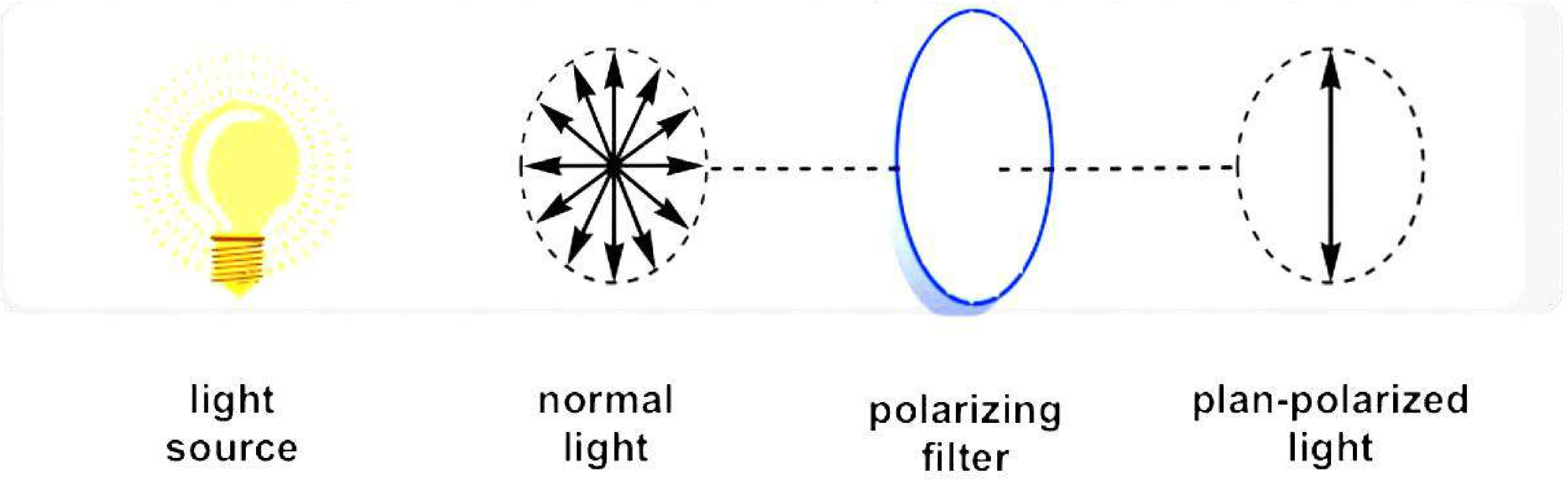
$$Rate \propto [R-X][Nu^{\ominus}]$$

Mechanism



Order of SN² reaction :- $CH_3X > 1° > 2° > 3°$

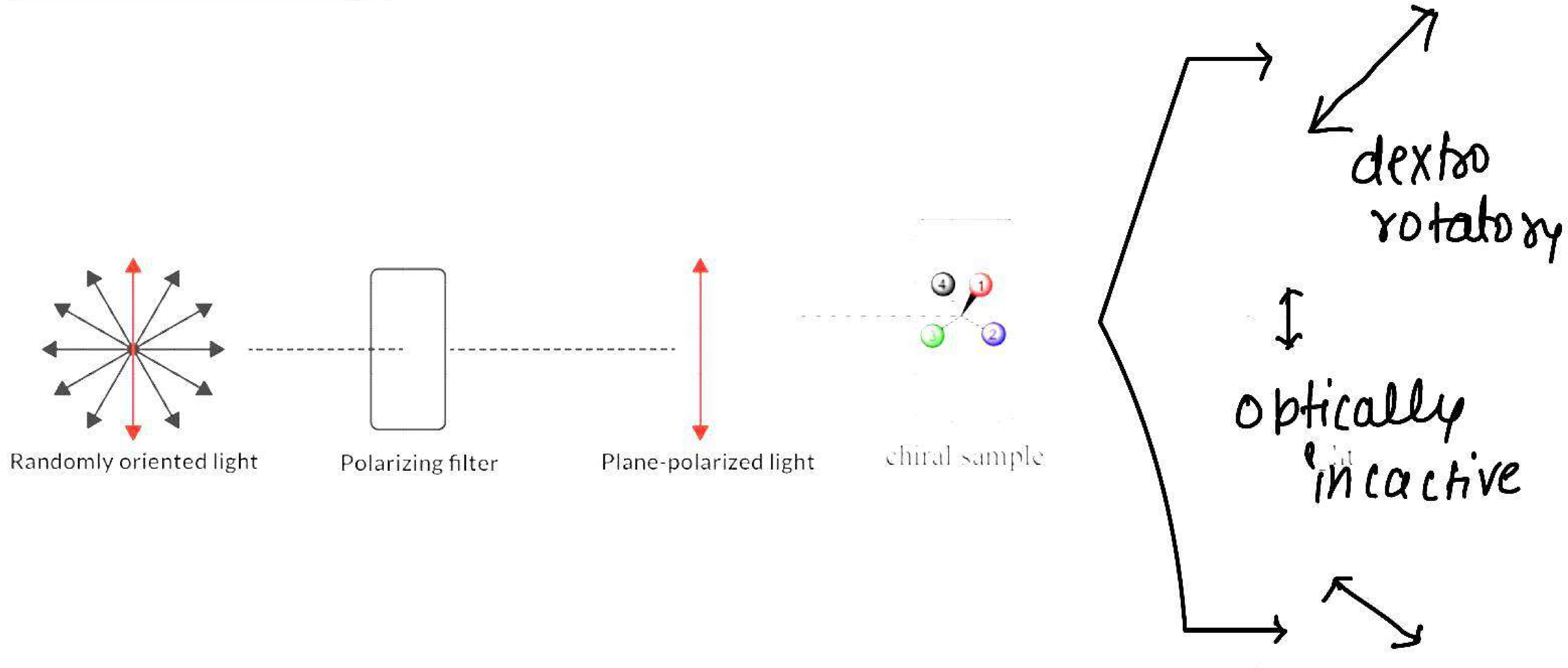
- inversion of configuration takes place



A beam of ordinary light consist of electromagnetic waves vibrating in all planes when pass through Nicol prism, vibrates in one plane called PPL (Plane polarised light)

Dextro-Rotatory - which rotate PPL towards right

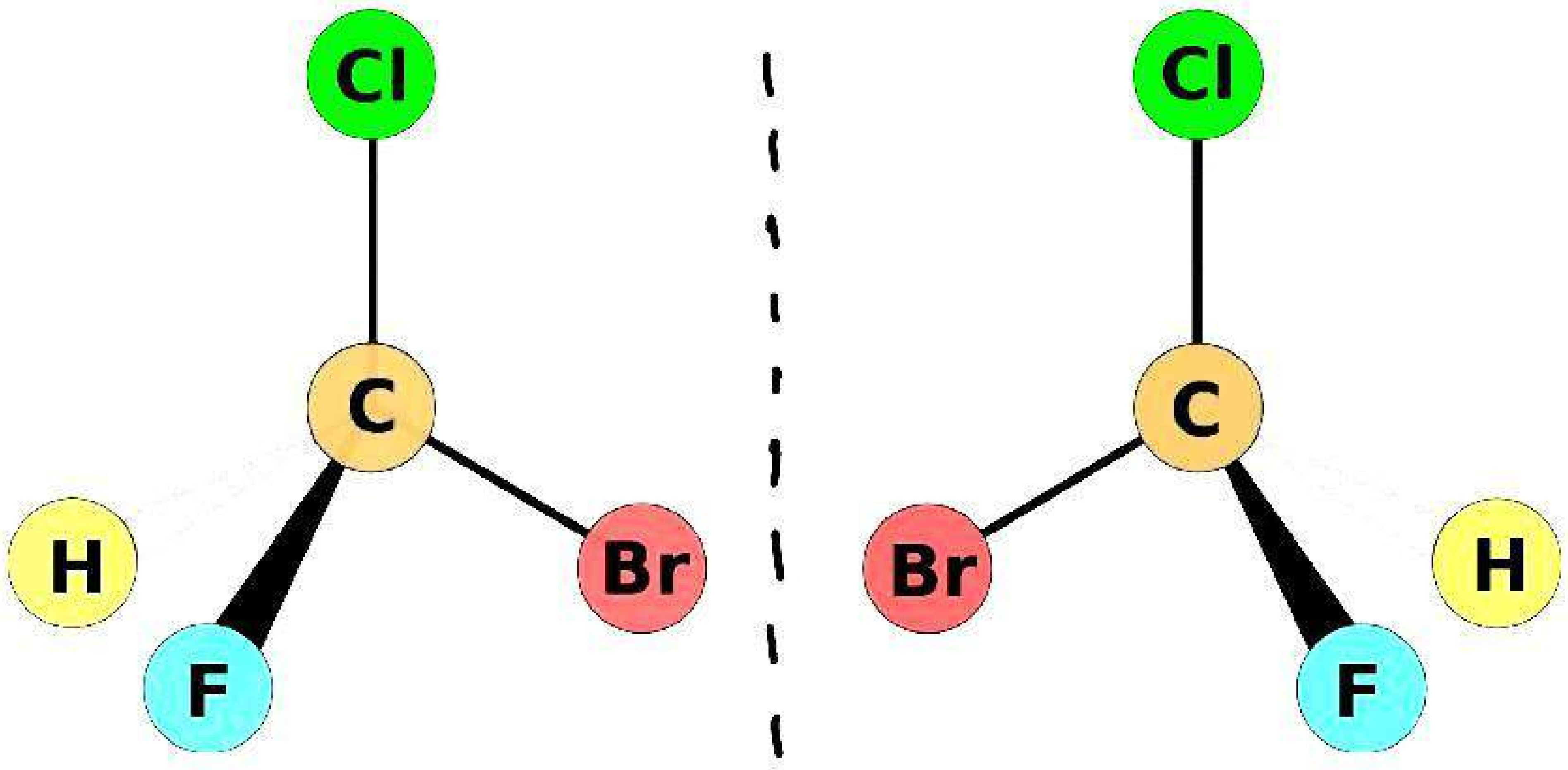
Levo-Rotatory - which rotate PPL towards left.



Racemic Mixture equimolar mixture of d and l, so that net rotation of PPL is zero.

Enantiomers

- The optical isomers are called enantiomers.
- These are distinguished by +/-, D/L or more correctly R/S.
- A 50/50 mixture of the two enantiomers is called a racemic mixture or a racemate.



Nucleophilic Substitution Reaction

Reagent	Nucleophile (Nu^-)	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
$R'^- M^+$	R'^-	RR′	Alkane

Substitution by Amino Group:

$$R-X + NH_3 \longrightarrow R-NH_2 + HX$$

when haloalkanes is in excess amount then all three of NH_3 is replaced by group (R)

$$\underset{(excess)}{R-X} + NH_3 \longrightarrow R_3N + HX$$

"Hoffman Ammonolysis reaction"

- $R-X + KNO_2 \xrightarrow{\Delta} R-O-N=O + KX$

$$R-X + AgNO_2 \xrightarrow{\Delta} R-N\overset{=O}{\underset{\rightarrow O}{}} + AgX$$

• Substitution by -OH group.

$$R\text{-}X + \underset{\text{AgOH}}{\overset{}{KOH}}\ (\text{or}) \xrightarrow{\Delta} R\text{-}OH + KX \text{ or } AgX$$

• Substitution by alkoxy group

$$R\text{-}X + \overset{\oplus}{Na}\text{-}OR \xrightarrow{\Delta} R\text{-}O\text{-}R' + NaX$$

This reaction is known as Williamson Synthesis

• Substitution by Cyano Group

$$R\text{-}X + KCN \longrightarrow R\text{-}CN + KX$$

$$C_2H_5\text{-}I + KCN \longrightarrow C_2H_5CN$$

$$C_2H_5CN \xrightarrow{\text{Conc. HCl}} CH_3CONH_2$$

$$C_2H_5CN \xrightarrow{\text{Dil. HCl or NaOH}} CH_3COOH$$

$$C_2H_5CN \xrightarrow[\text{LiAlH}_4,\ \text{Ni/H}_2]{\text{Na, }C_2H_5\text{-}OH} CH_3CH_2NH_2$$

Mendius Reaction: The formation of 1° amines by reduction with nascent hydrogen obtained by the action of sodium on alcohol.

Substitution by Isocyanide group:

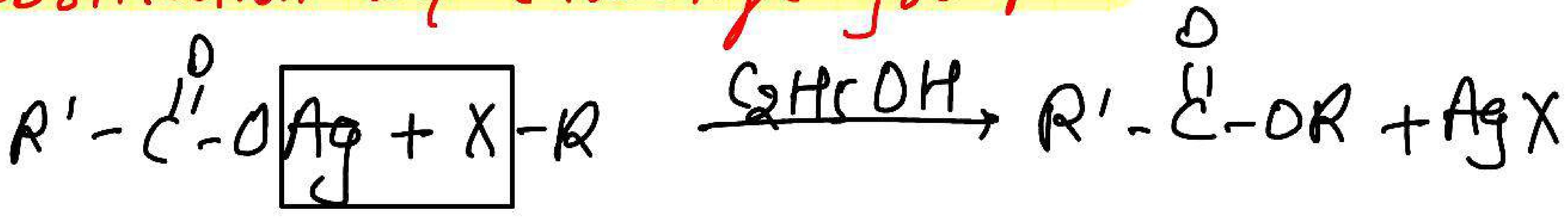
$$R\text{-}X + AgCN \longrightarrow R\text{-}NC + AgX$$

Note Ag activate N-group & K activate C-group

• Substitution by azide group:

$$R\text{-}X + NaN_3 \longrightarrow R\text{-}N_3 + NaX$$

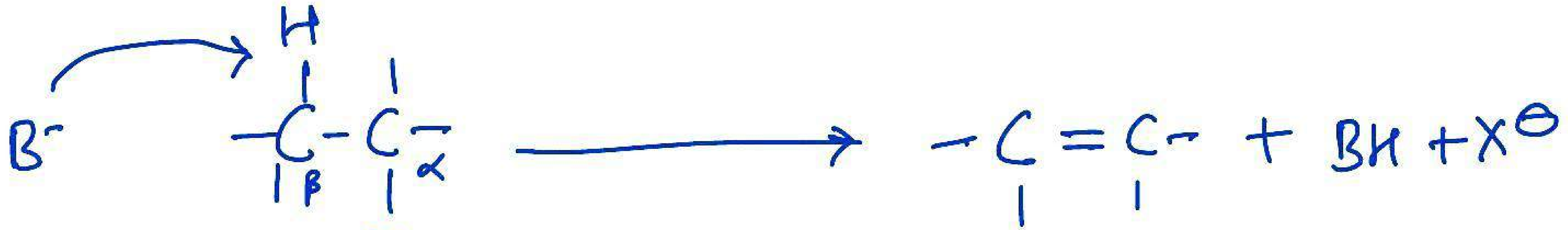
• Substitution by Carboxyl group:



$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\boxed{Ag + X}\text{-}R \xrightarrow{C_2H_5OH} R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR + AgX$$

· Elimination Reaction (Dehydrogenaton)

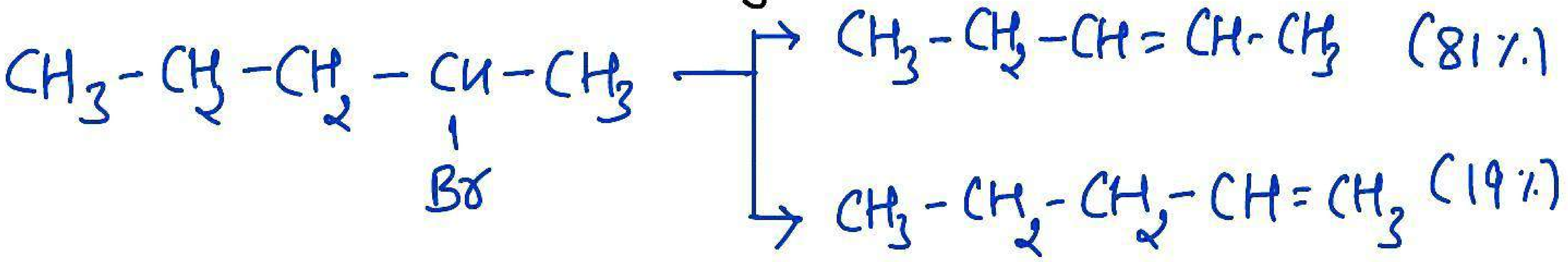
when a haloalkane with β-H atom is heated with alc. KOH there is an elimination of H-atom from β-C and a halogen from α-C, result an alkene is formed



$$B^{-}\quad -\overset{H}{\underset{\beta}{C}}-\overset{|}{\underset{X}{C}}-_{\alpha} \longrightarrow -\underset{|}{C}=\underset{|}{C}- + BH + X^{\ominus}$$

(here B- base, X- leaving group)

If there is a possibility of formation of more than one alkene due to availability of more than one β-H usually one alkene is formed as major product.



$$CH_3-CH_2-CH_2-\underset{Br}{CH}-CH_3 \longrightarrow \begin{cases} CH_3-CH_2-CH=CH-CH_3 \ (81\%) \\ CH_3-CH_2-CH_2-CH=CH_3 \ (19\%) \end{cases}$$

- Acc. to "Saytzeff's Rule", the alkene with greater no. of alkyl group is preferred [$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH_2$]

Note → A primary alkyl halide prefer a S_N2 reaction.

→ A sec. halide prefer S_N2 & S_N1 depending upon the strength of base/$Nu^{\ominus}$ and a tert. halide prefer S_N1

Reactivity → 3° > 2° > 1° > CH_3-X cas carbocation

→ Alcoholic KOH causes elimination, while aqueous solution of base leads to substitution

⇒ Reaction with active metals-

⇒ Reaction with Magnesium

$$R-X + Mg \xrightarrow[\text{ether}]{\text{Dry}} R-Mg\cdot X \quad (X \rightarrow Cl, Br, I)$$

Grignard Reagent

→ These grignard reagents are very reactive compounds. They react with any source of proton to form hydrocarbons. So it is very necessary to avoid traces of moisture from grignard reagent.

$$R-MgX + \underset{(H^+ \cdot OH^-)}{H_2O} \longrightarrow \underset{\text{Hydrocarbon}}{\underline{\underline{R-H}}} + Mg\begin{matrix} X \\ OH \end{matrix}$$

⇒ Reaction with Na (Wurtz Rxn)

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

used to prepare Symmetrical alkanes.

⇒ Reaction with Zn (Frankland Reaction)

$$2\,C_2H_5-Br + 2\,Zn \longrightarrow C_2H_5-Zn-C_2H_5 + ZnBr_2$$

diethyl zinc (frankland Reagent)

⇒ Reduction Reaction:

$$R-X + 2[H] \longrightarrow R-H + HX$$

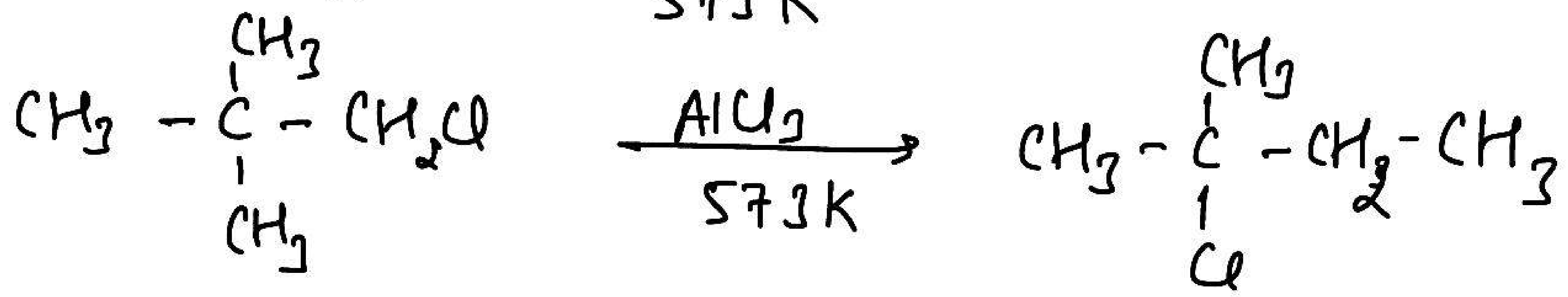
$$C_2H_5Cl + 2[H] \longrightarrow C_2H_6 + HCl$$

⇒ Following reagents are used for reduction

Zn/HCl, Na/C_2H_5OH, $LiAlH_4$, Red P/HI

Rearrangement Reaction

$$CH_3CH_2CH_2Cl \xrightarrow[573\,K]{AlCl_3} CH_3-\overset{Cl}{CH}-CH_3$$



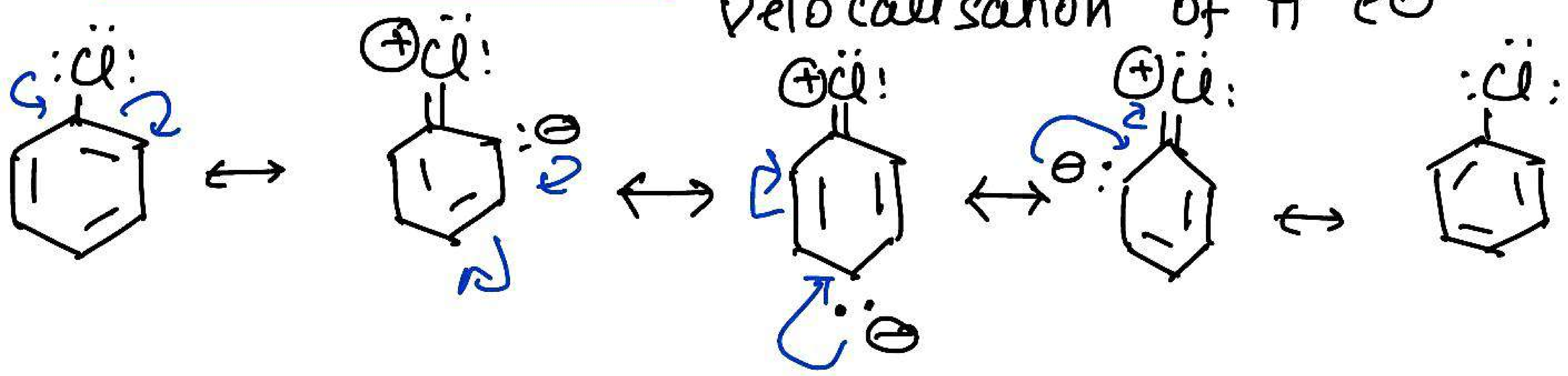
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl \xrightarrow[573\,K]{AlCl_3} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2-CH_3$$

Chemical Proberties of Haloarenes:

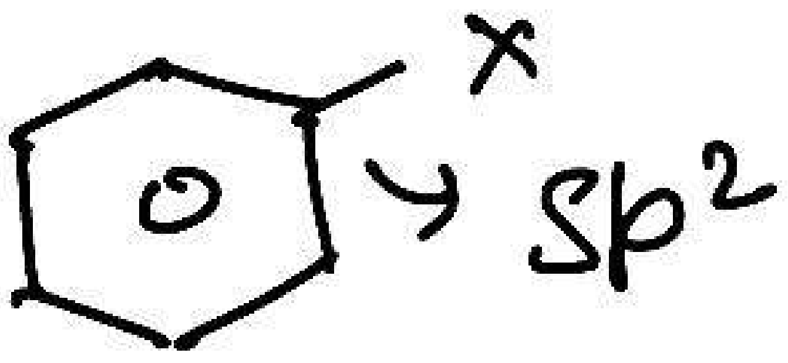
Haloarenes are less reactive than Halo alkanes due to

1. Resonance Effect →

Delocalisation of π e⊖



2. Difference in hybridisation of C-X Bond



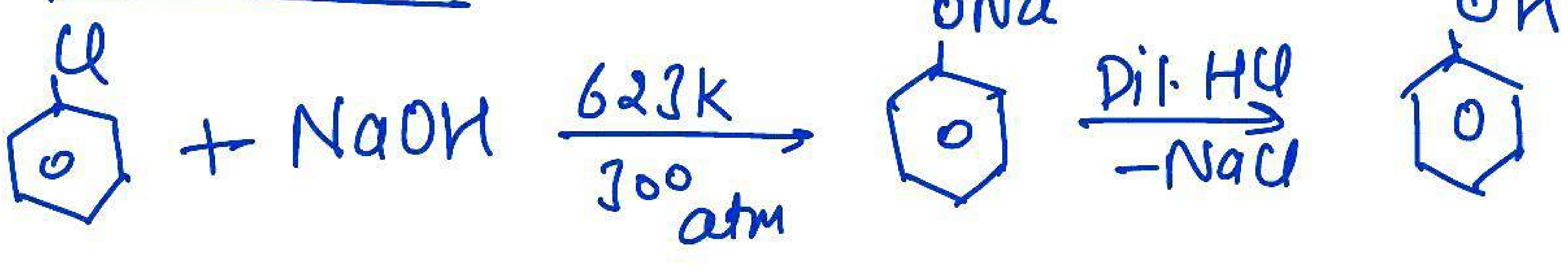
$R-\overset{sp^3}{CH_2}-X$

more s-character more electronegative, so hold e⊖ pair more tightly, so less reactive

3. Polarity of C-X Bond In C-X bond of aryl halide polarity is less, so reactivity is less

Ce→ Nucleophilic Substitution Reaction

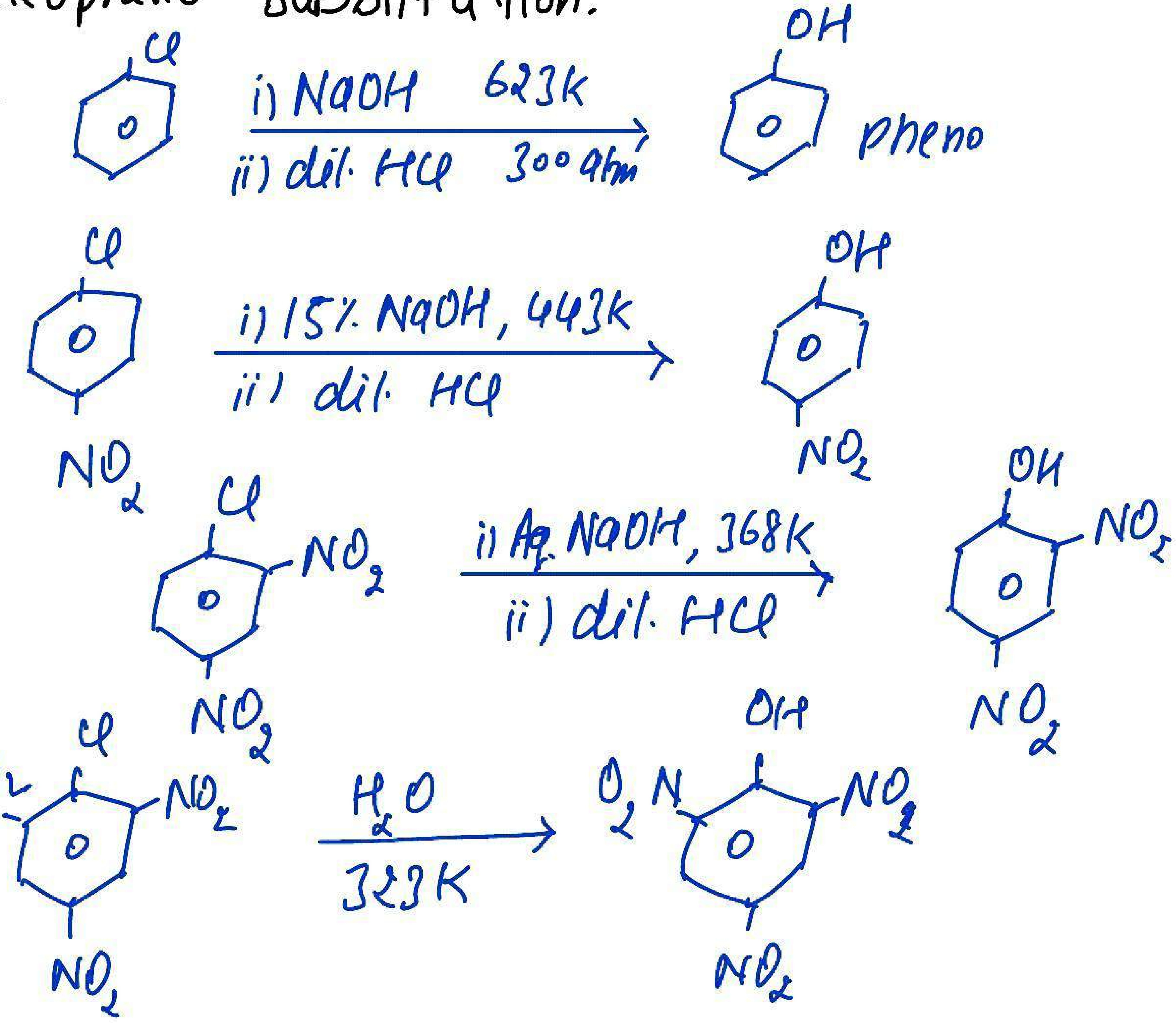
- Dow's Process



Effect of Substituent in Haloarenes on Reactivity:

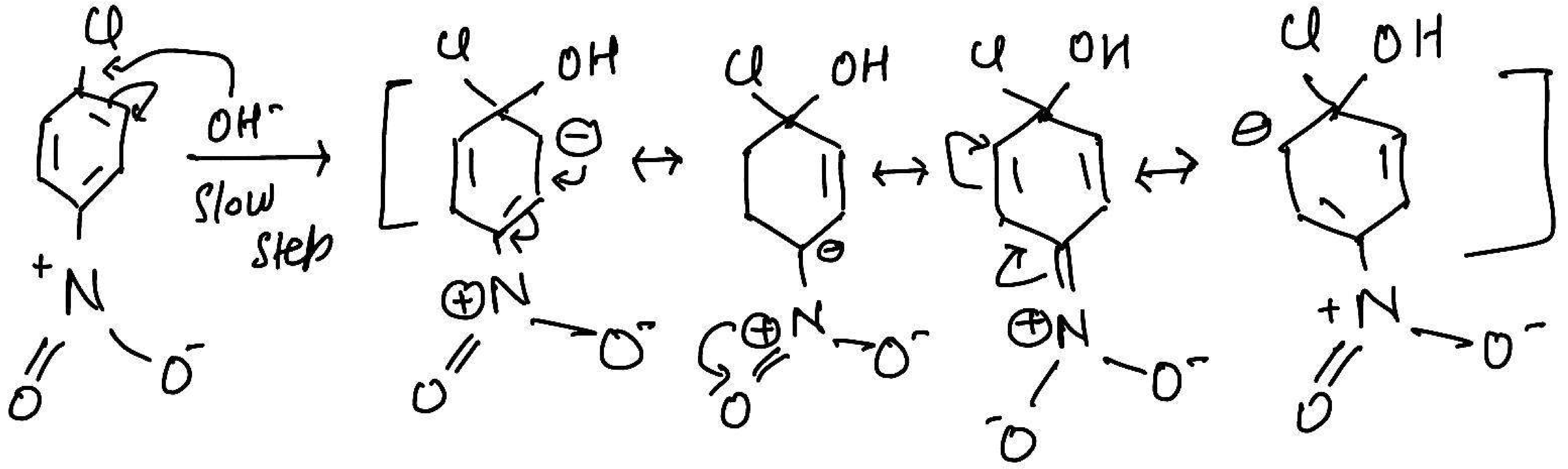
→ The presence of e⊖ withdrawing groups such as $-NO_2$, $-CN$, $-COOH$ etc. at ortho and para position to the halogen atom greatly activates the halogen towards Nucleophilic substitution.

e.g



NOTE → Nitro group ($-NO_2$) meta to the chlorine has no effect on reactivity.

Explanation :- NO_2 at para positions.



In case of ortho and para structures, one of the resonating structures bears a negative charge on the C-atom bearing the $-NO_2$ group.

These carboanions are stabilized by the $-NO_2$ group as well as π $e^{\ominus}$ of benzene ring.

However in case of m-structure, none of the resonating str. bear the -ve charge on carbon atom. bearing the $-NO_2$ group.

$\therefore$ The $-NO_2$ groups does not stabilise the carboanion and thus has no effect towards Reactivity.

Q Out of chlorobenzene and cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why?

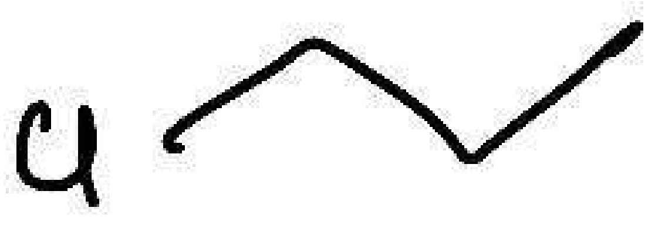
Ans. Cyclohexyl chloride is more reactive towards nucleophilic substitution reaction because C-Cl bond strength is less in cyclohexyl chloride than chlorobenzene.

In Cyclohexyl chloride, Cl-atom is bonded to sp^3 hybrid C-atom while in chlorobenzene Cl is bonded to sp^2 hybrid C-atom

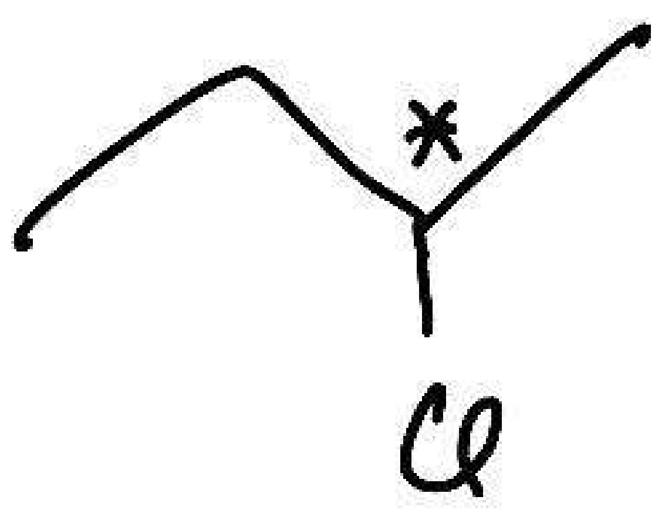
C-Cl bond is more strong in chlorobenzene and less reactive towards nucleophilic sub.

Q Identify the chiral molecule in the following pairs.

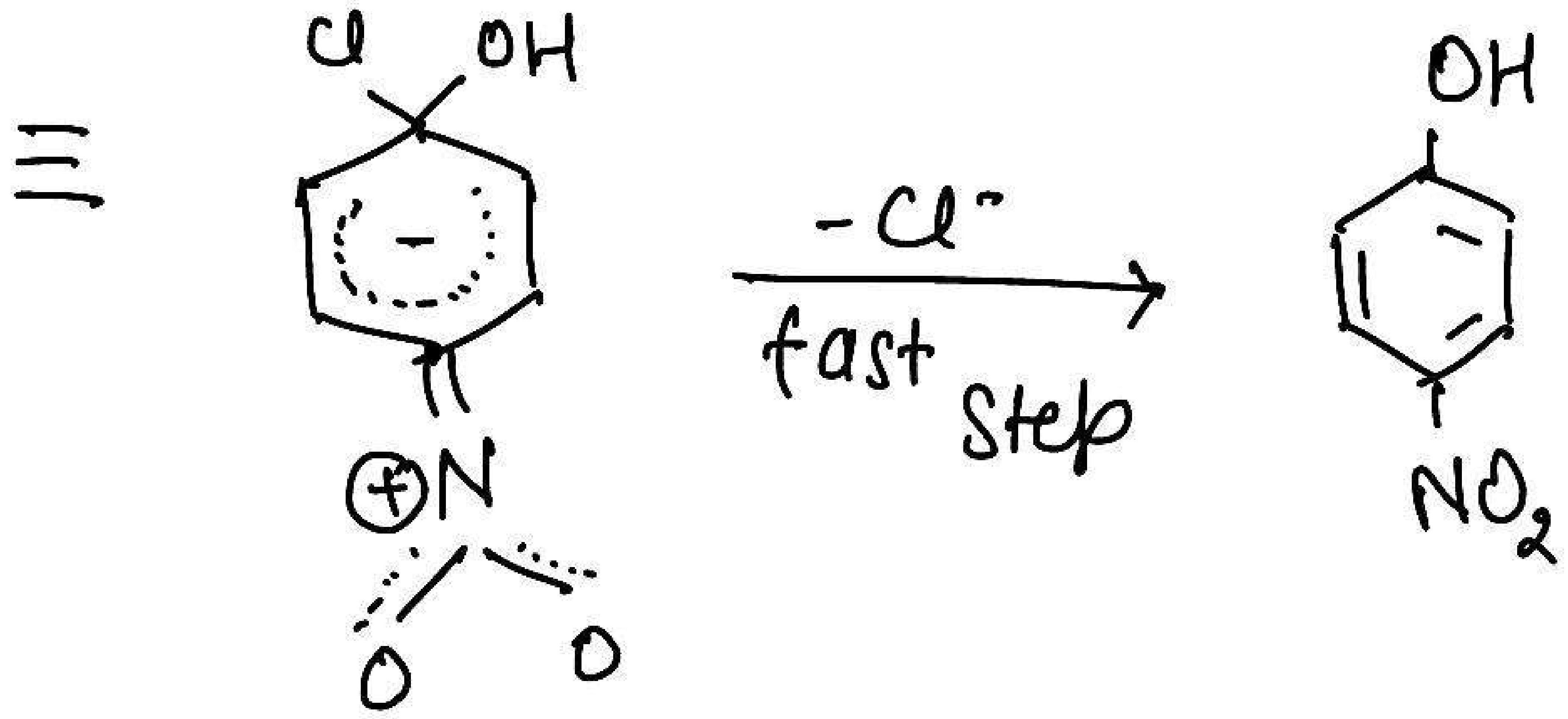
and



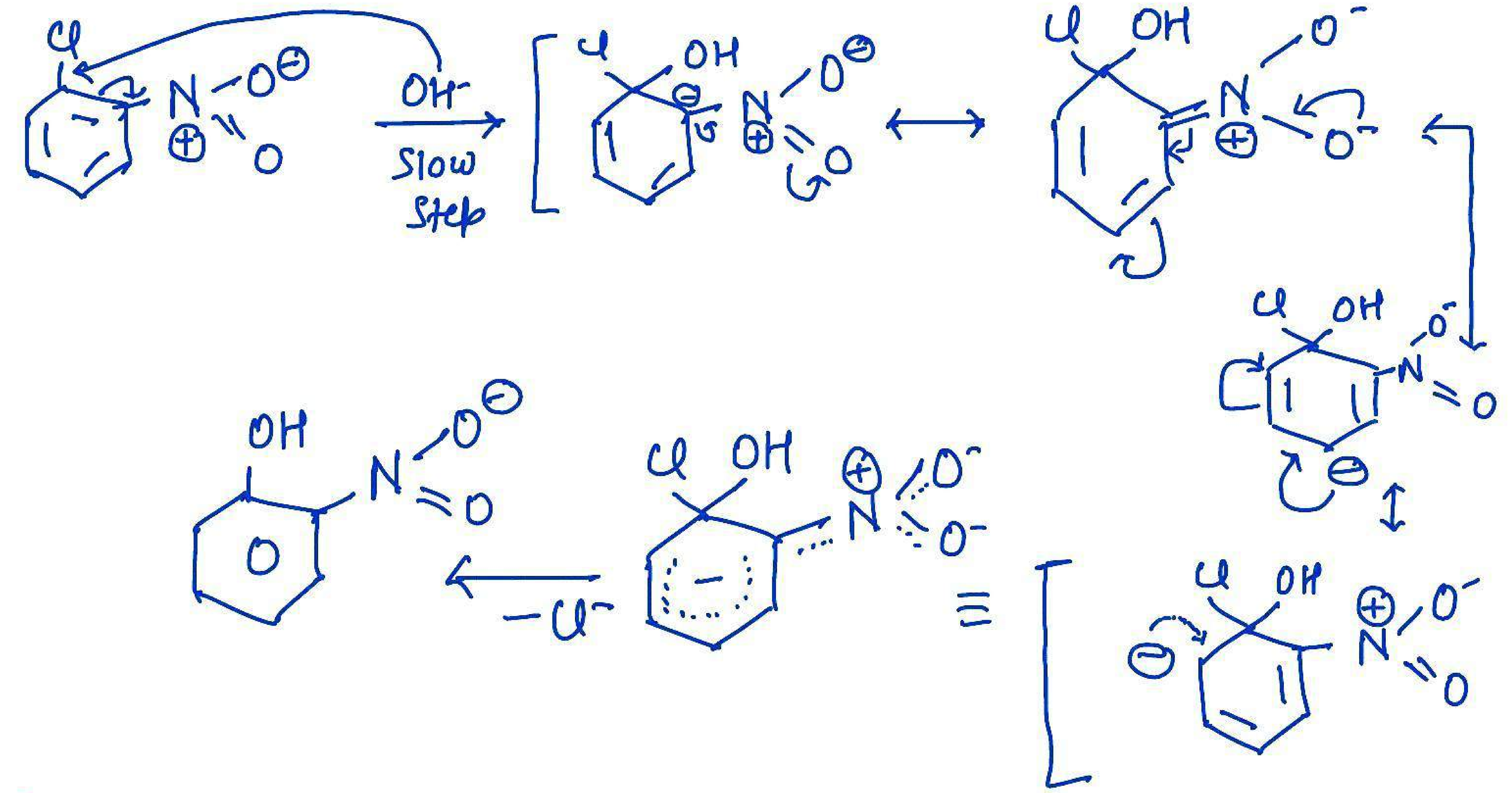
Ans.



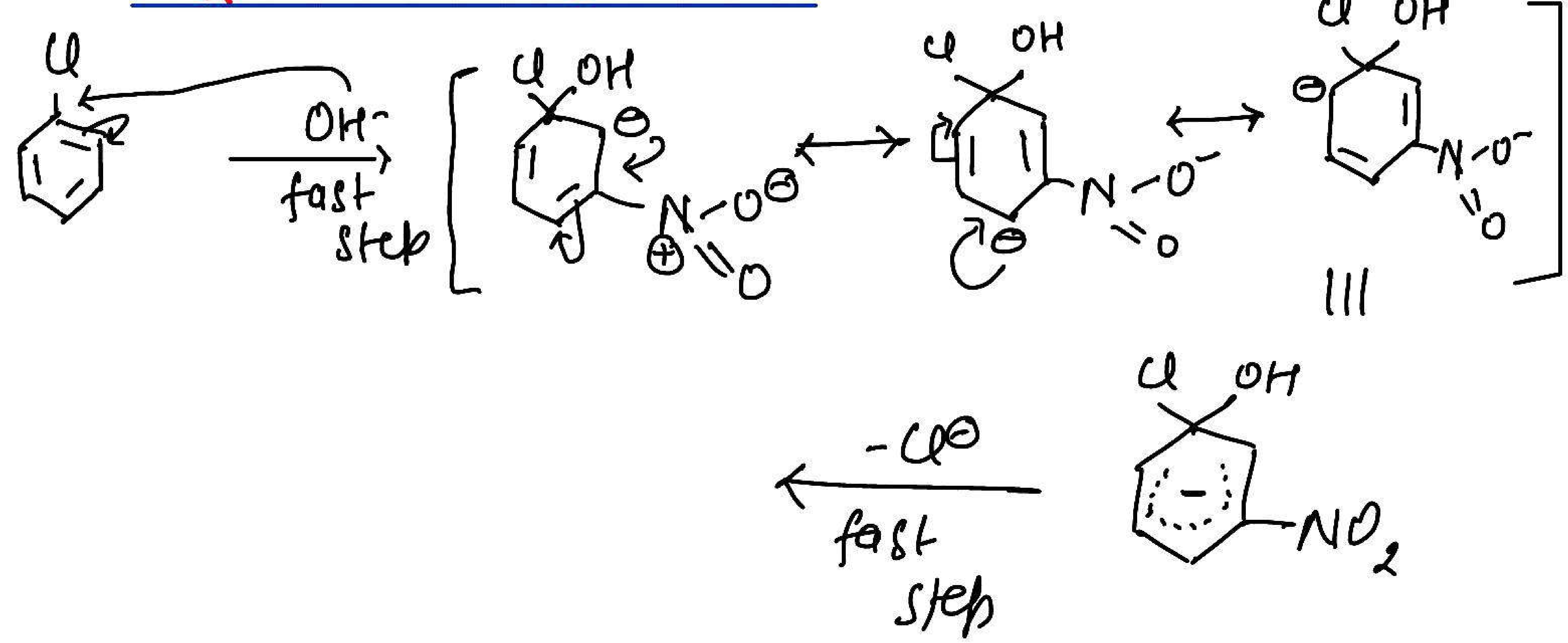
is chiral molecule as it contains an asymmetric C-atom which is denoted by *.



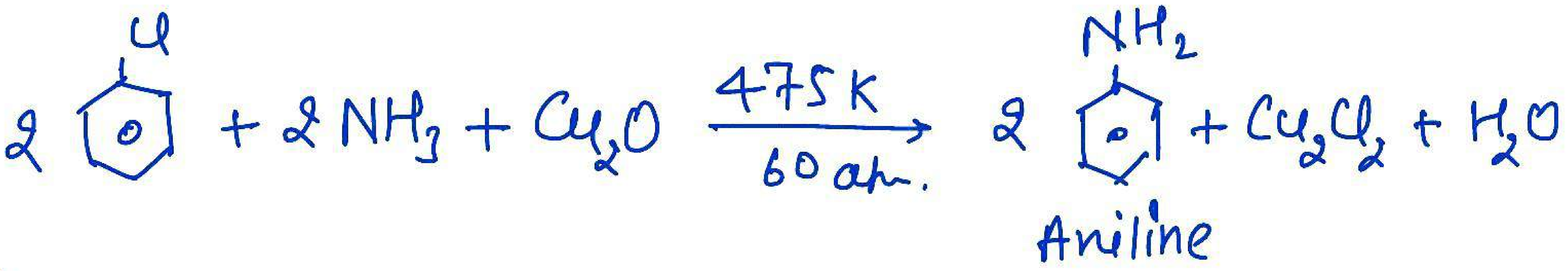
Ce → NO_2 at Ortho position :



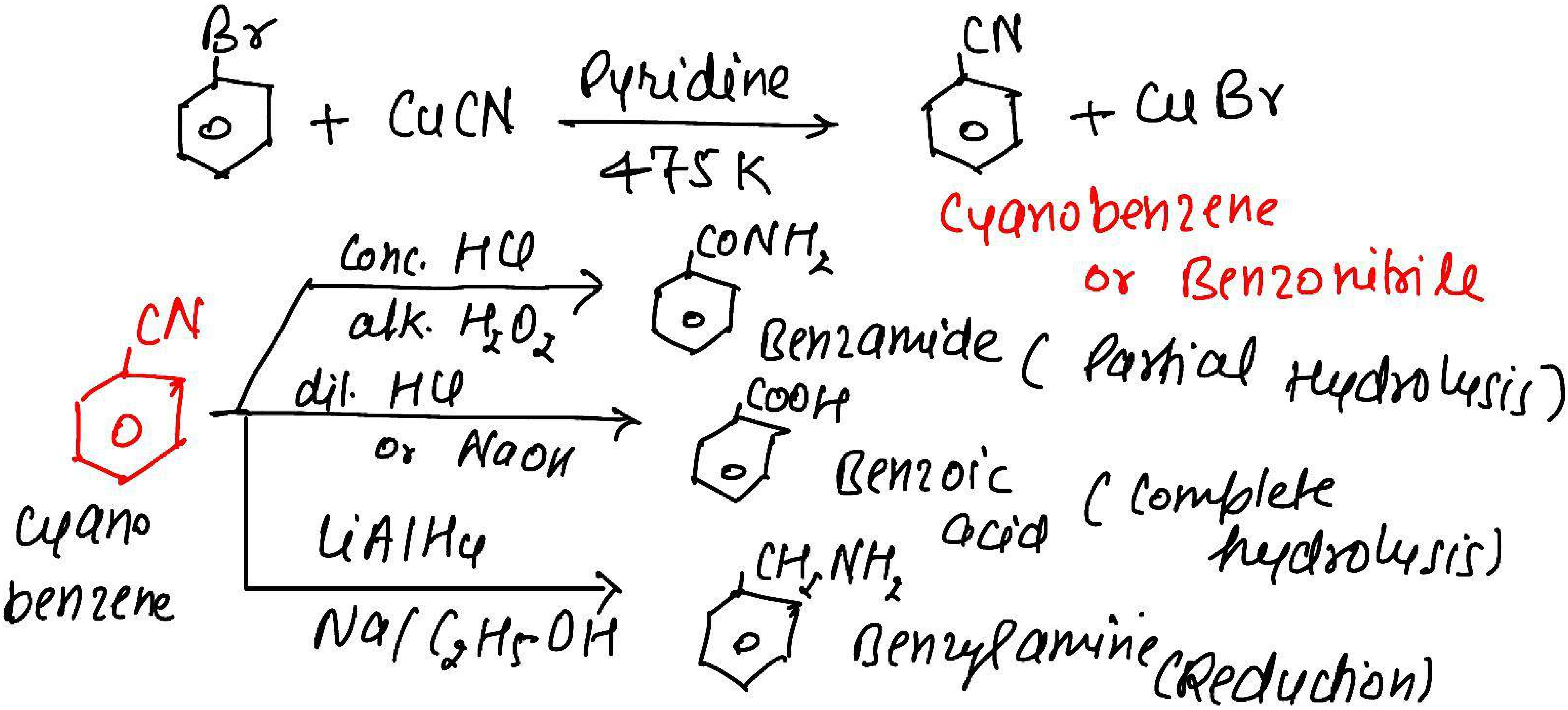
Ce → NO_2 at meta position



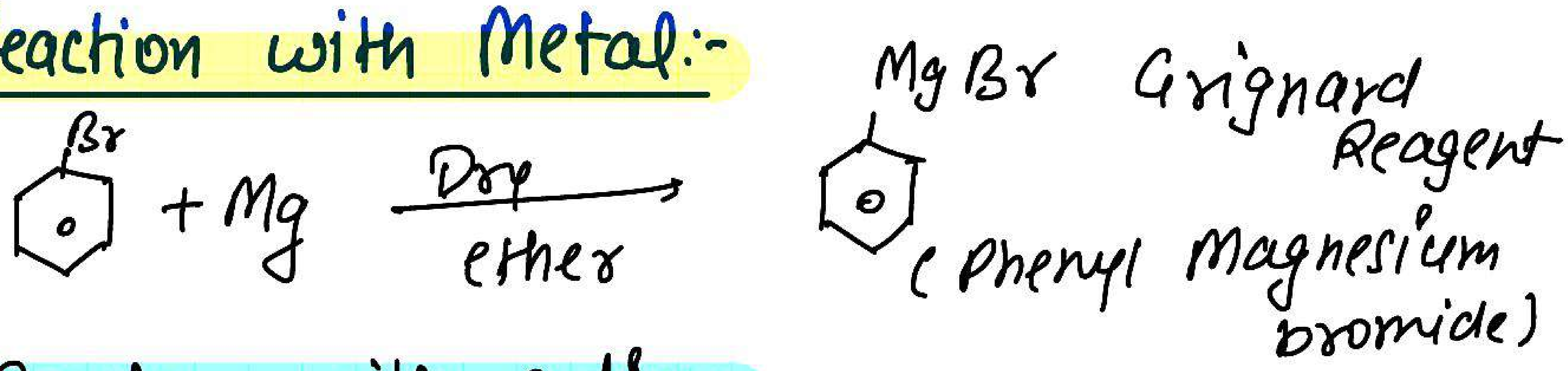
Substitution of Amino Group :



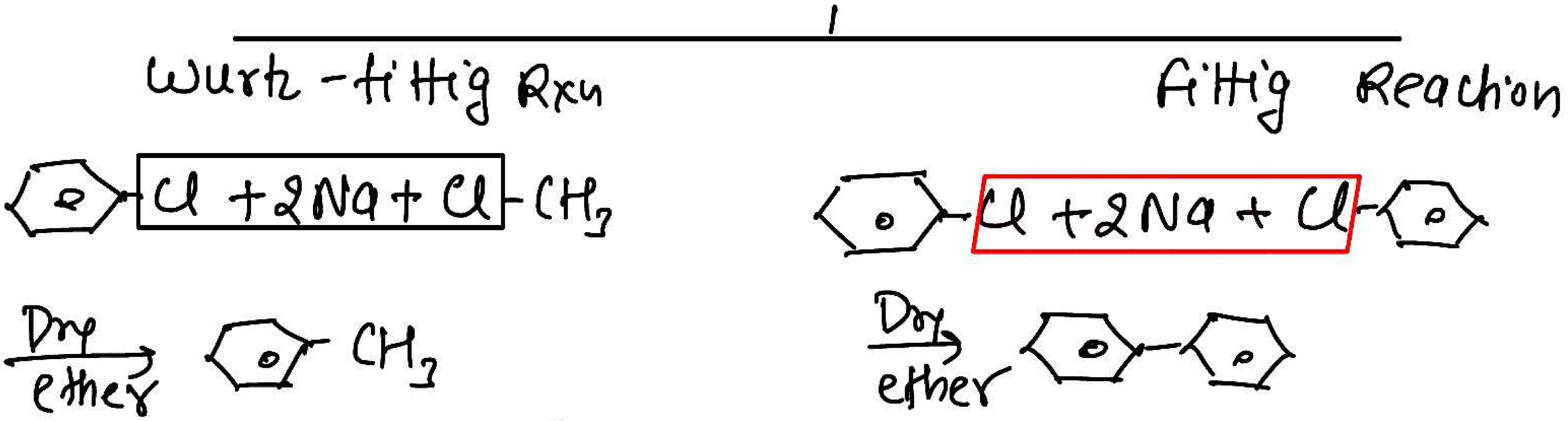
Substitution by Cyano Group



Reaction with Metal:-



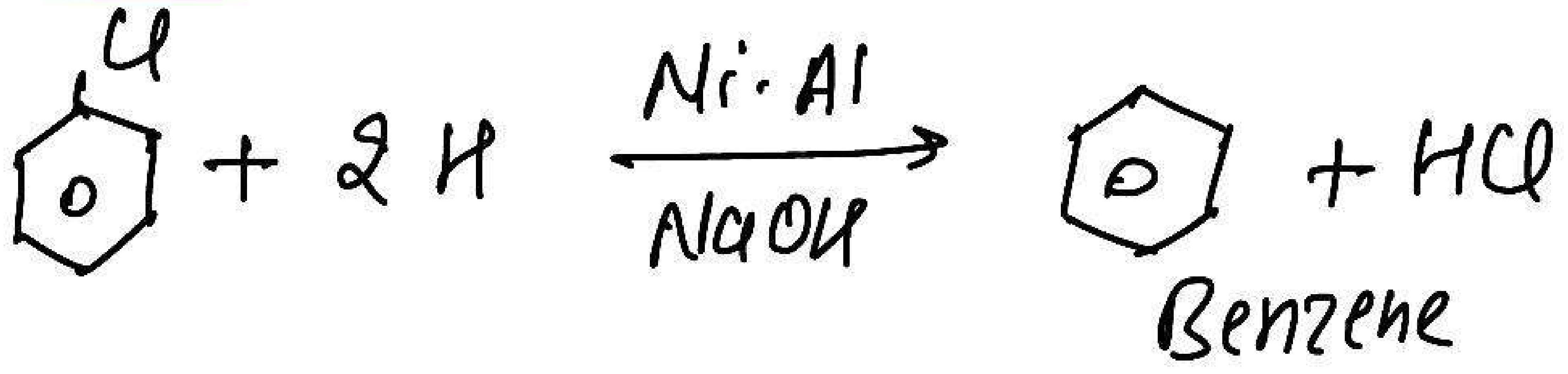
Reaction with sodium



Reaction with Copper

Ullmann Reaction

Cl▸ Reduction

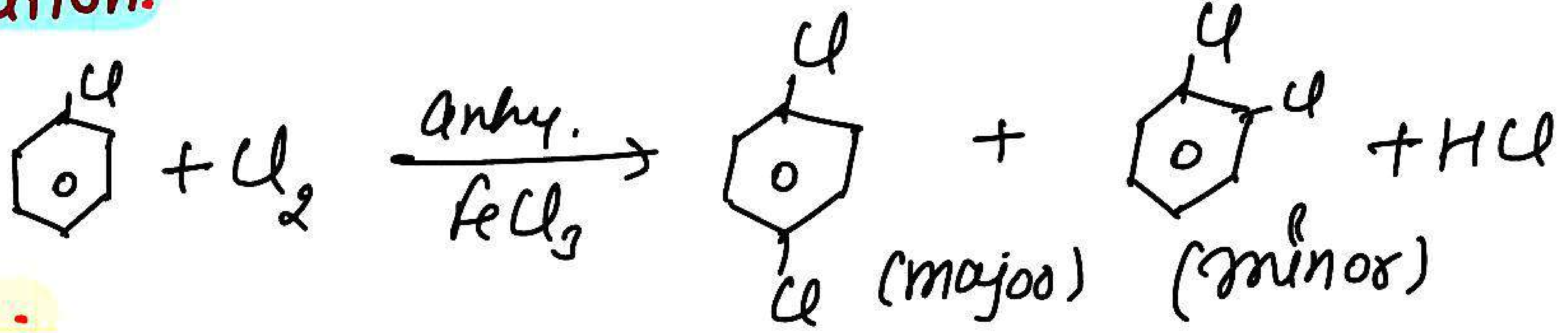


Cl▸ Electrophilic Substitution Reaction

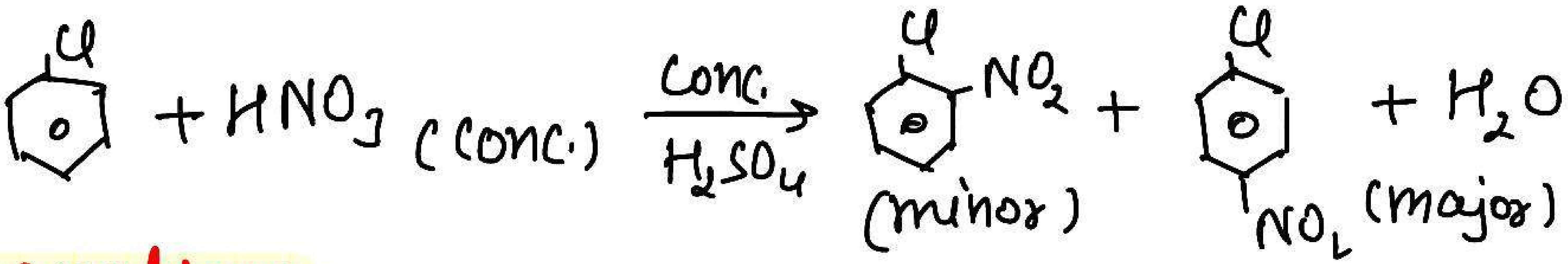
Note (i) Haloarenes undergo electrophilic substitution reaction slowly as compared to benzene

(ii) Halogen group is ortho and para directing

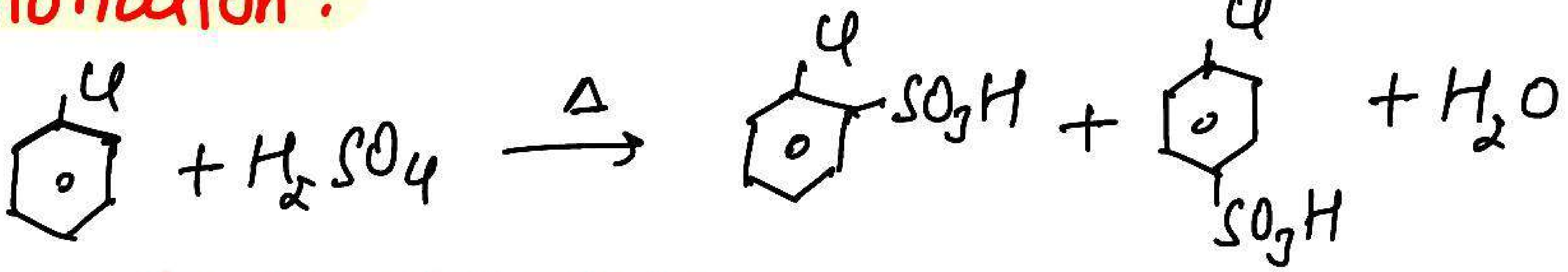
Halogenation:



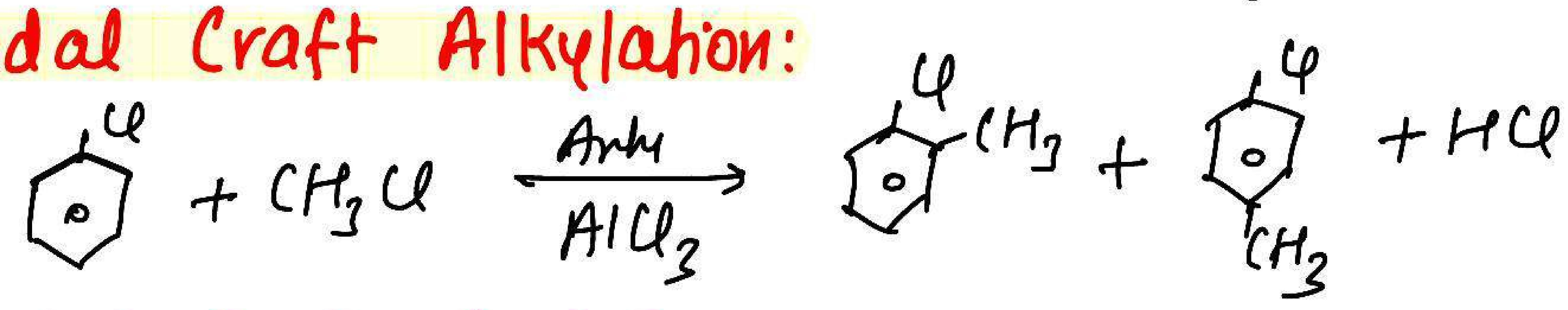
Nitration:



Sulphonation:



Friedal Craft Alkylation:



Friedal Craft Acylation: