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Handwritten Notes

on

Haloalkanes and Haloarenes

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Haloalkanes and Haloarenes

- Haloalkanes are organic compounds obtained by replacement of one or more H-atoms of aliphatic hydrocarbon by halogen atoms.

- Haloarenes are organic compounds obtained by replacement of one H-atom of aromatic compounds by halogen atoms. Haloalkanes are commonly known as alkyl halides.

- In alkyl halides the halogen atom of the is attached to sp^3 hybridised atom of the hydrocarbon.

- In aryl halide the halogen atom is attached to sp^2 hybridised atom of the aromatic compound.

→ Classification of haloalkanes →

(i) Based on type of C-atom to which halogen atom is attached.

; CH_3-CH_2-Cl : Primary alkyl halide

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(ii) $CH_3-\underset{Cl}{\underset{|}{C}}H-CH_3$: Secondary alkyl halide

(iii) $CH_3-\underset{Cl}{\overset{Cl}{\overset{|}{\underset{|}{C}}}}-Cl$: Tertiary alkyl halide

(ii) Based on no. of halogen atoms attached to C-atom in a molecule :

- $CH_3-CH_2-CH_2-Cl$: monohaloalkane.
- $CH_3-\underset{CH_2-Cl}{\underset{|}{CH}}-Cl$: dihaloalkane
- $CHCl_3$, $\underset{CH_2Cl}{\underset{|}{\overset{CH_2Cl}{\overset{|}{C}}}}H$: Polyhaloalkane.

→ Dihaloalkanes are further classified as.

- Vicinal halides have halogen atoms attached to adjacent C-atoms.

$\underset{CH_2-Cl}{\underset{|}{CH_2-Cl}}$: 1-2 dichloroethane.
Ethylene chloride
(Alkylene halide)

(ii) gem dihalides have both the halogen atoms attached to the same C-atom.

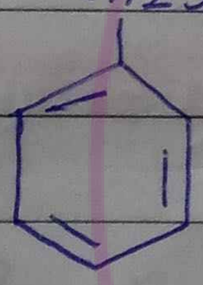
CH_3-CHCl_2 : 1,1-dichloro ethane.

Ethylidene chloride

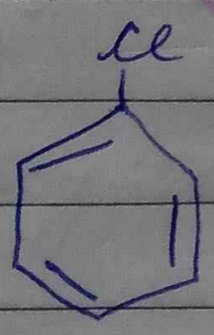
(Alkylidene halides)

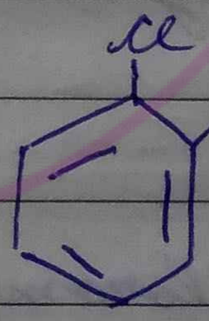
(iii) Based on the type of sp^3 hybridised C-atom

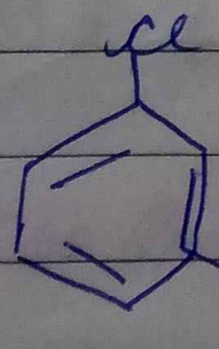
(i) $CH_2=CH-CH_2-Cl$ Allyl chloride

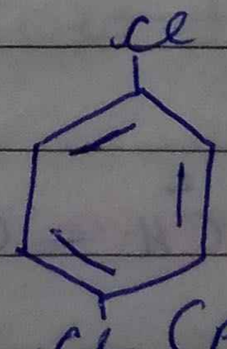
(ii)  : Benzyl chloride.

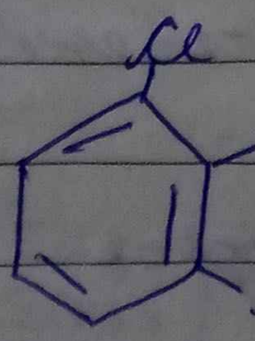
- Classification of haloarenes:

 : Chlorobenzene.

 1,2 dichlorobenzene (o-dichlorobenzene)

 : 1,3 dichlorobenzene (m-dichlorobenzene)

 : 1,4-dichlorobenzene (p-dichlorobenzene)

 (1,2,3 trichlorobenzene)

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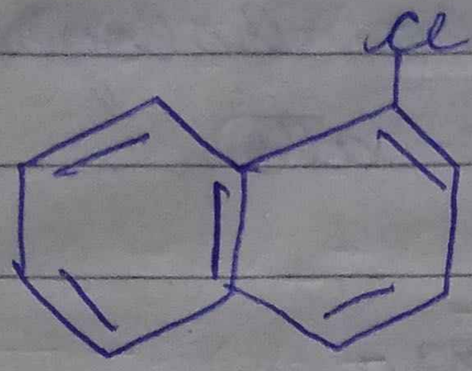
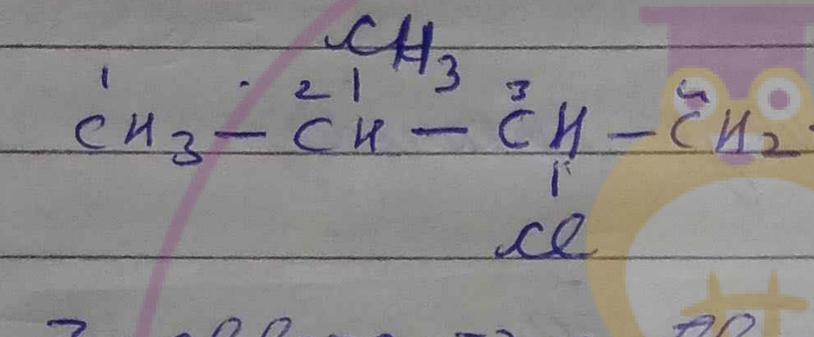
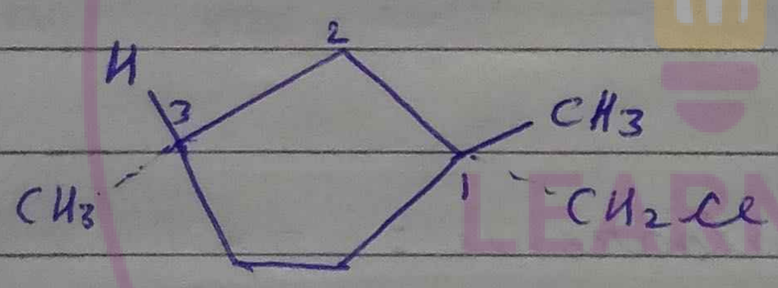


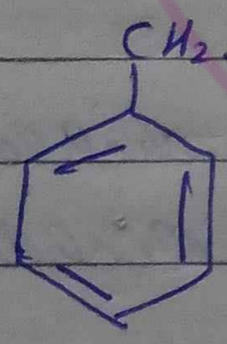
: 1 chloronaphthalene

- $CH_2 = CH - Cl$: vinyl chloride
- IUPAC nomenclature of haloalkanes and haloarenes.
- 

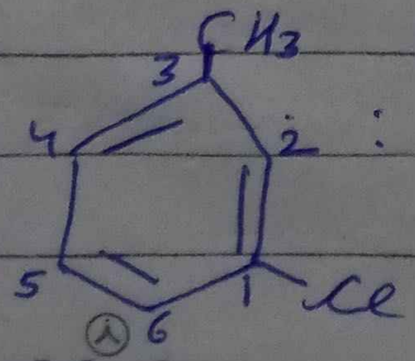
3 - chloro - 2 - methyl pentane.

- 

1 - chloromethyl - 1 - 3, dimethyl cyclopentane.

- 

: chloromethyl benzene.

- $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - Cl$: 3 chloropropene.
- $\overset{4}{C}H_3 - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_2 - Cl$: 1 chlorobut - 2 - ene
- 

: 1 - chloro - 3 methyl benzene.

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- Preparation of monohaloalkanes

1 From alcohols.

(i) By using Hydrogen halides.

$$R-OH + HX \longrightarrow R-\overset{+}{O}H_2 + X^- \xrightarrow[SN_1]{} \overset{+}{R} + X^{-1} \longrightarrow RX + \text{Rearranged Product}$$

$$R-\overset{+}{O}H_2 \xrightarrow{SN_2} RX + H_2O$$

- Reactivity order among HX →

HI > HBr > HCl

- Reactivity order among ROH

3° ROH > 2° ROH > 1° ROH

- Syntheses of HX

- $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$.

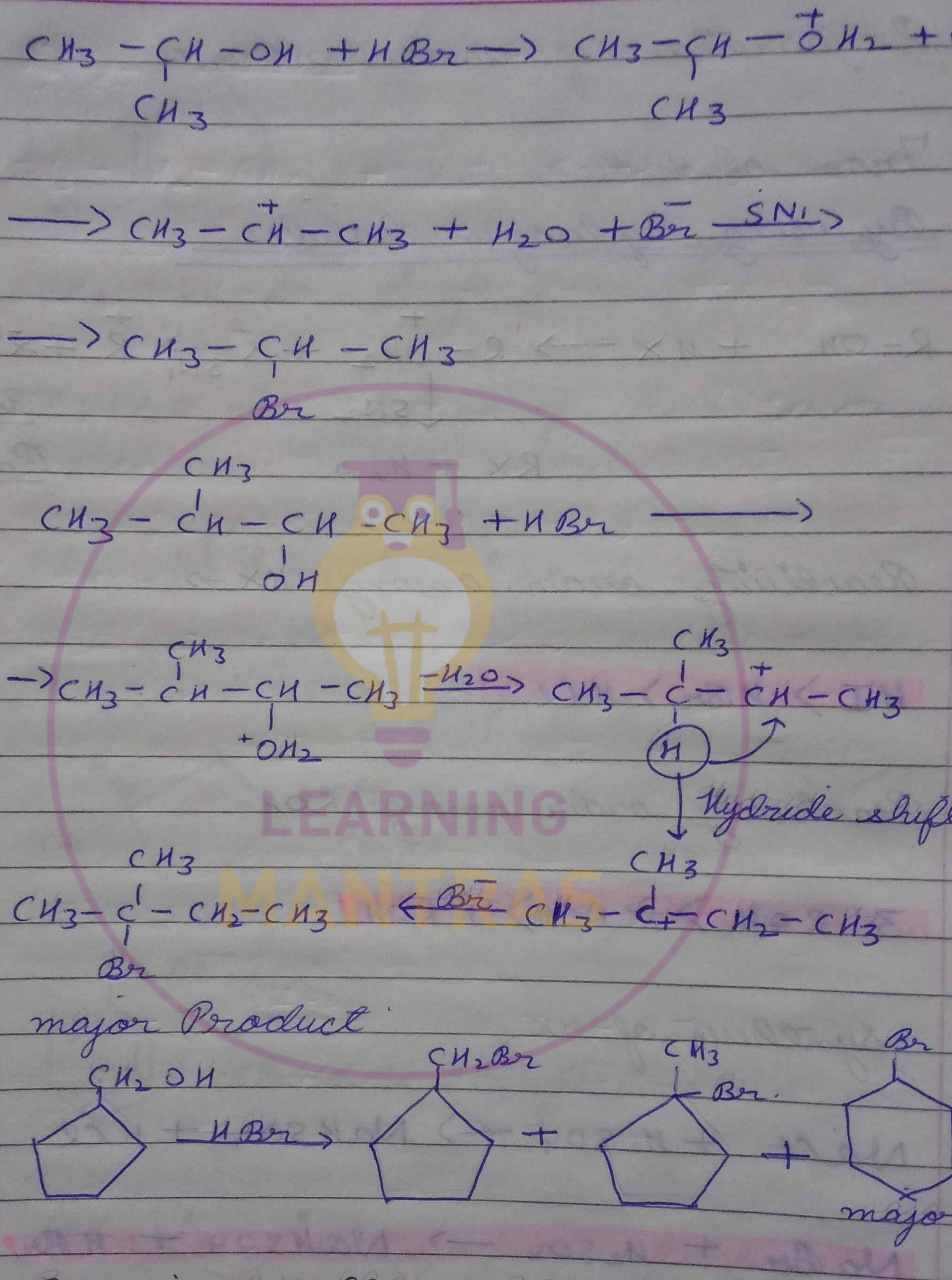
- $NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$.

- $NaI + H_3PO_4 \longrightarrow NaH_2PO_4 + HI$

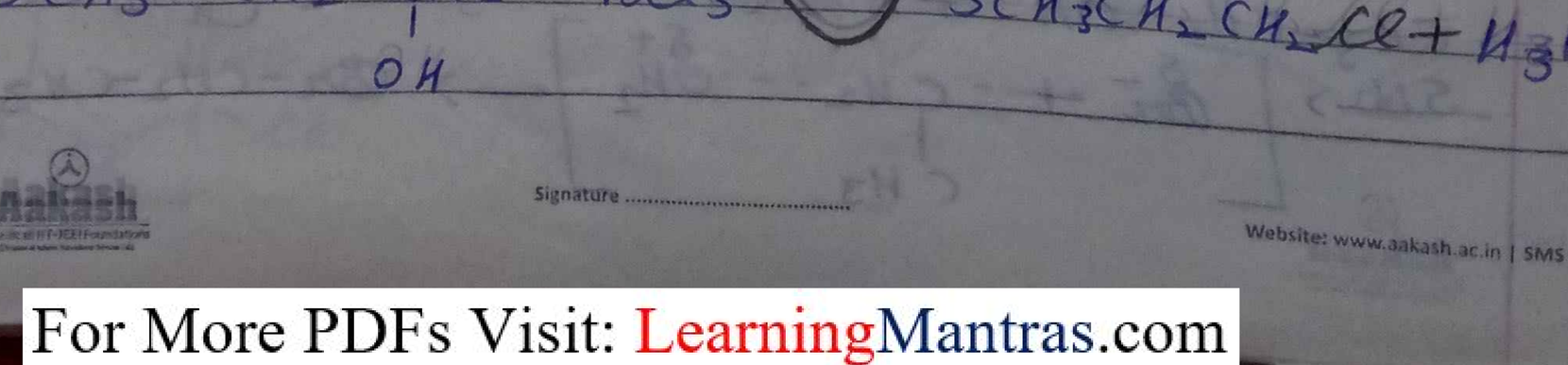
e.g. $CH_3-CH_2-OH + HBr \longrightarrow CH_3-CH_2-\overset{+}{O}H_2 + Br^-$

$\xrightarrow{SN_2}$ $\left[\overset{\delta-}{Br^-} + - CH_2(CH_3) - - - \overset{\delta+}{O}H_2\right] \longrightarrow Br-CH_2-CH_3 + H_2O$

•



major Product



(ii) By using PX_3 (PCl_3, PBr_3, PI_3) and PX_5 (PCl_5, PBr_5)

-

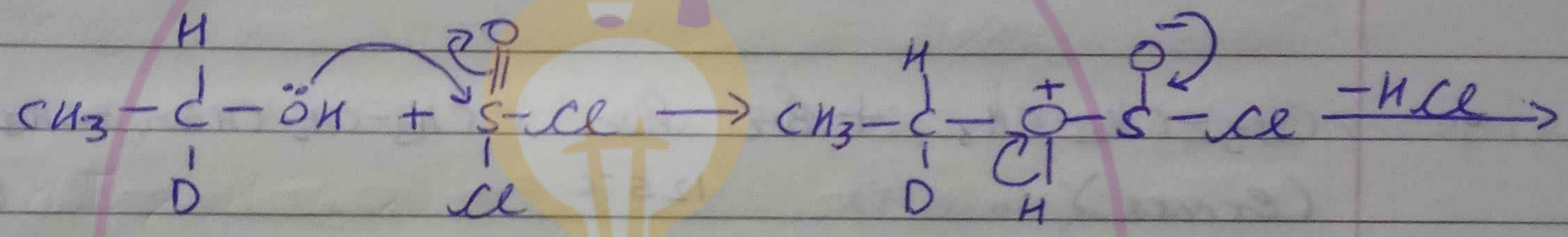
- $CH_3-CH_2-OH + PCl_5 \xrightarrow{SN_2} CH_3-CH_2-Cl + POCl_3 + HCl$

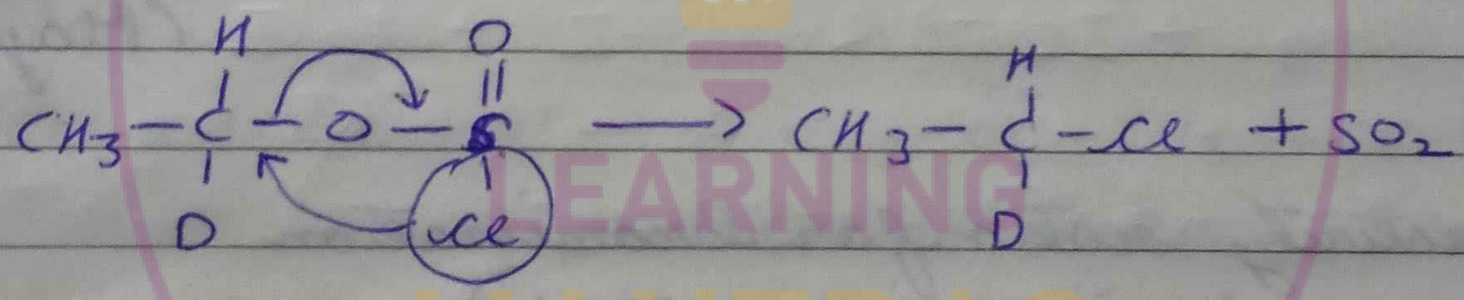
(iii) By using $SOCl_2$ (Darzens Reaction)

- $CH_3-\underset{\underset{D}{|}}{CH}-OH + SOCl_2 \xrightarrow{SNi} CH_3-\underset{\underset{D}{|}}{CH}-Cl + SO_2\uparrow + HCl\uparrow$

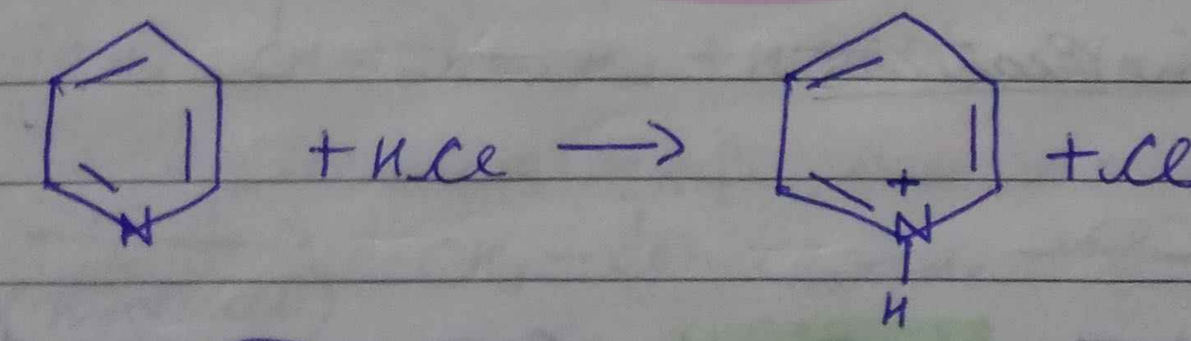
→ configuration is retained

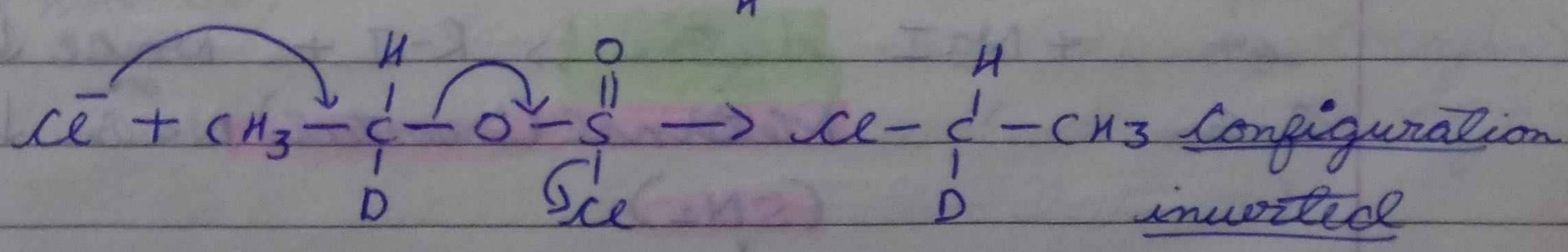
Mechanism:





★ In presence of pyridine the same reactions results in inversion of configuration.





Configuration inverted

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- From alkanes

- $CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{hv} CH_3-CH_2-CH_2Cl +$ $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$
  Excess, Room temp. (Major)

→ For chlorination, the reactivity ratio ($3^\circ H : 2^\circ H : 1^\circ H = 5 : 3.8 : 1$)

- $CH_3-CH_2-CH_3 + Br_2 \xrightarrow[125^\circ C]{hv} CH_3-CH_2-CHBr + CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$
  (Excess) (Major)

→ Reactivity ratio for bromination ($3^\circ H : 2^\circ H : 1^\circ H = 1600 : 82 : 1$)

- $CH_4 + I_2 \underset{HIO_3}{\rightleftharpoons} CH_3I + HI$

→ Finkelstein Reaction

$R-Cl$ (or $R-Br$) $+ NaI \xrightarrow[\text{or Methanol (inverted)}]{\text{Acetone}} R-I +$ $NaCl \downarrow$ (or $NaBr \downarrow$)

(S_N2)

→ Swarts Reaction:

$$\left.\begin{matrix} R-Cl \\ \text{or} \\ R-Br \end{matrix}\right. + AgF \longrightarrow R-F + \left.\begin{matrix} AgCl \\ \text{or} \\ AgBr \end{matrix}\right.$$

Hg_2F_2, CoF_2 and SbF_3 can also be used.

- From alkenes

- $CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\overset{Br}{\overset{|}{C}}H-CH_3 + CH_3-CH_2-CH_2Br$
  (Major)

Mechanism

$CH_3-CH=CH + H^+ \longrightarrow CH_3-\overset{+}{C}H-CH_3 + CH_3-CH_2-\overset{+}{C}H_2$
(More stable) (less stable)

$CH_3-\overset{+}{C}H-CH_3 + CH_3-CH_2-\overset{+}{C}H_2 \xrightarrow{\bar{Br}} CH_3-CHBr-CH_3$ (Major) $+ CH_3-CH_2-CH_2Br$

- $CH_3-\overset{CH_3}{\overset{|}{C}}H-CH=CH_2 + HCl \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{+}{C}H-CH_3$

$\xrightarrow[\text{(Hydride Shift)}]{\sim H^-} CH_3-\overset{CH_3}{\overset{|}{C}}{\oplus}-CH_2-CH_3 \xrightarrow{Cl^-} CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3$ (Major)

(2-chloro-3methyl butane)

☆ Birankumsimanini Reaction

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★ Hundsdicker Reaction

$$R-COOAg + Br_2 \xrightarrow{CCl_4} R-Br + AgBr + CO_2$$

$$R-COOAg + Br_2 \longrightarrow R-COO-Br + AgBr$$

$$R-COO-Br \xrightarrow{RDS} R-COO^{\cdot} + Br^{\cdot}$$

$$R-COO^{\cdot} \longrightarrow R^{\cdot} + CO_2 \longrightarrow R^{\cdot} + Br^{\cdot} \longrightarrow R-Br$$

→ If I_2 is used:

$$R-COOAg + I_2 \rightarrow R-COO-I + AgI$$

$$R-COO-I \longrightarrow R-COO^{\cdot} + I^{\cdot}$$

$$R-COO^{\cdot} \longrightarrow R^{\cdot} + CO_2$$

☆ $\Rightarrow R-COO^{\cdot} + R^{\cdot} \longrightarrow R-COOR$ (Major)

Ester

Allyl halides or Benzyl halides

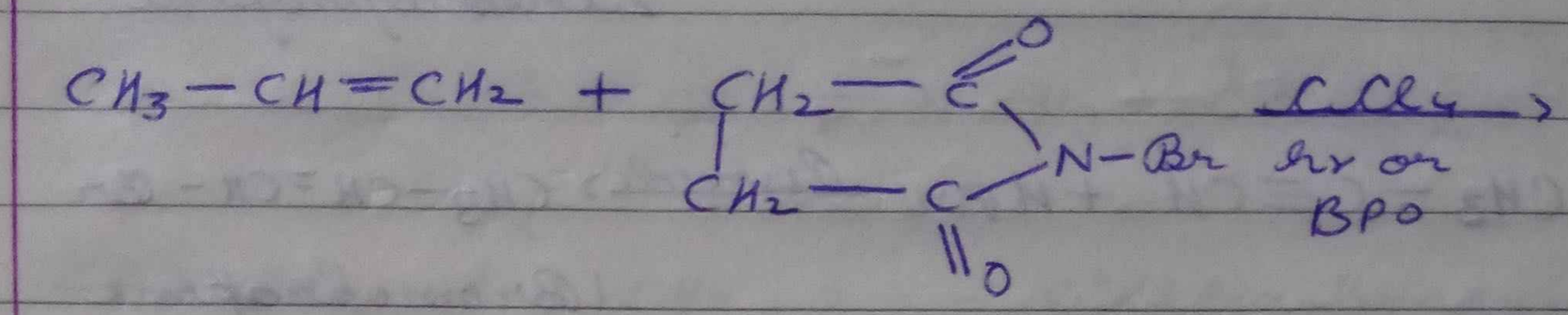
$$CH_3-CH=CH_2 + Cl_2 \xrightarrow{400^{\circ}C-500^{\circ}C} CH_2Cl-CH=CH_2 + HCl$$

(Major)

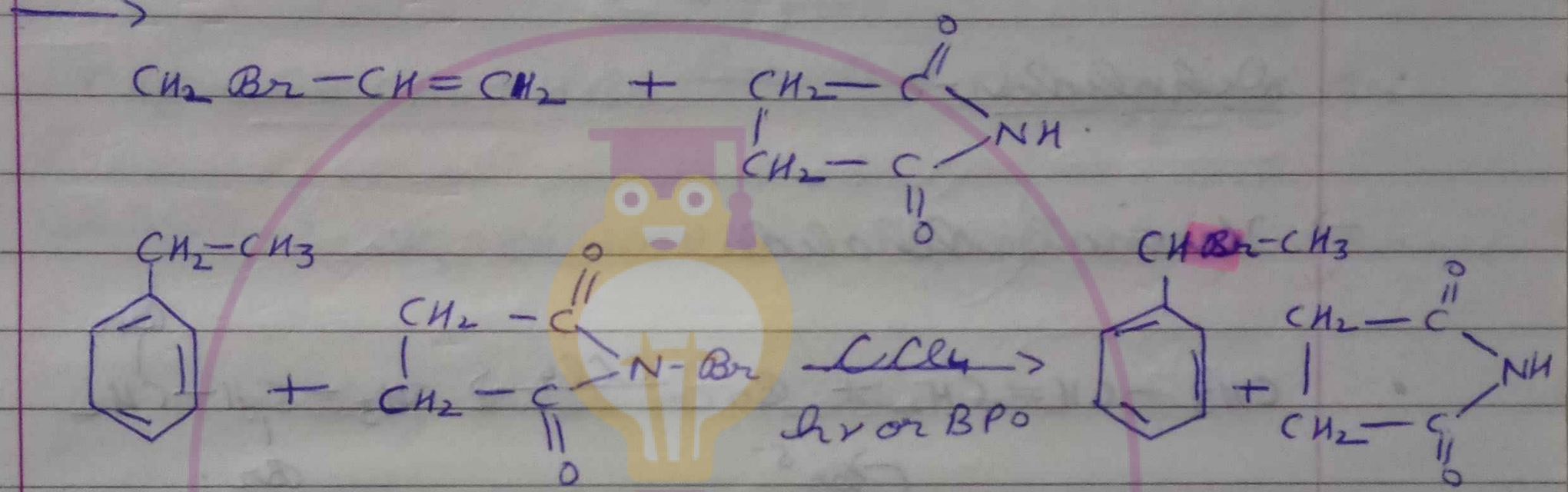
$$Cl-Cl \xrightarrow{\Delta} 2Cl^{\cdot}$$

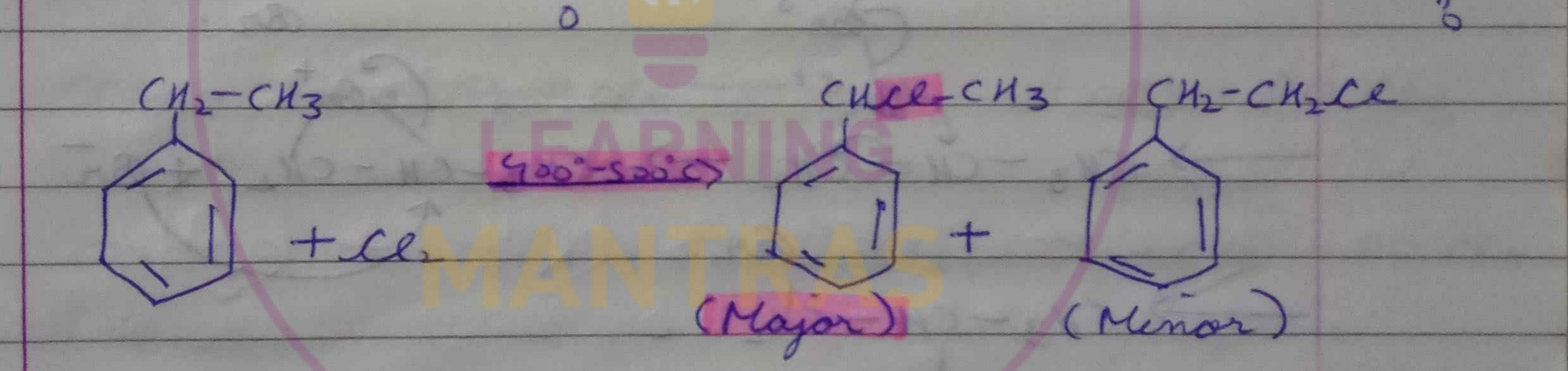
$$CH_3-CH=CH_2 + Cl^{\cdot} \longrightarrow \dot{C}H_2-CH=CH_2 + HCl$$

$$\dot{C}H_2-CH=CH_2 + Cl_2 \rightarrow CH_2Cl-CH=CH_2 + \dot{C}l$$



(NBS)



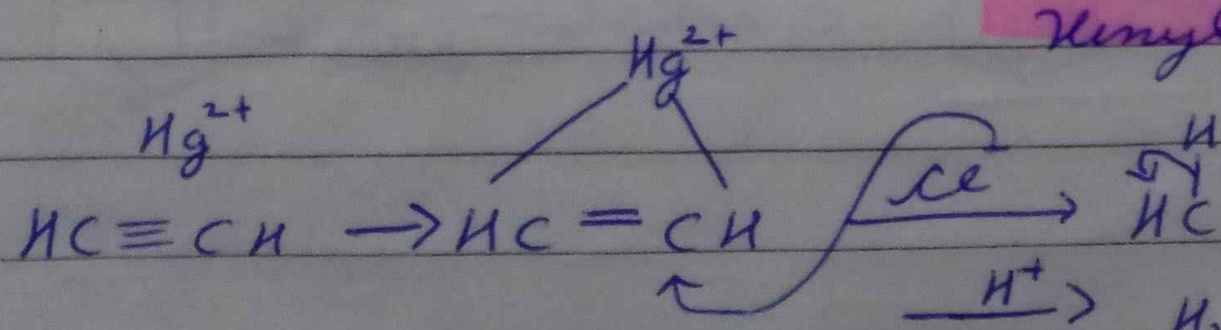


Vinyl halides

From alkynes

$$HC\equiv CH + HCl \xrightarrow{HgCl_2} CH_2=Cl-Cl$$

Vinyl chloride.



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- $CH_3-C\equiv CH + HCl \xrightarrow{HgCl_2} CH_3-\underset{Cl}{\underset{|}{C}}=CH_2$

  2 Chloropropene

- $CH_3-C\equiv CH + HBr \xrightarrow{Peroxide} CH_3-CH=CH-Br$

  1 Bromopropene

  (Kharash Effect)

- <u>Dihalides</u> ->

→ Vicinal dihalides

- $CH_3-CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\underset{|}{CH}}-CH_2Br$

$\longrightarrow CH_3-CH=CH_2 \longrightarrow CH_3-CH-CH_2 + Br^-$

$\longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-CH_2Br$

- $CH_3-C\equiv CH + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\underset{|}{C}}=CHBr \xrightarrow{Br_2}$

$\longrightarrow CH_3-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CHBr_2$: 1,1,2,2 Tetrabromopropane

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→ Gem dihalides:

- $CH_3-C\equiv CH + HCl \longrightarrow CH_3-\underset{Cl}{\overset{|}{C}}=CH_2 \xrightarrow{HCl}$

$\longrightarrow CH_3-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-CH_3$: 2,2-dichloropropane

- $CH_3-C\equiv CH + HBr \xrightarrow{Peroxide} CH_3-CH=CH_2Br$

$\xrightarrow{HBr} CH_3-CH_2-CHBr_2$: 1,1 dichloropropane.

- from aldehydes and ketones

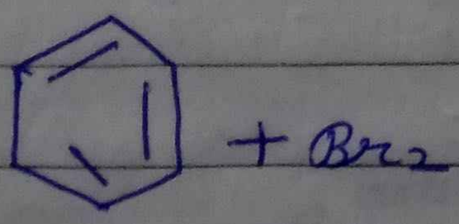
- $CH_3-CH=O + PCl_5 \longrightarrow CH_3-CHCl_2 + POCl_3$

- $CH_3-CO-CH_3 + PCl_5 \longrightarrow CH_3-CCl_2-CH_3 + POCl_3$

2,2 dichloropropane.

→ Haloarenes:

1 By direct halogenation of aromatic compounds:

-  $+ Br_2 \xrightarrow{FeBr_3}$  $+ HBr$

Mechanism:

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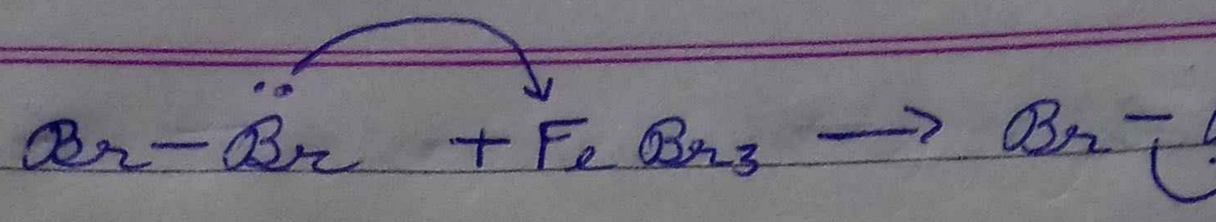
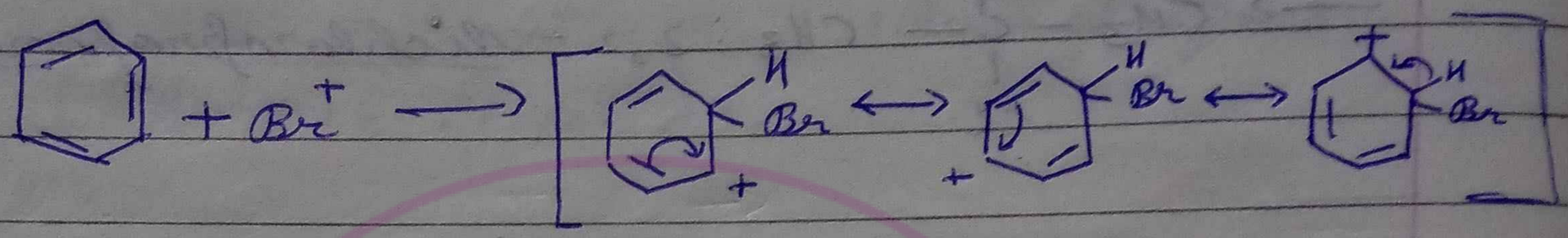
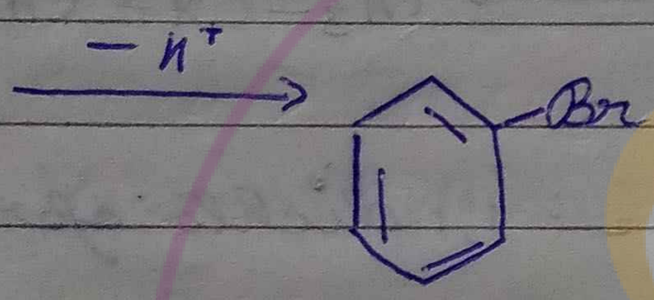


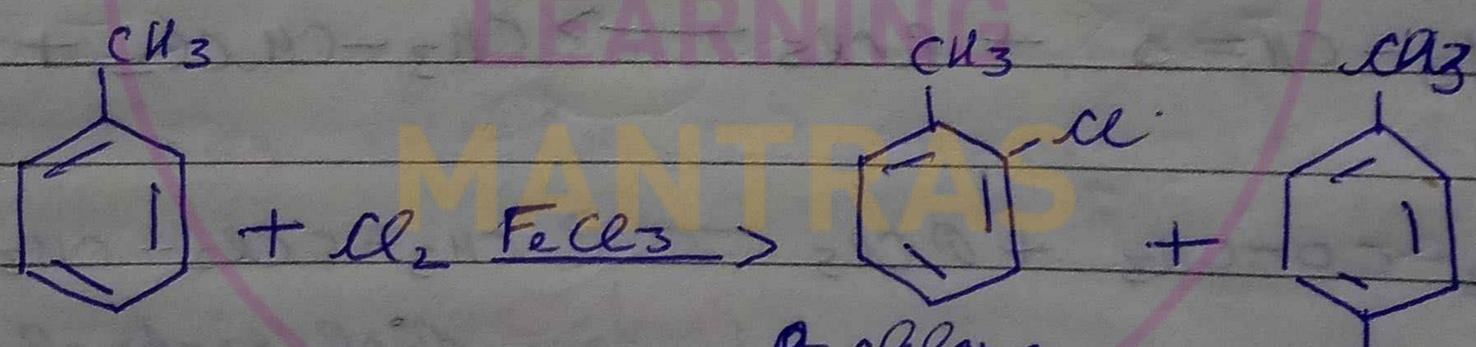
$$\longrightarrow Br^+ + FeBr_4^-$$



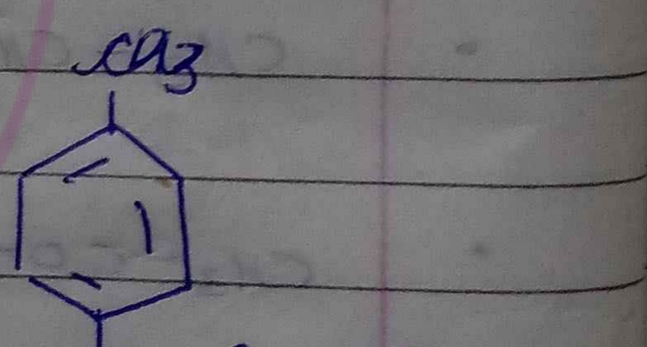
Arrenium ion



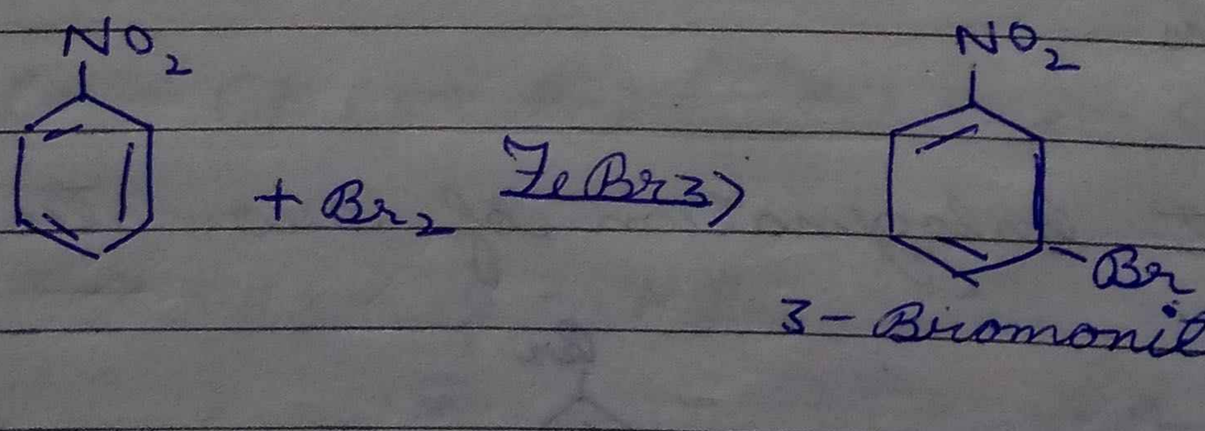
$$H^+ + Br-\bar{F}eBr_3 \longrightarrow HBr + FeBr_3$$



o-chloro toluene



p-chloro toluene



3-Bromonitrobenzene.

From aniline

$\Longrightarrow$

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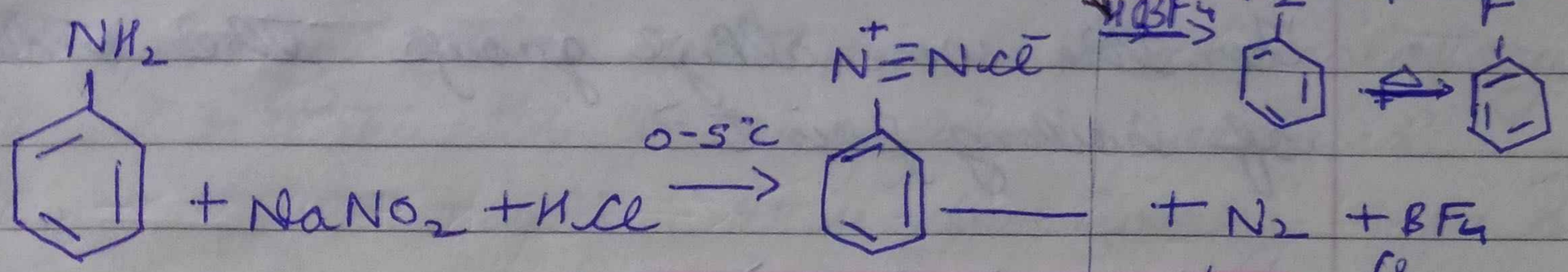
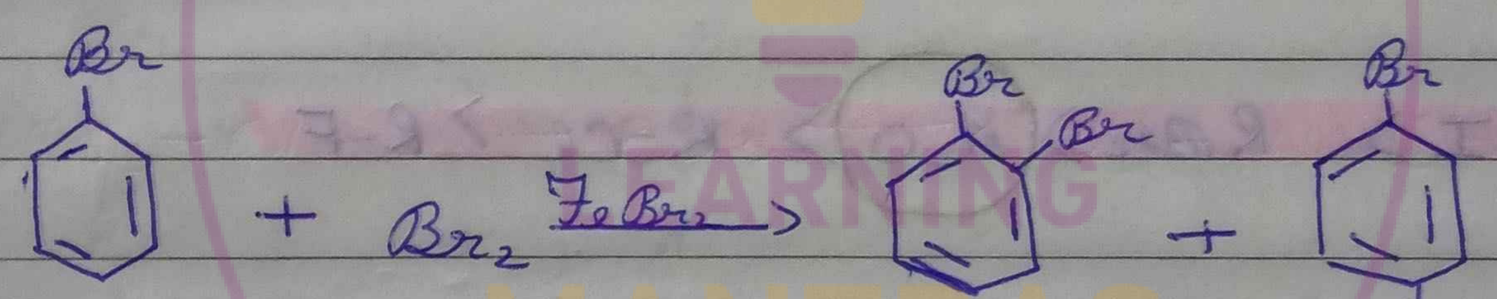
★ Balz schiemann reaction



Dihalides



Physical Properties

- $R\overrightarrow{-X}$ is a polar molecule having permanent dipole moment →
  decreasing order of dipole moment.

⇒ $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$

- They are not soluble in water because they do not form H-bonds with H_2O.

☆ Because here distance of C–Cl bond is more than C–F bond., here distance is a more dominating factor than charge.

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- For the same alkyl groups the order of boiling point →

$RI > RBr > RCl > RF$

- Among polyhaloalkanes the order of boiling point is →

$CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$

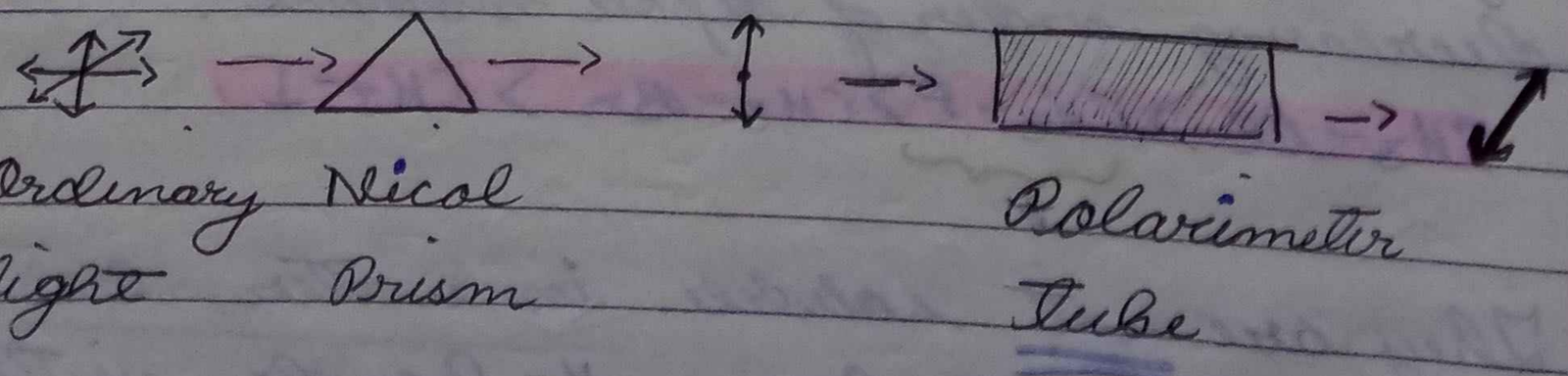
- The density of monohaloalkanes follows the order

☆ $RI > RBr > H_2O > R-Cl > R-F$

- Density among polyhaloalkanes →

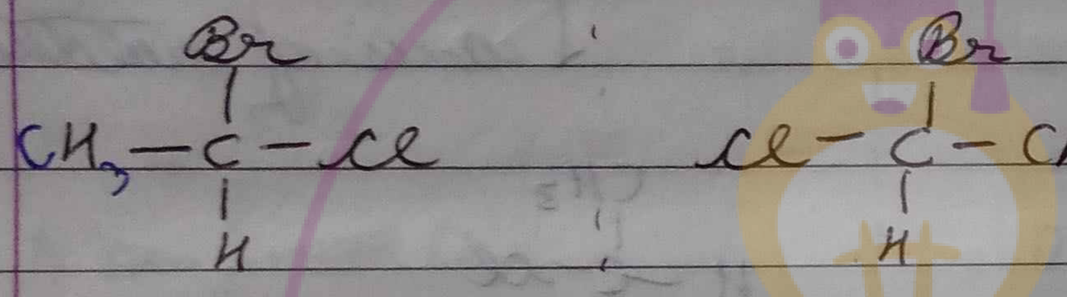
☆ $CCl_4 > CHCl_3 > CH_2Cl_2 > H_2O > CH_3Cl$

→ Chemical Properties

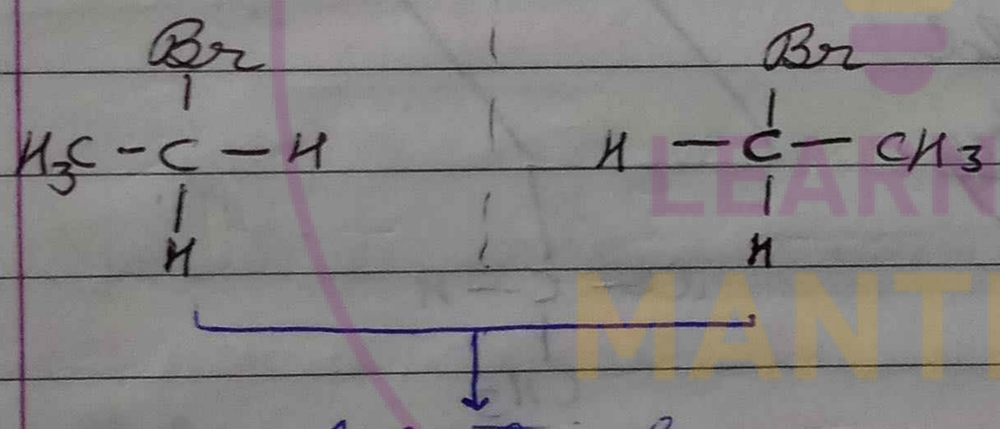


- The optically active substance is dextrorotatory if it rotates the plane of plane polarised light to the right. It is denoted by + or d

- The optically active substance is laevorotatory if it rotates the plane of plane polarised light to the left. It is denoted by (−) or l.

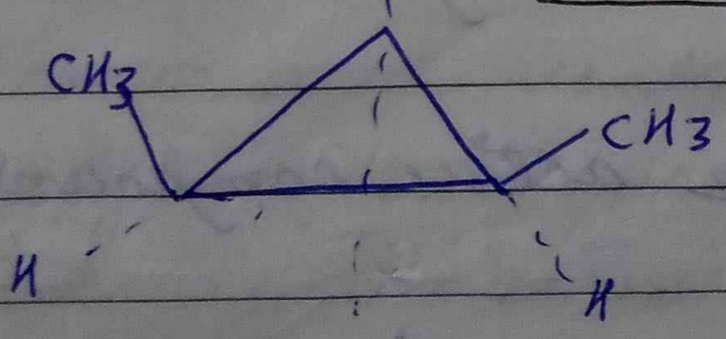


Mirror image isomers are called enantio-mers.



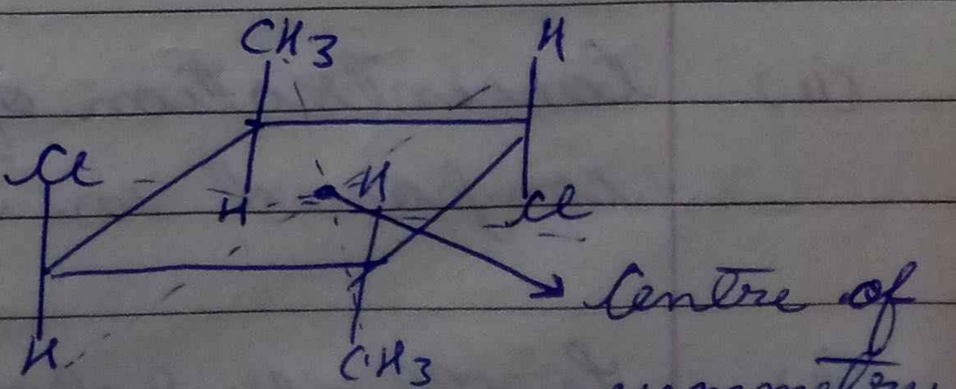
- Symmetry Elements

(i) ← Plane of symmetry

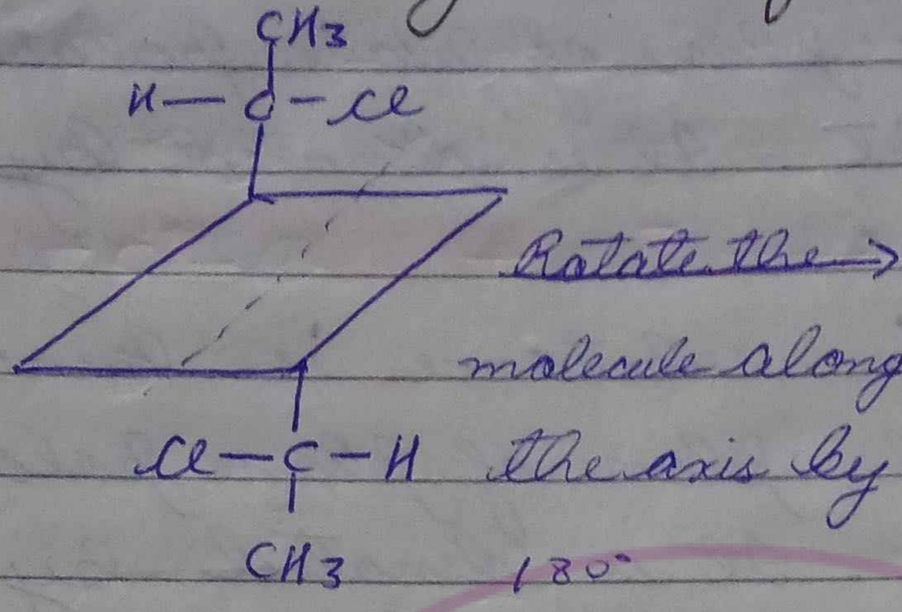


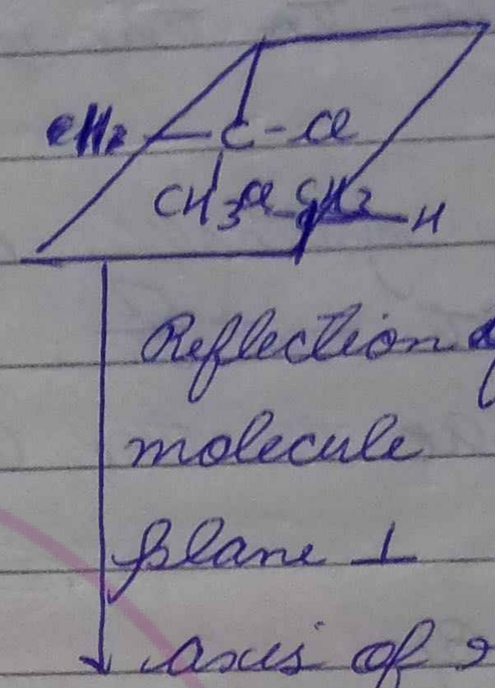
cis-1,2 dimethylcyclopropane

(ii) Centre of symmetry :

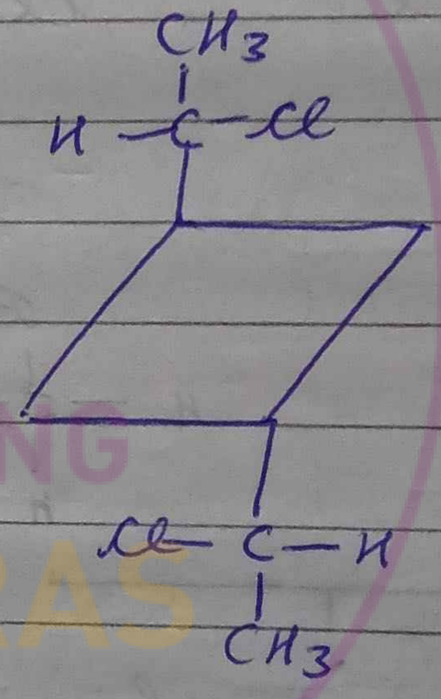


3 Alternating axis of symmetry →





This is called 1 alternating 2 fold axis of symmetry.



- Optical Isomerism

- Angle of rotation (α) depends on:

(i) Nature of optically active compound.

(ii) Concentration of the optically active compound in solution.

(iii) Length of polarimeter tube.

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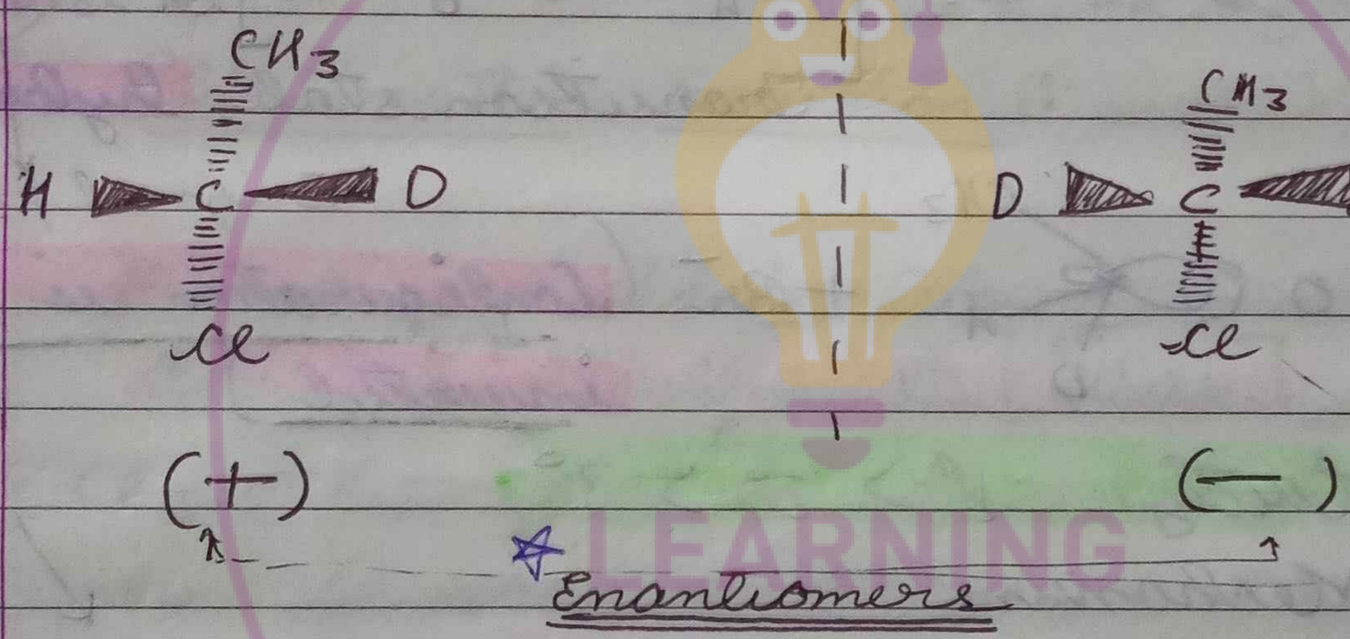
(iv) Temperature.

(v) Wavelength of the incident light.

- Specific rotation, $[\alpha]_\lambda^T = \frac{\alpha \text{ observed}}{c \times l}$

where c is conc. in gm/ml

l is the length of polarimeter tube in decimeter.



☆ Enantiomers

- Diastereomers are non-mirror image, non-superimposation isomers of the same compound.

- Racemic mix is equimolar mix of (+) and (−) of the same compound. It will be optically inactive.

- Nucleophilic substitution reaction:

$$R-X + Na^- \longrightarrow R-Na + X^-$$

- Leaving group

Leaving ability : $I^- > Br^- > Cl^-$

Name of the Chapter

☆ S_N1 reaction : The nucleophile plays no kinetic role

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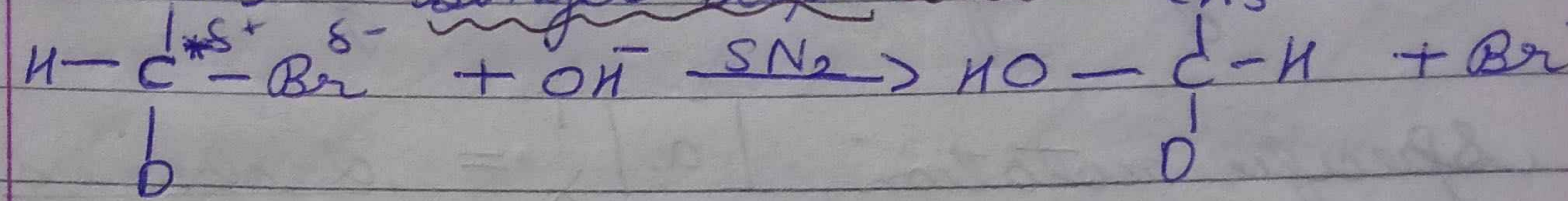
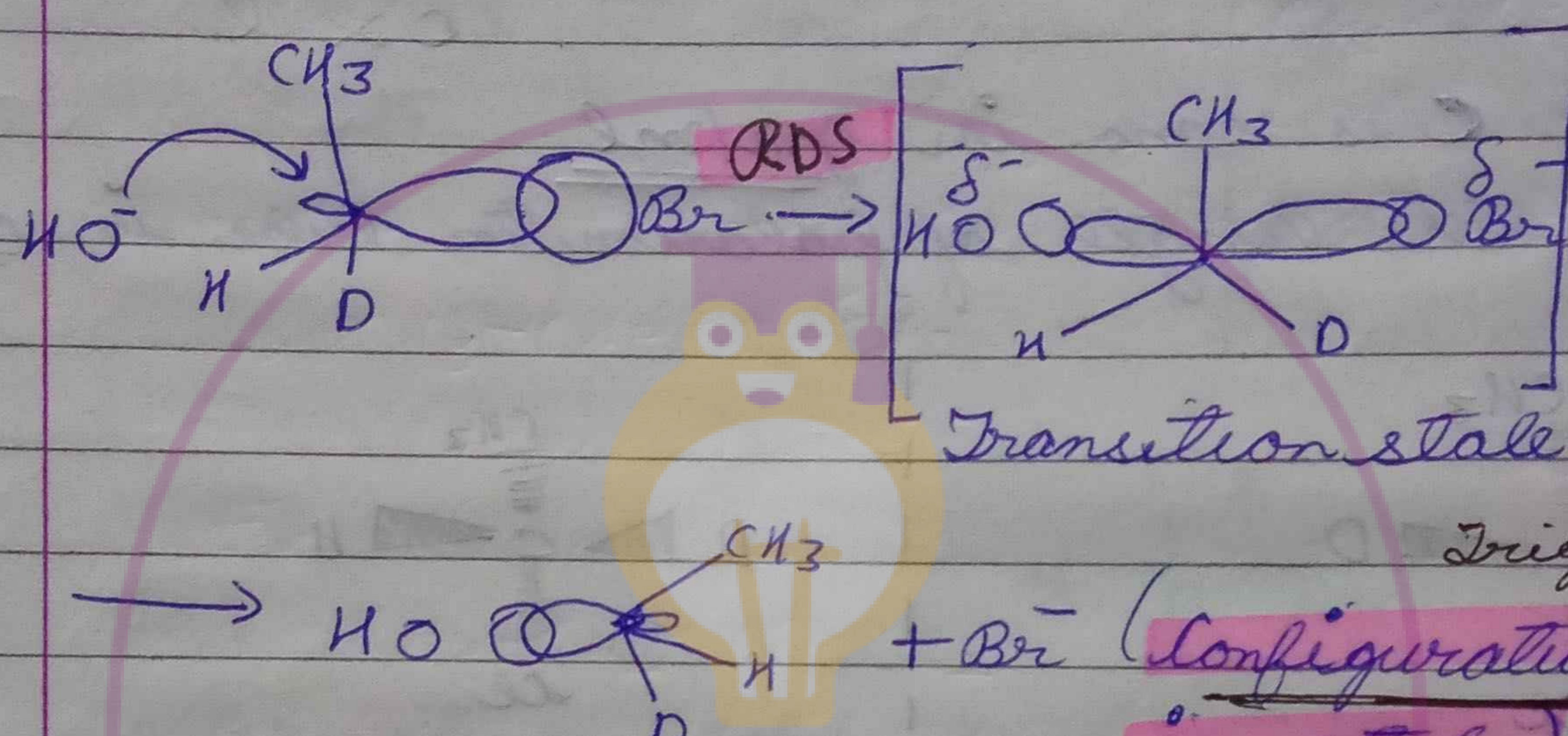
1 S_N2 mechanism :

Rate = K[alkyl halide][Base] ⇒ order = 2

- ☆ single step reaction





Transition state

(C-atom contg. Br, OH^- is sp^2 hybridised) → Trigonal planar

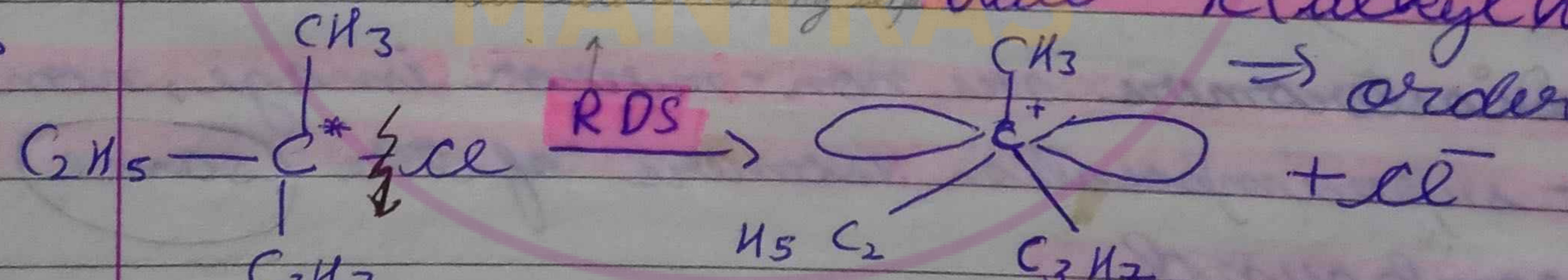
(Configuration is inverted)

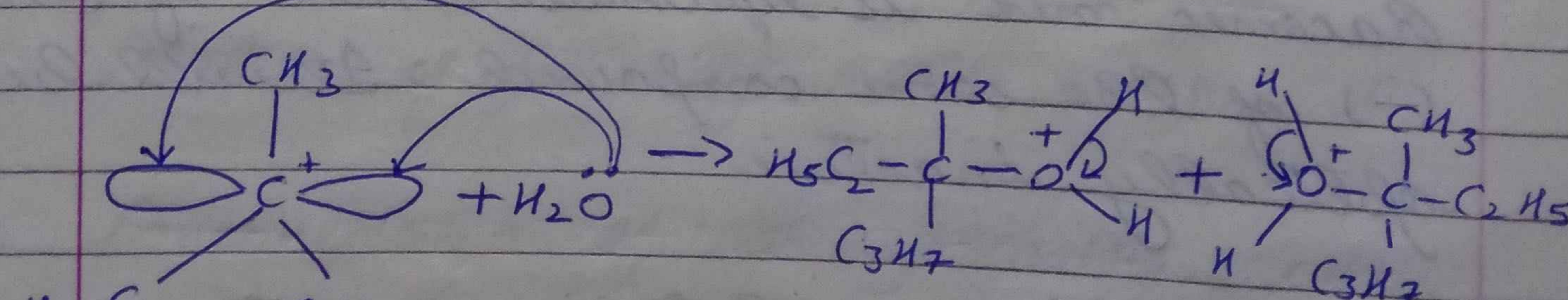
Reactivity : 1° > 2° > 3°

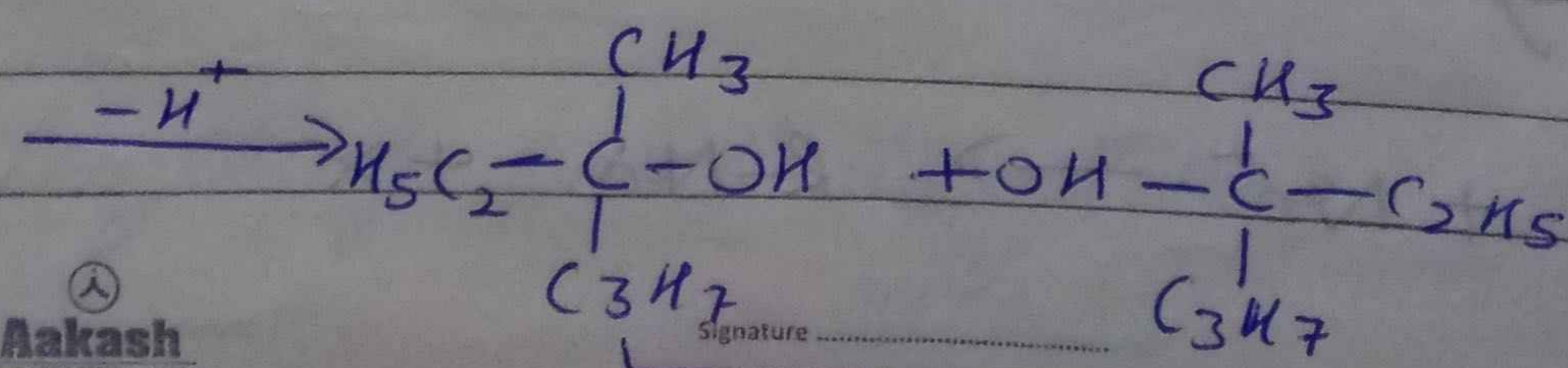
2 S_N1 Mechanism

Rate = K[alkyl halide] ⇒ order = 1

Rate determining step ← RDS







Enantiomers

* In S_N1 mechanism reaction proceed via racemisation which is partial.

3 **S_Ni mechanism**
→ intramolecular

- $CH_2(OH)-CH_2-Cl + AgKOH \longrightarrow$ CH_2-CH_2 (bridged by O)

Ethylene oxide

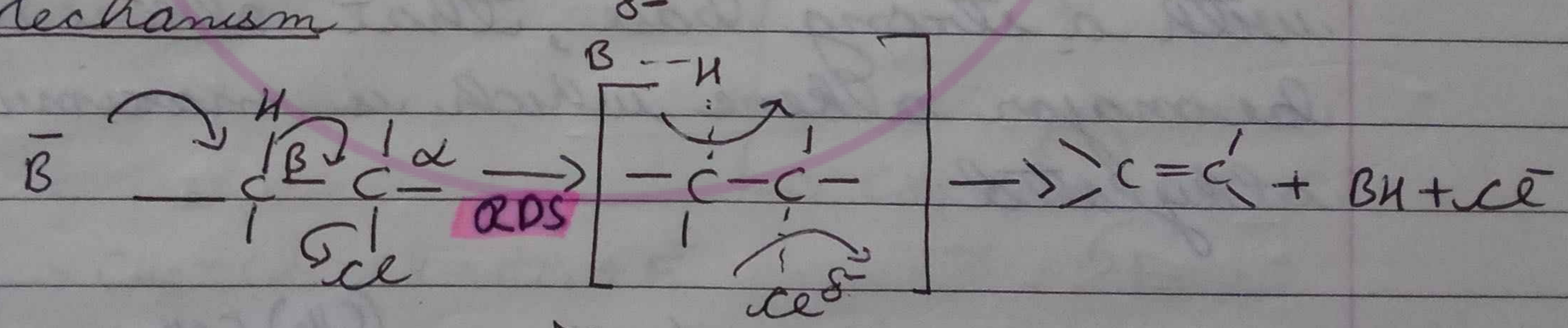
$CH_2(OH)-CH_2(Cl) + OH^- \xrightarrow{-H_2O} CH_2(O^-)-CH_2(Cl) \xrightarrow{S_Ni} CH_2-CH_2$ (bridged by O) $+ Cl^-$

- **Elimination reaction:**

1 E_2 or β elimination
Rate = K [Alkylhalide] [Base]

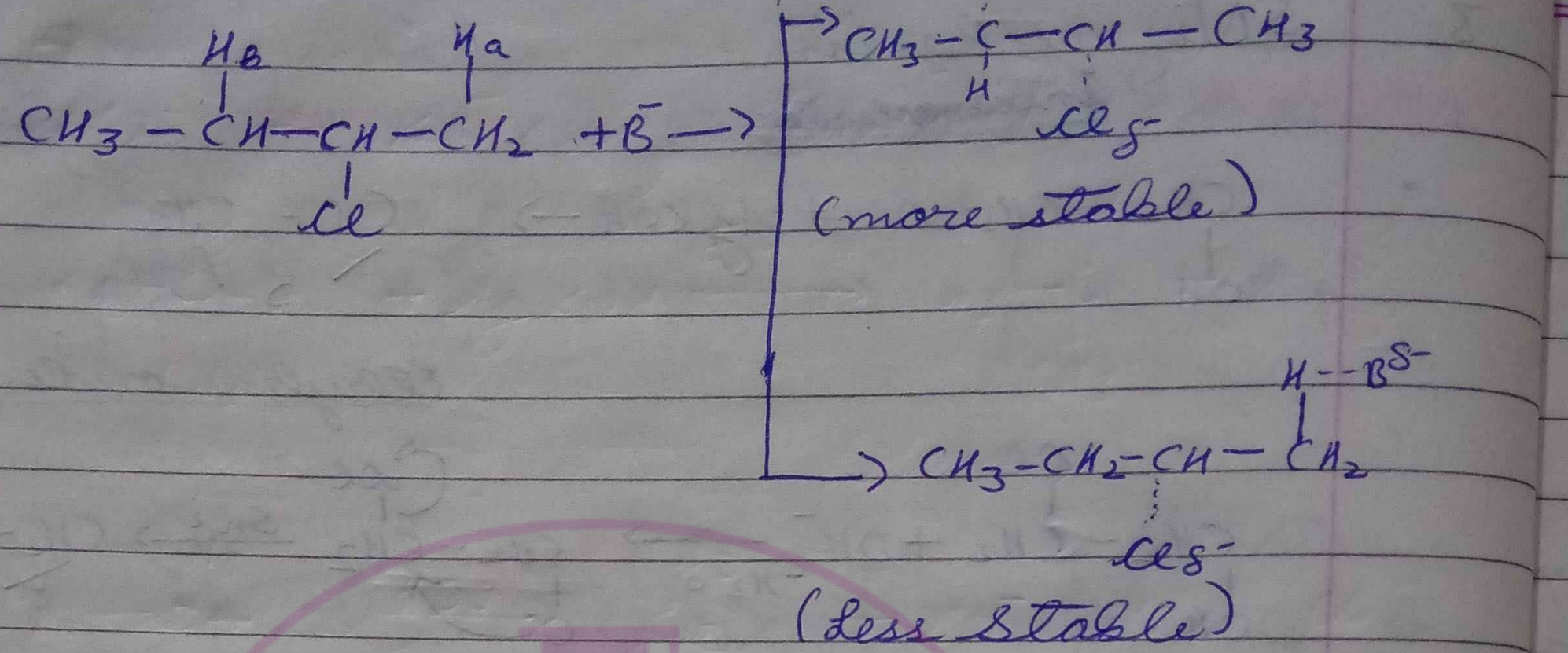
- $\overset{\beta}{CH_3}-\overset{\beta}{CH_2}-\overset{\alpha}{CH}(Cl)-\overset{\beta}{CH_3} + \text{alc. KOH} \longrightarrow CH_3-CH=CH-CH_3$ (maj) $+ CH_3-CH-CH=CH_2$

Mechanism



Transition state

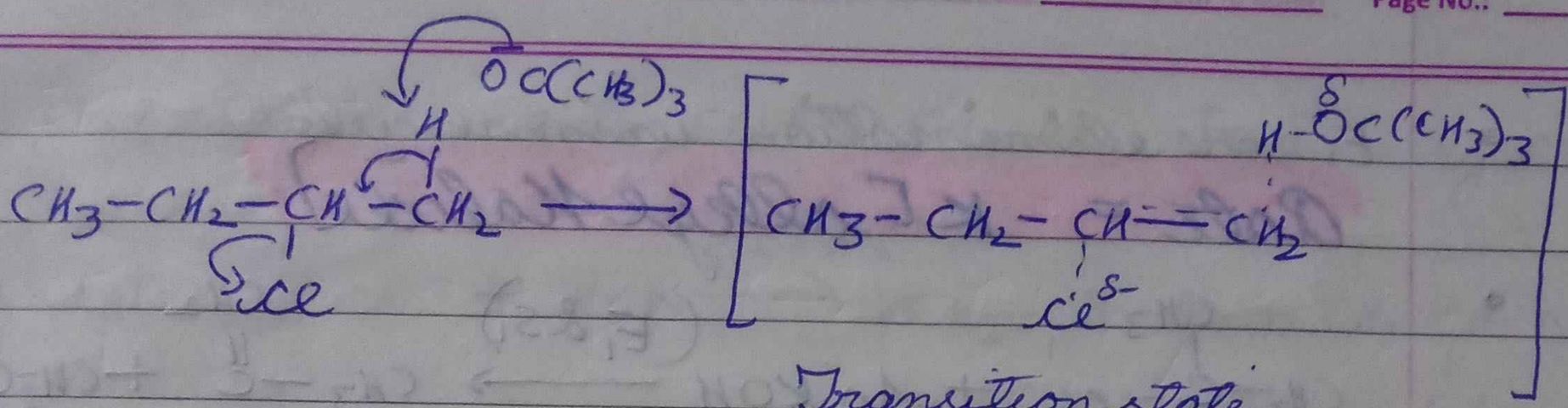
- For the same alkyl group reactivity order towards E_2
R–I > R–Br > R–Cl.



Saitzeff rule: states that when alkyl halides undergoes elimination reaction with a strong base, that alkene will be major alkene which is maximum alkylated.

$$CH_3-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3 + (CH_3)_3COK \xrightarrow{(CH_3)_3COH} \text{(Bulky base)}$$

$$\longrightarrow \underset{\text{(Major)}}{CH_3-CH_2-CH=CH_2} + CH_3-CH=CH-CH_3$$



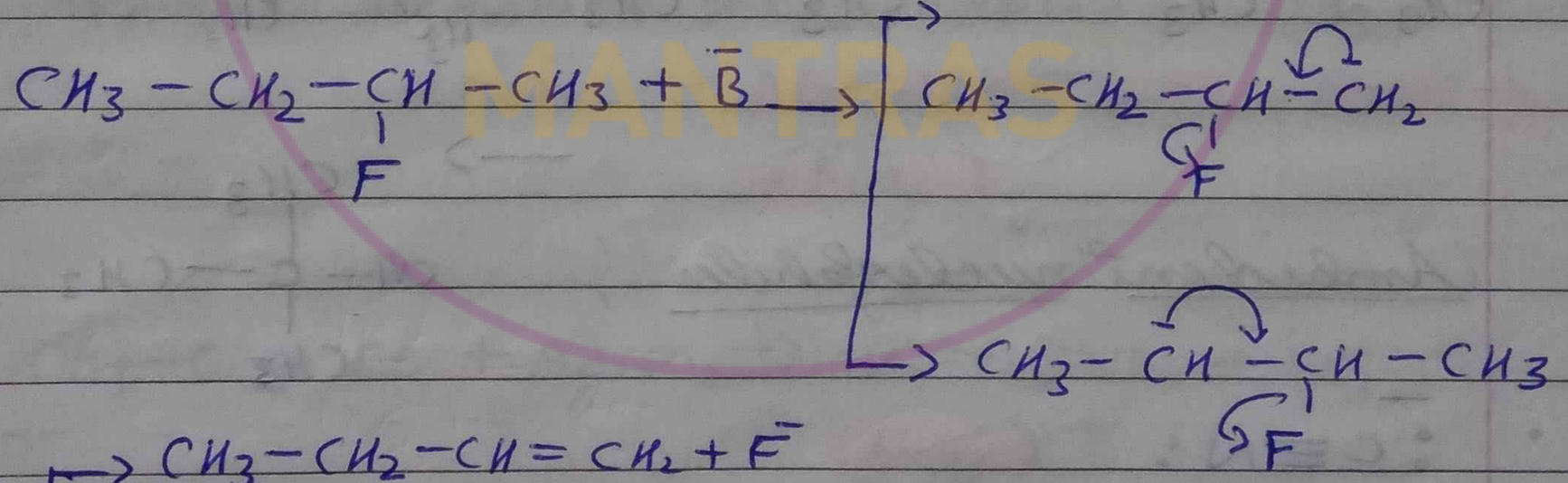
$\longrightarrow CH_3-CH_2-CH=CH_2$

(Hoffmann product)

2 E1cb : elimination unimolecular through conjugate base.

$CH_3-CH_2-\underset{F}{CH}-CH_3$ + alc. KOH $\longrightarrow CH_3-CH_2-CH=CH_2$ (Major)

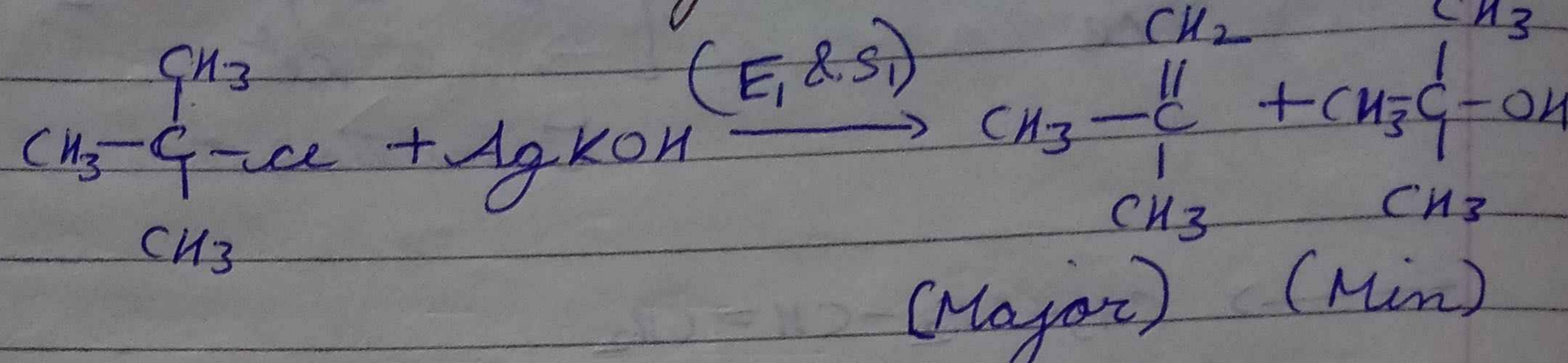
+ $CH_3-CH=CH-CH_3$



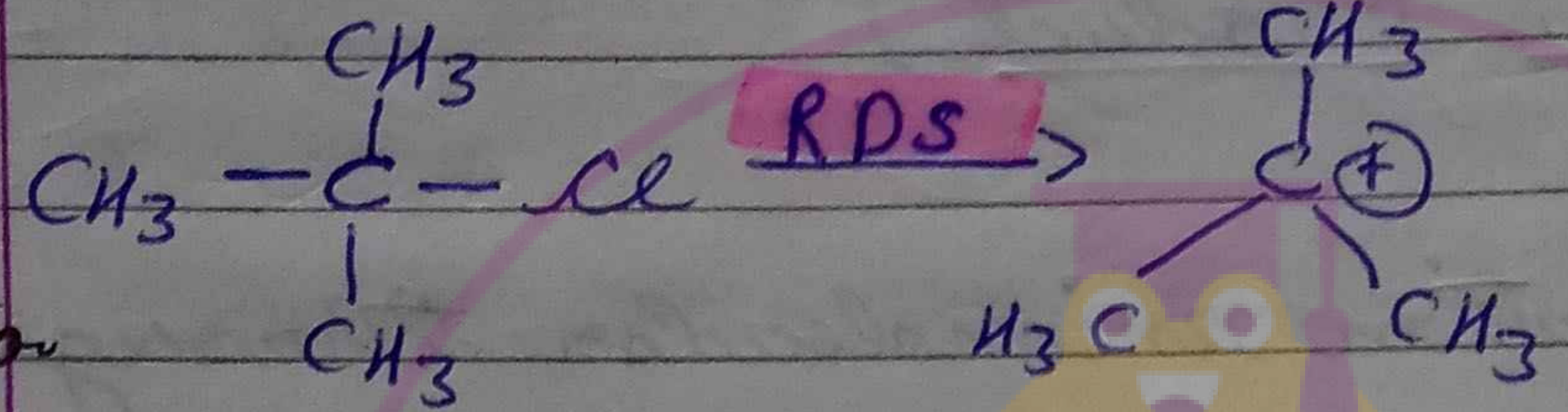
- This reaction requires very high activation energy.

- E_1 or elimination unimolecular.

Rate = K[alkyl Halide]

- 

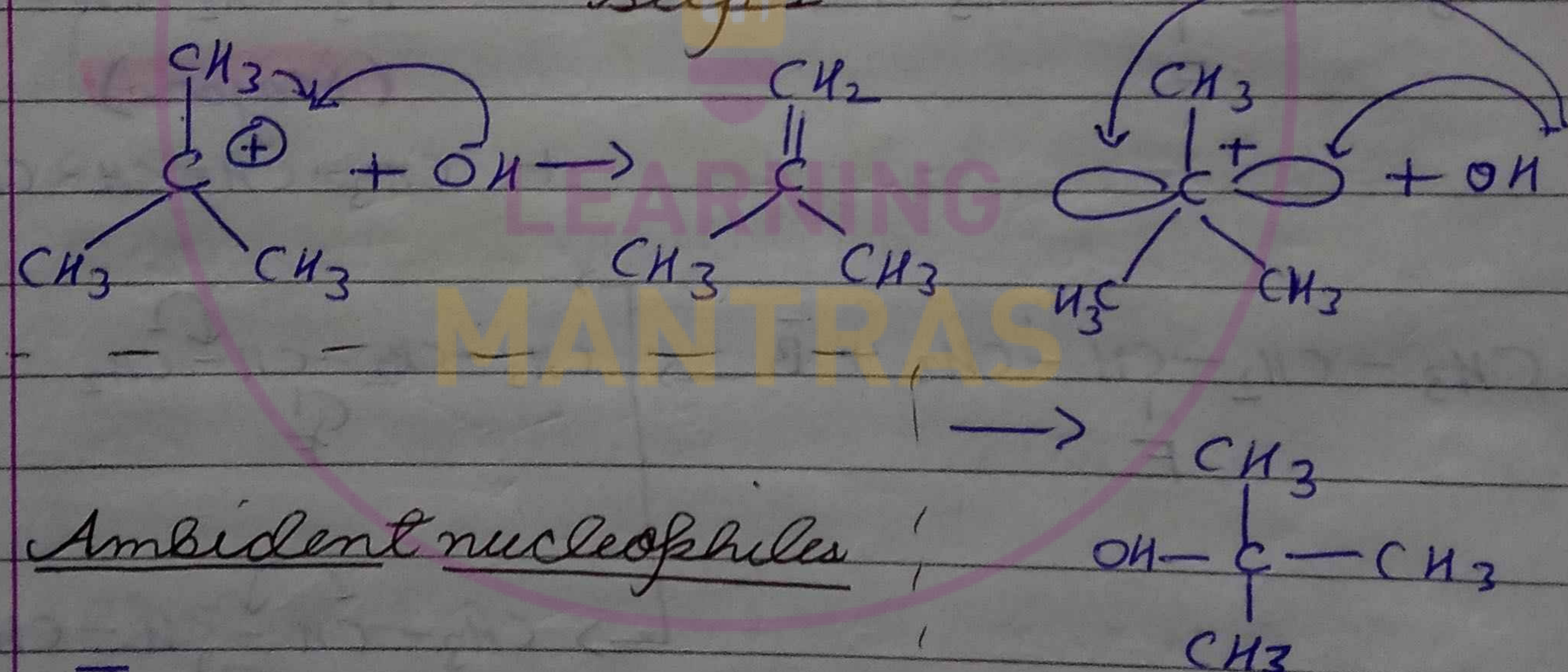
Step I
Formation of carbocation



Rate ∝ stability of carbocation

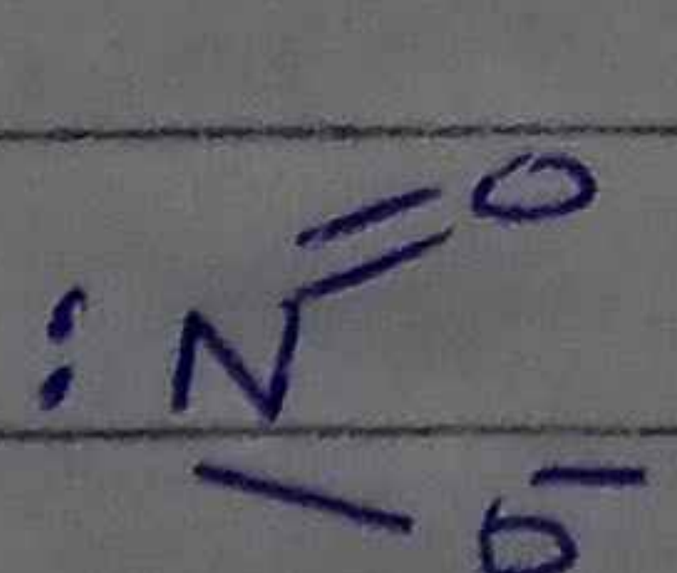
E_1 S_1

step 2



- Ambident nucleophiles

- $\overline{:C\equiv N:}$

- 

- $CH_3-CH_2-Cl + KCN \xrightarrow{SN_2} CH_3-CH_2-CN + KCl$
(Maj)

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- $CH_3-CH_2-Cl + AgCN \longrightarrow CH_3-CH_2-\overset{+}{N}\equiv\overset{-}{C} + AgCl$

- $CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl + KCN \xrightarrow{SN_1+SN_2} CH_3-\underset{\underset{CH_3}{|}}{CH}-CN + CH_3-\underset{\underset{CH_3}{|}}{CH}-NC$

  (Major) (Min)

- $CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl + AgCN \xrightarrow{SN_1+SN_2} CH_3-\underset{\underset{CH_3}{|}}{CH}-NC$

  2^0 (Major)

- $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + KCN \text{ or } AgCN \rightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}=CH_2$

  3^0 (Major)

- $CH_3-CH_2-Cl + NaNO_2 \xrightarrow{\text{or } KNO_2} CH_3-CH_2-ONO + CH_3-CH_2-NO_2$

  Nitritoethane (min)

  (Maj)

- $CH_3-CH_2-Cl + AgNO_2 \rightarrow CH_3-CH_2-NO_2 + CH_3-CH_2-ONO$

  (Maj)

  Nitroethane

- $CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl + NaNO_2 \xrightarrow[SN_2]{SN_1} CH_3-\underset{\underset{CH_3}{|}}{CH}-ONO$

  (Major)

- $CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl + AgNO_2 \xrightarrow[SN_1]{SN_2+} CH_3-\underset{\underset{CH_3}{|}}{CH}-NO_2$

  (Major)

☆ $4C_2H_5Cl + Pb \longrightarrow (C_2H_5)_4Pb$

Tetraethyllead → petrol antiknocking

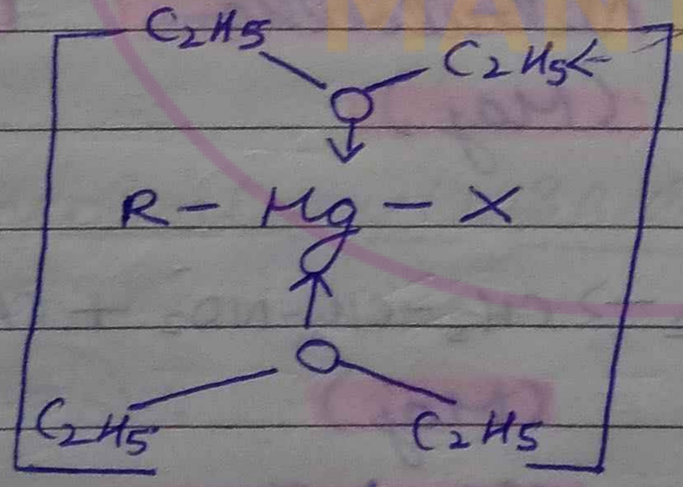
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + NaNO_2 \text{ or } AgNO_2 \xrightarrow{SN1} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-NO_2 \text{ (Major)}$$

Reaction with metals

★ $R-X + 2Li \xrightarrow[\text{ether}]{\text{Dry}} \overset{-}{R}\overset{+}{Li} + LiX$

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

$R-X + Mg \xrightarrow[\text{ether}]{\text{Dry}} R-Mg-X$ (Grignards reagent)



Reactivity = R-I > R-Br > R-Cl

Reduction Reactions

$R-X \xrightarrow{Zn/HCl} R-H$

1°, 2°, 3° / Zn/CH_3COOH

$Zn-Cu/C_2H_5OH$

$Na-C_2H_5OH$

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- $R-X \xrightarrow{LiAlH_4} R-H$

1° or 2°

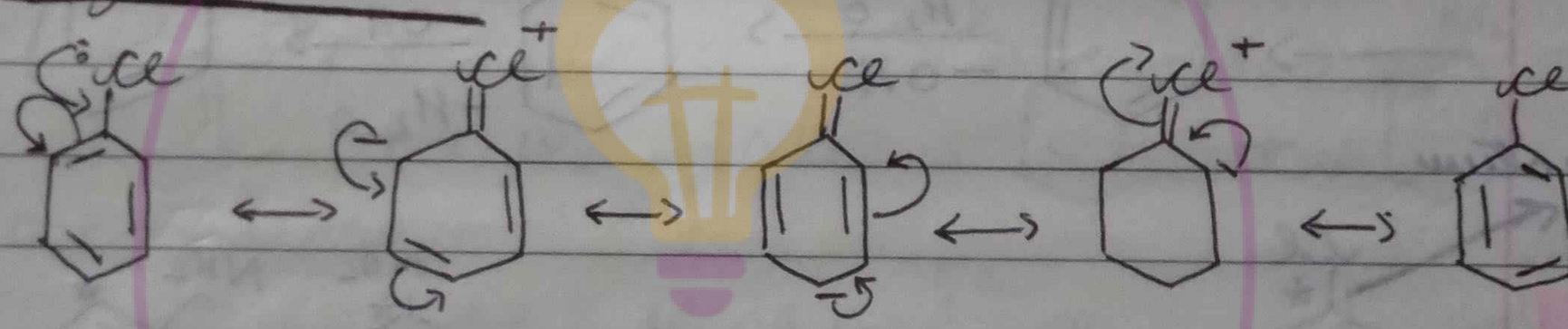
- $R-X \xrightarrow{NaBH_4} R-H$

2° or 3°

- $R-X \xrightarrow{(C_6H_5)_3SnH} R-H$

1°, 2°, 3°

- **Aryl Halides**



(i) Halogen is bonded to sp^2 hybridised C-atom

(ii) There is partial double bond character between C and halogen.

(iii) The π cloud of benzene repels any nucleophile approaching towards aryl halide.

(iv) Heterolytic cleavage of C-X bond in aryl halide results in the formation of phenyl cation which is less stable.

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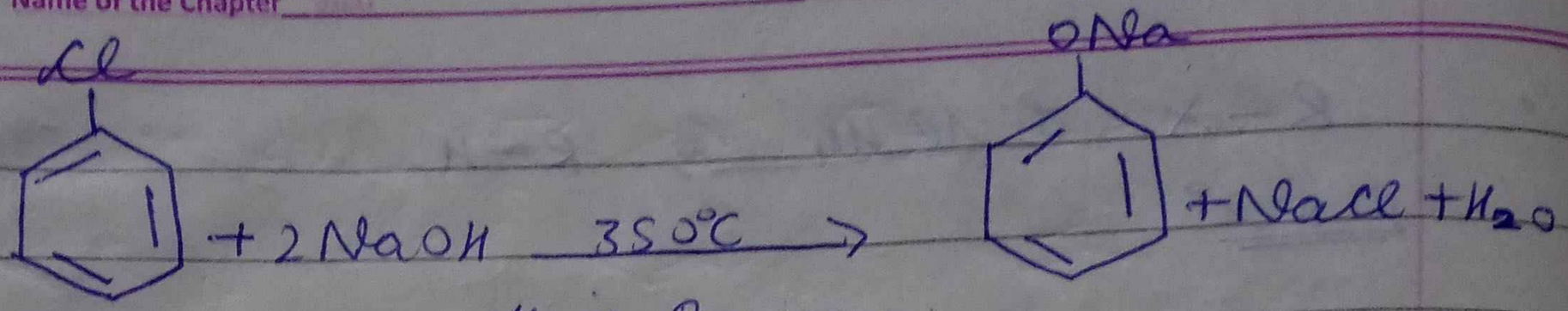
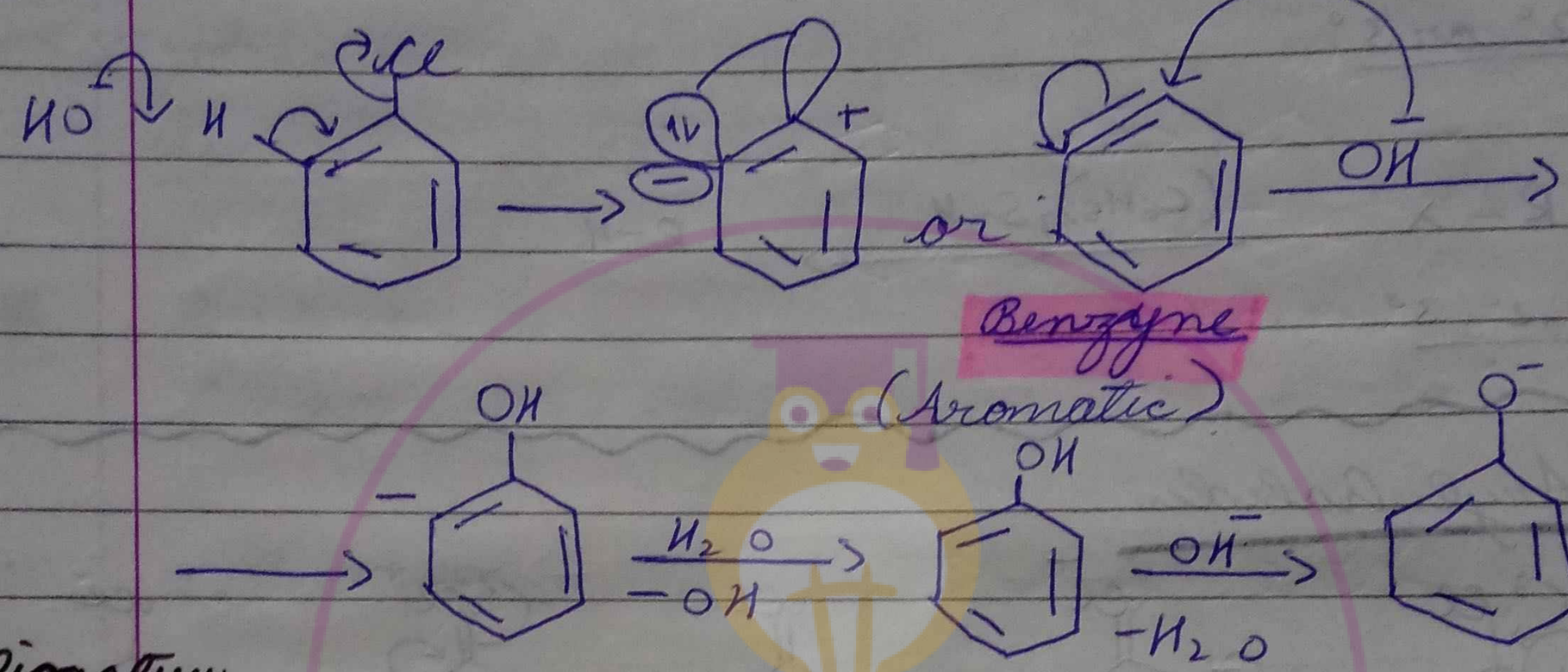
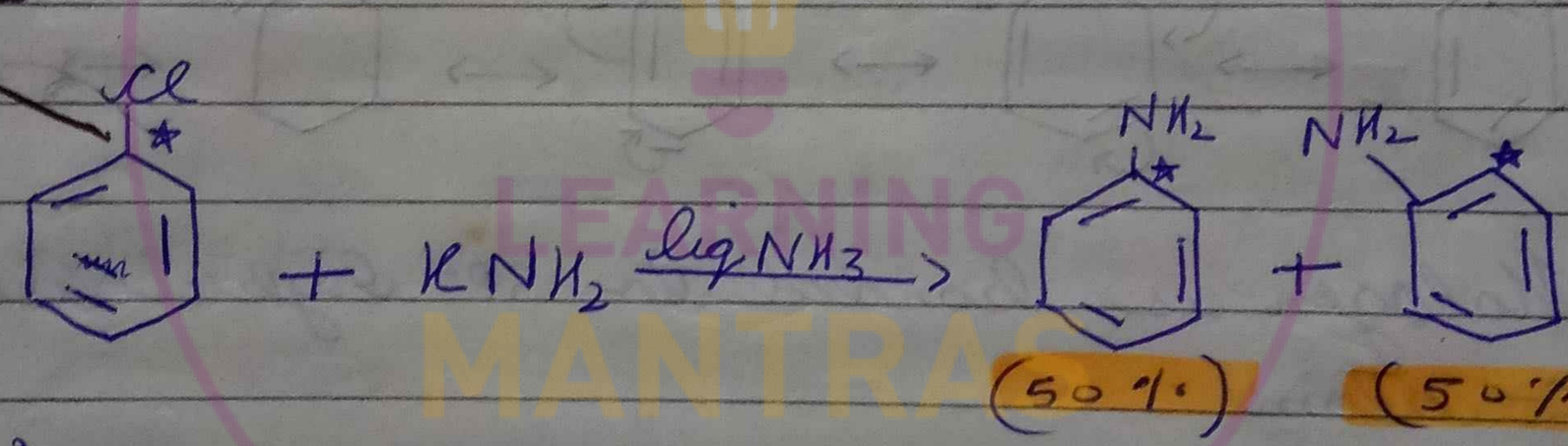
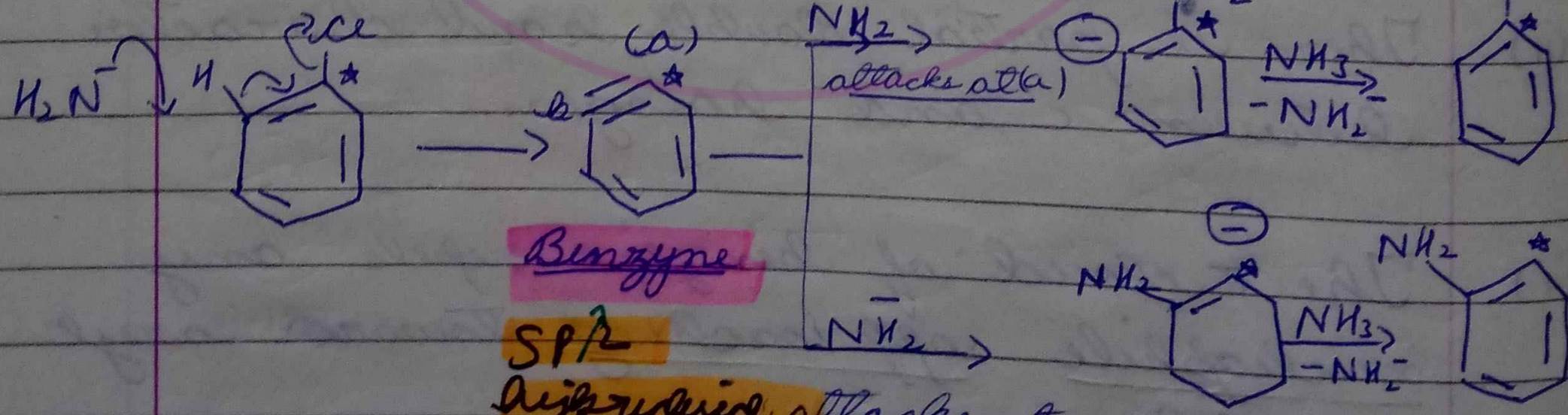




Radioactive carbon



Mechanism:



Hence planar molecule, attack from both sides will equal probability.

Signature .....

☆ In benzyne the $-NH_2$ closer to the methyl group is more stable and is the major product.

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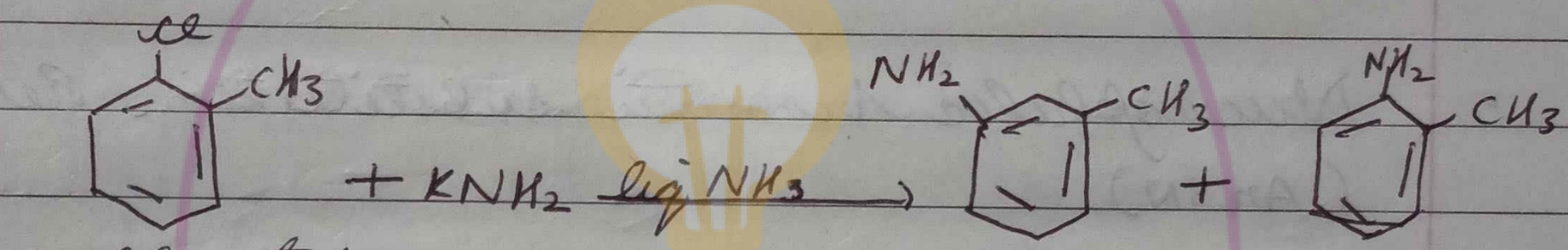
• Conditions favouring benzyne intermediate are

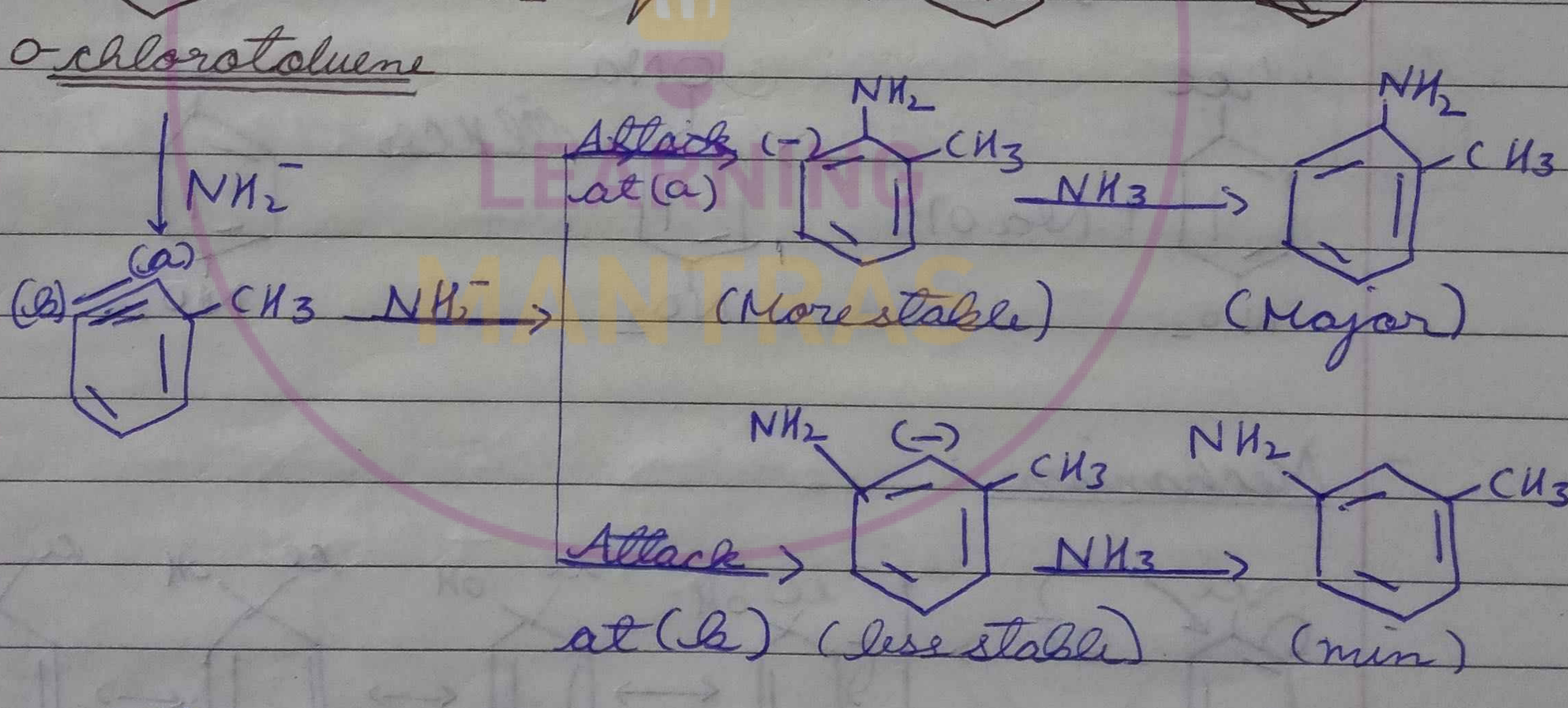
(i) Unsubstituted aryl halides.

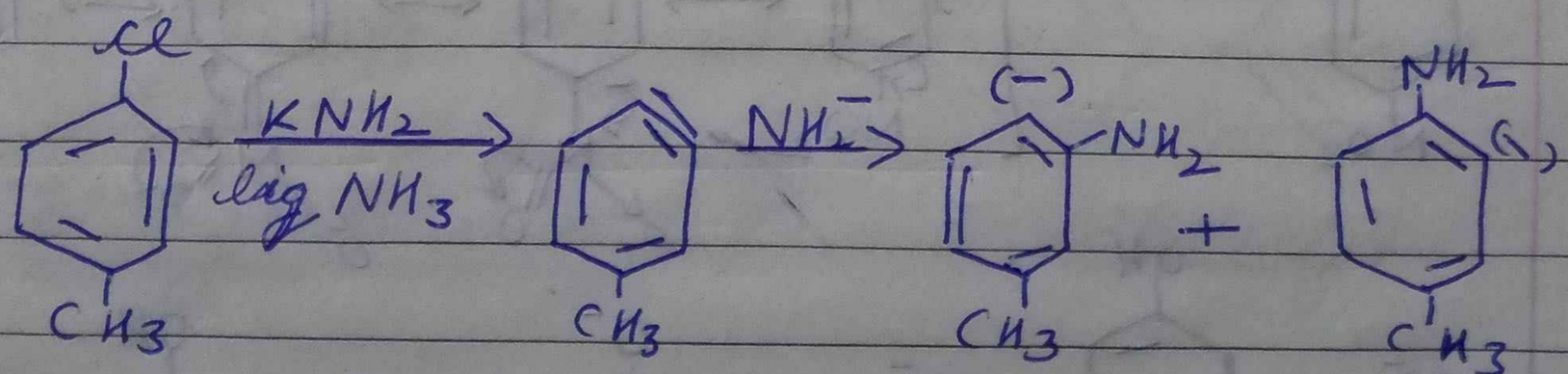
(ii) Aryl halide containing electron releasing groups.

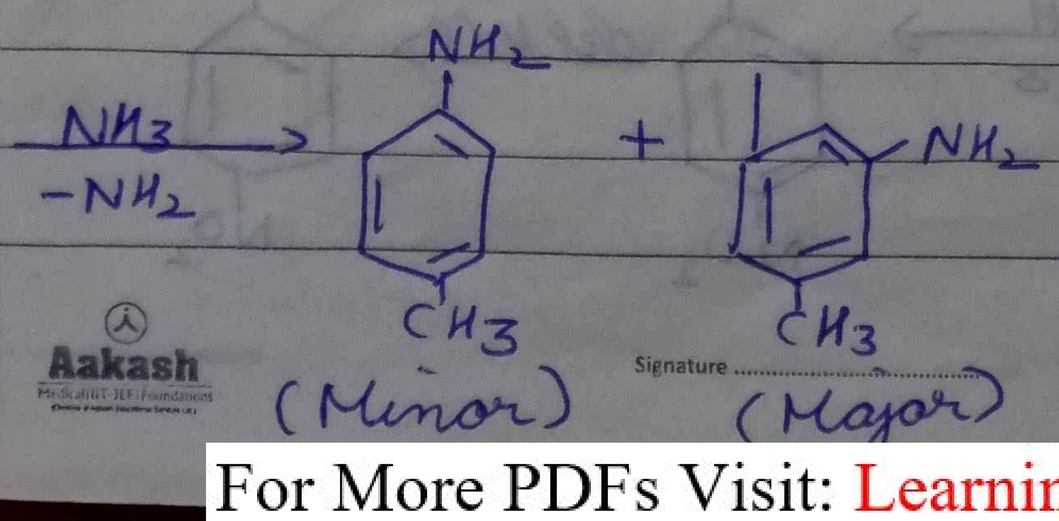
(iii) Aryl halides containing electron withdrawing groups at meta position only.



o-chlorotoluene







Signature .....

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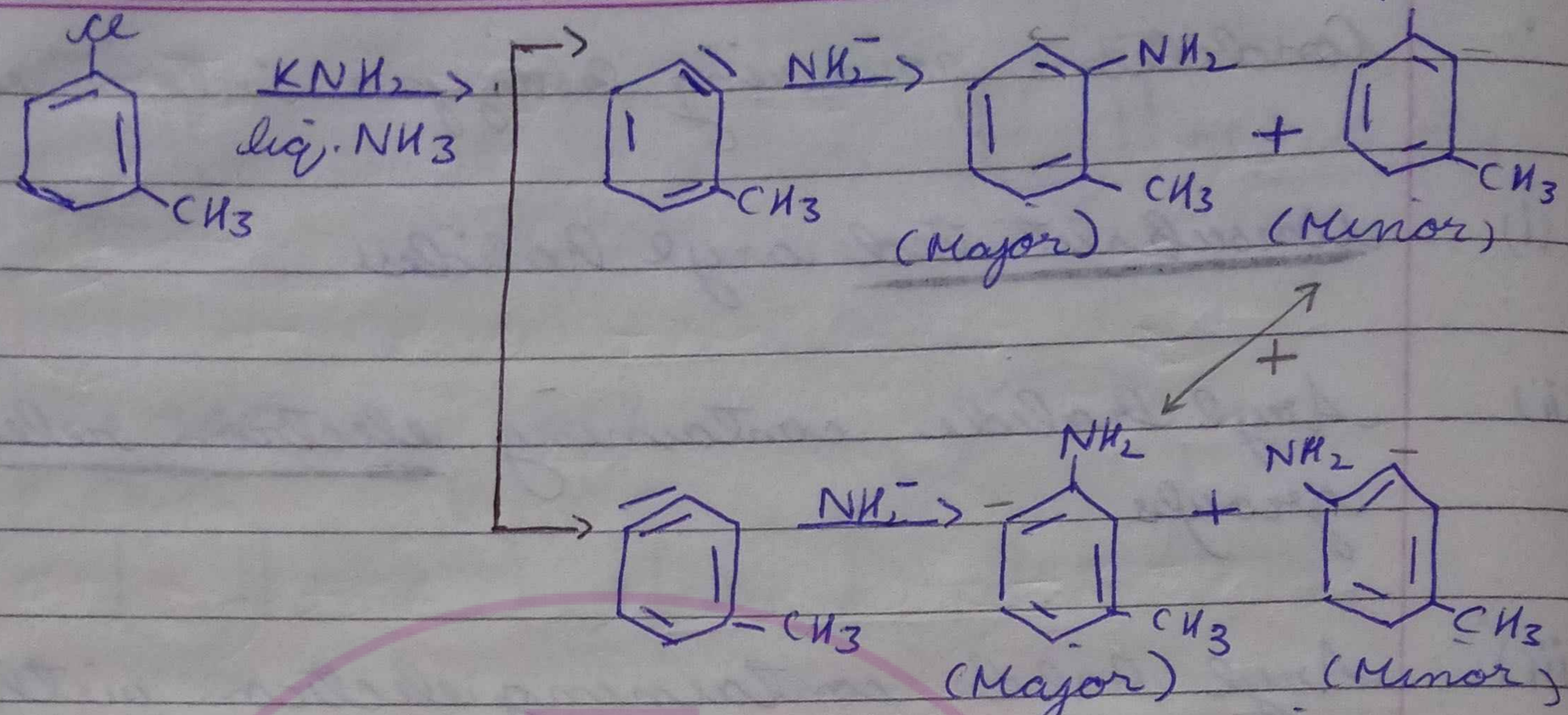
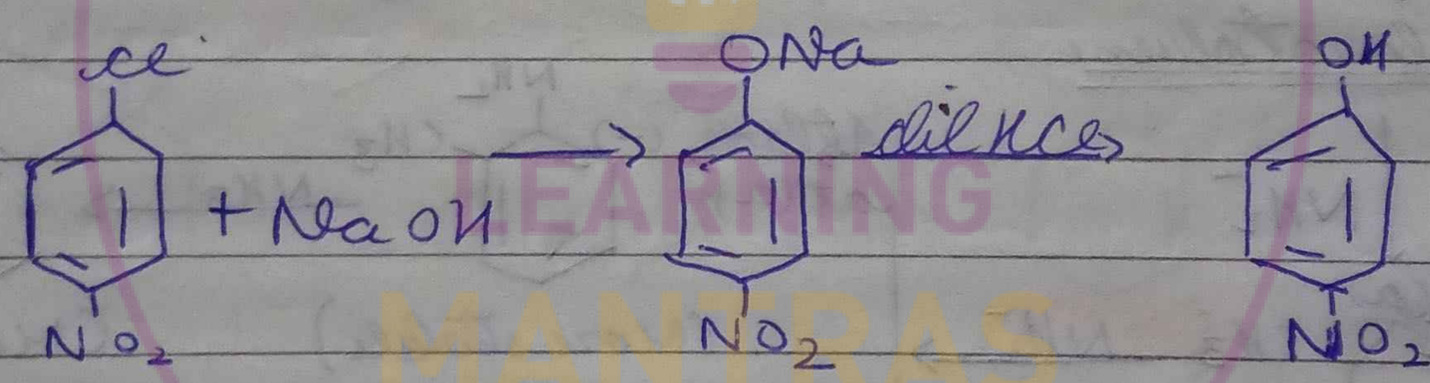
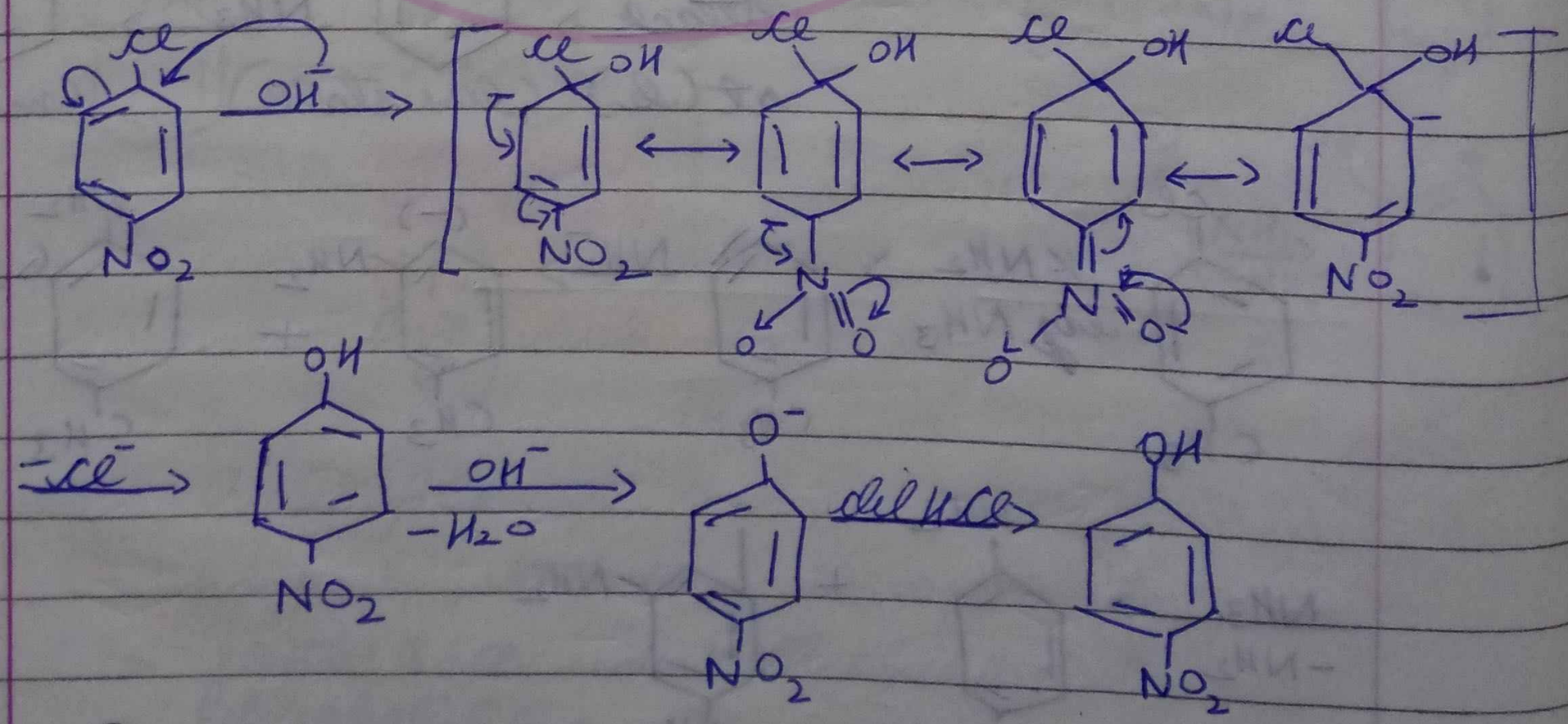


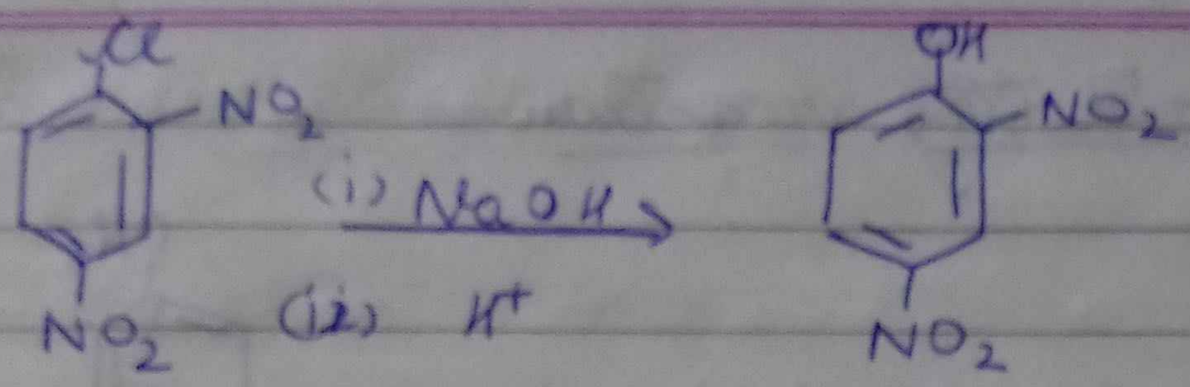
Overall yield of m-isomer will be high.

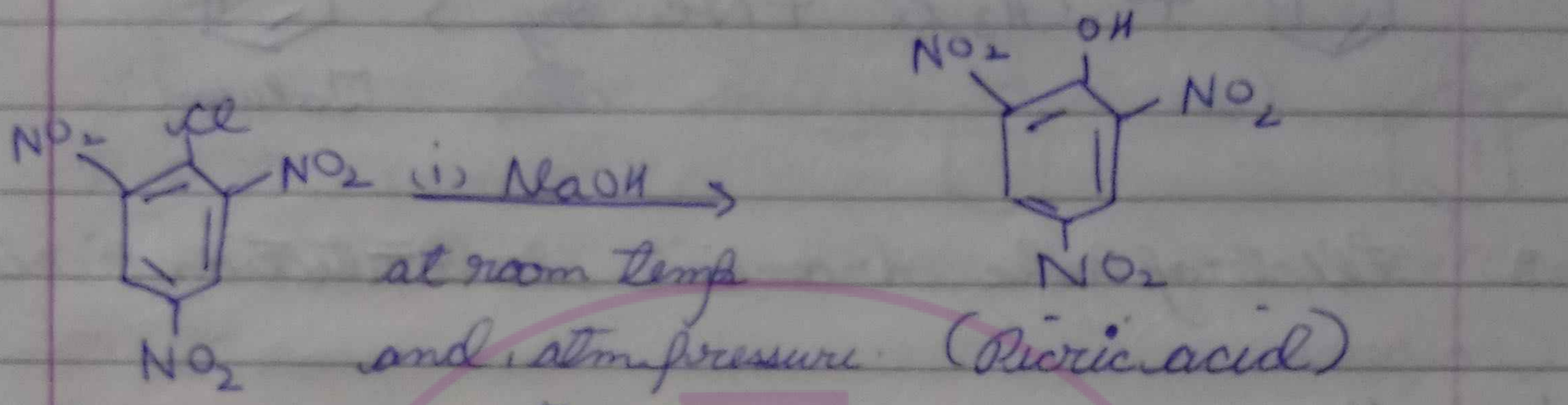
- Nucleophilic Aromatic substitution Reaction (ArSN)



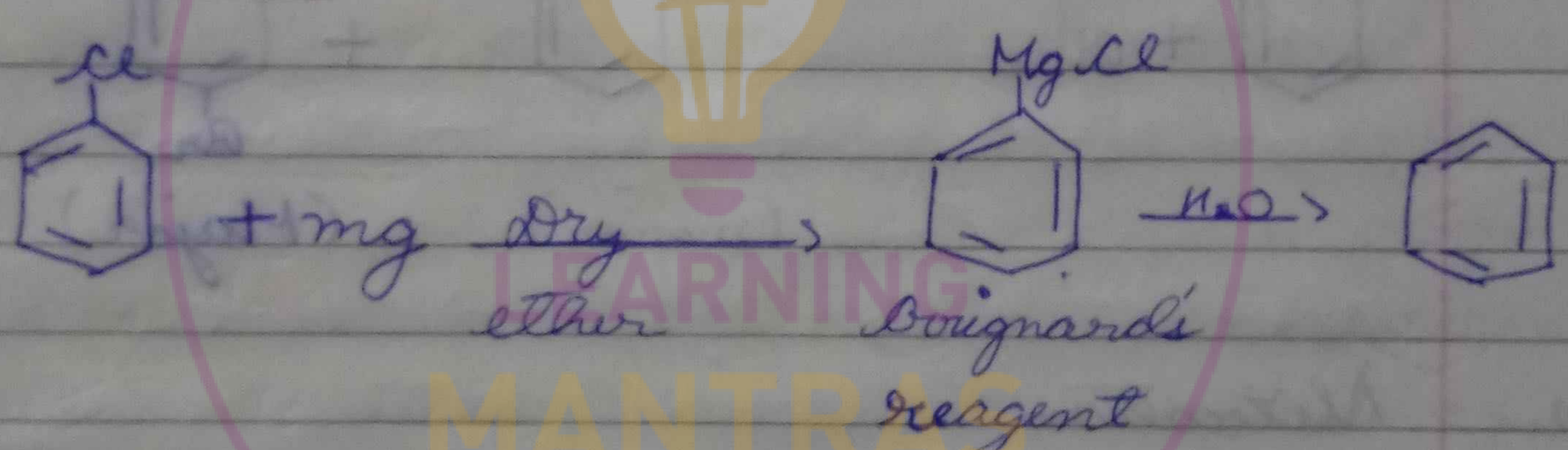
- Mechanism:



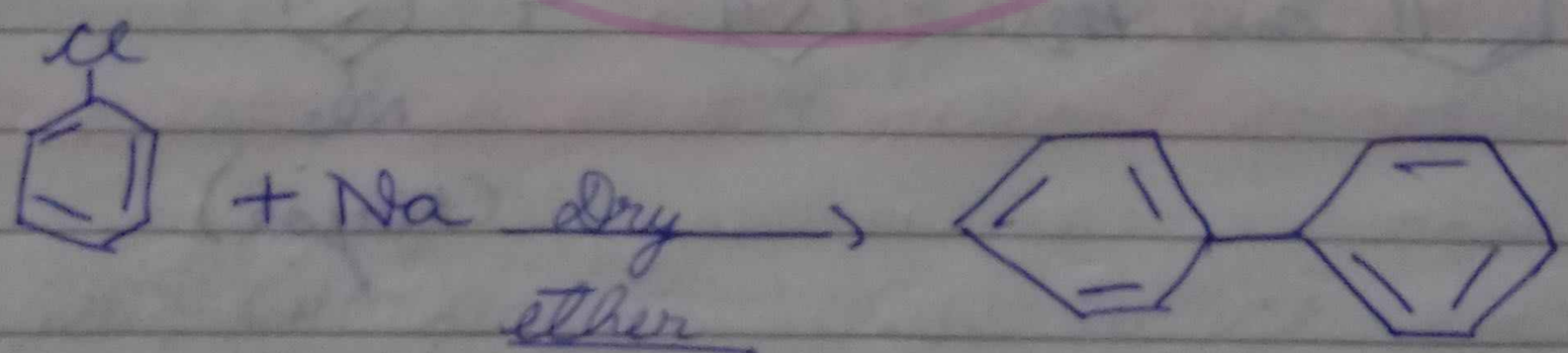




→ Reduction reactions:



→ Reaction with sodium



Fittig Reaction

Biphenyl

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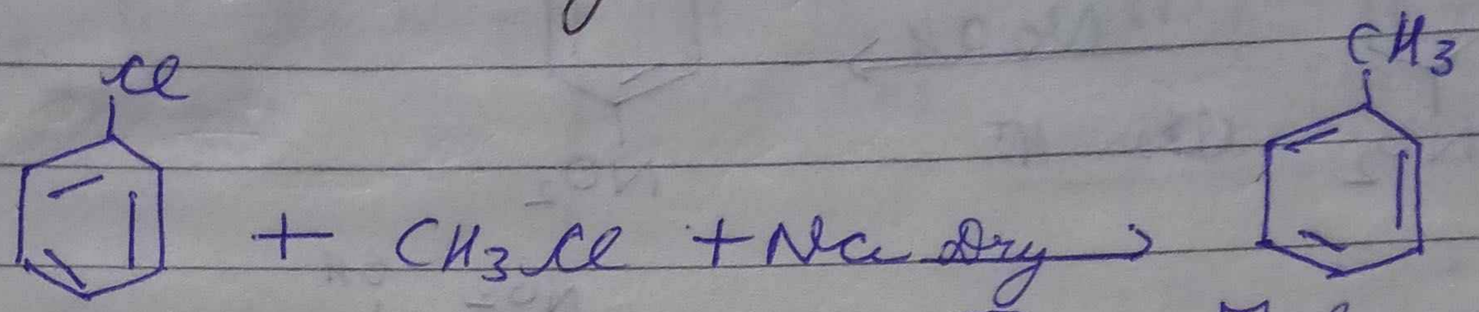
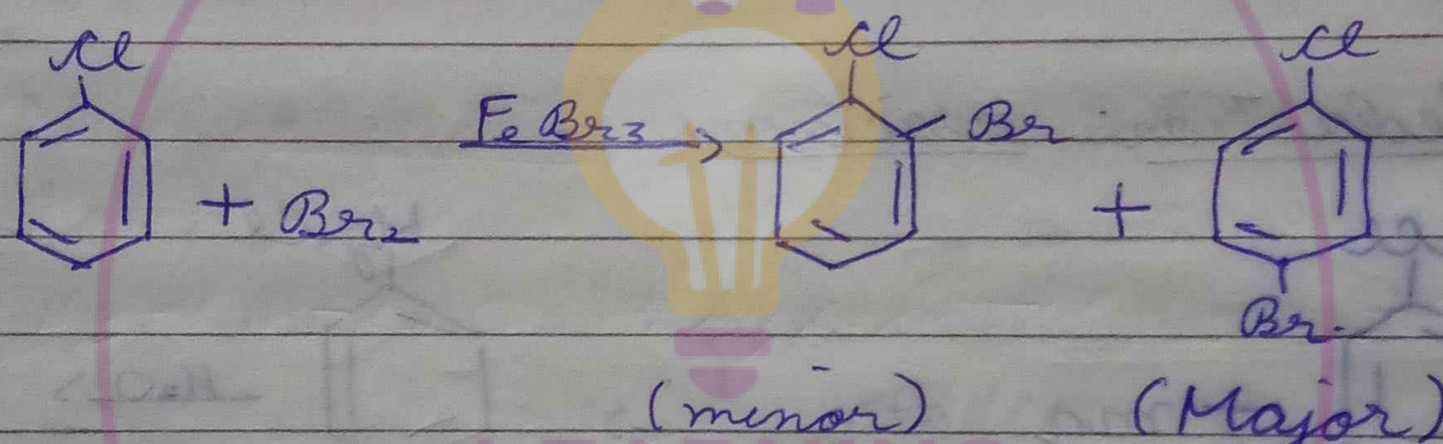
- **Wurtz – Fittig reaction**

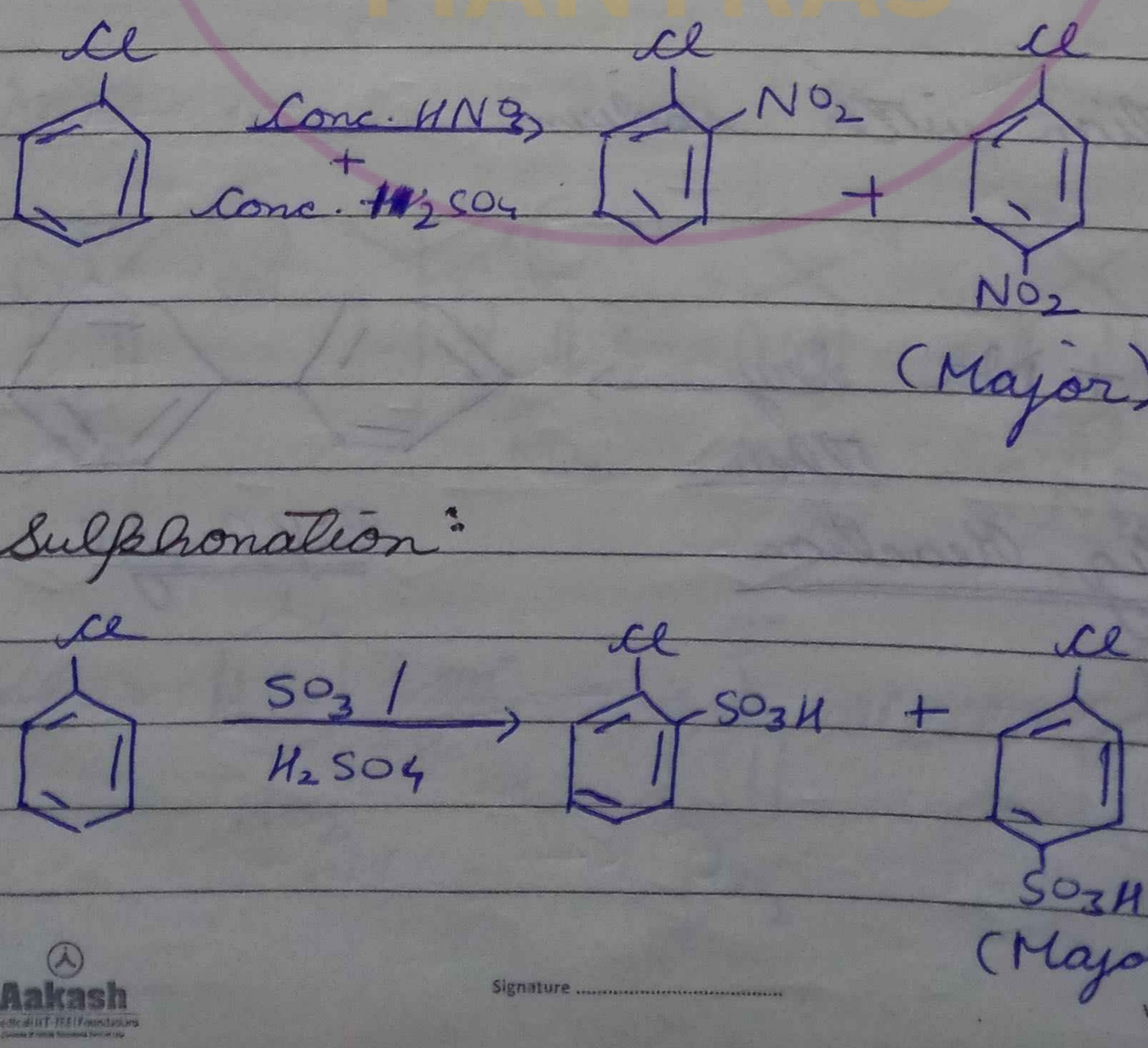


- **Electrophilic Aromatic Substitution Reactions:**

(i) **Halogenation:**



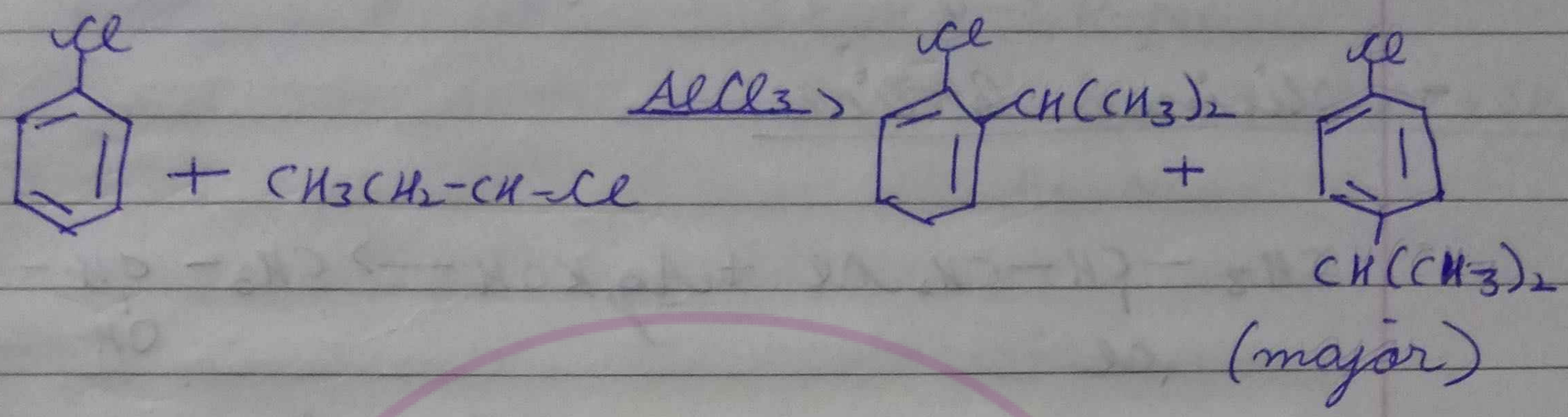
(ii) **Nitration:**



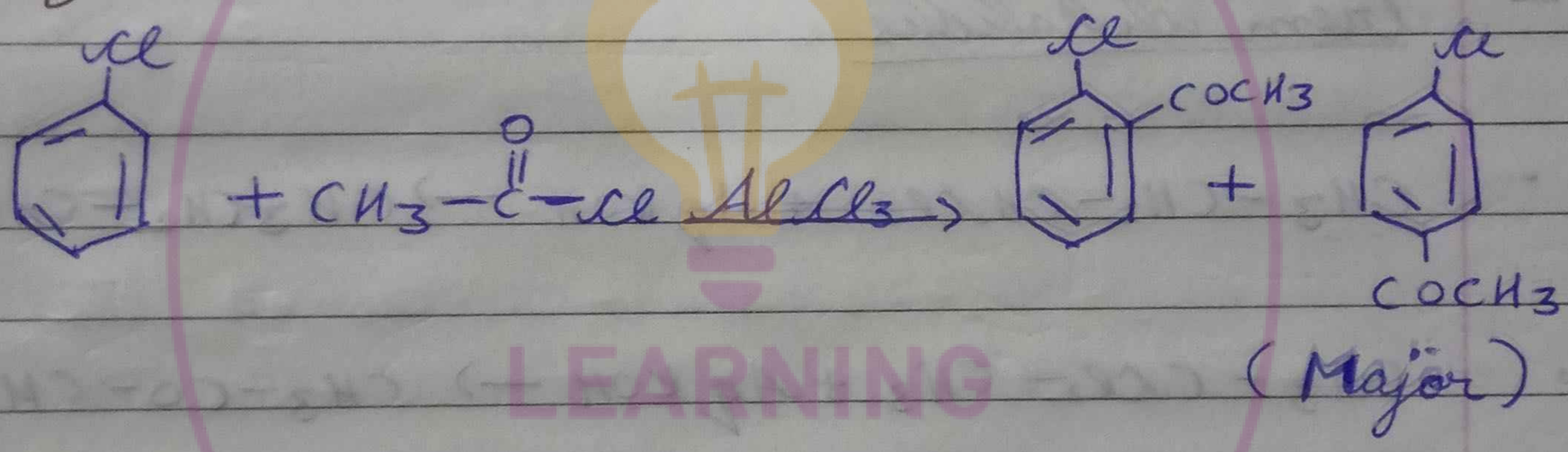
(iii) **Sulphonation:**

(iv) Friedal Crafts

(a) Alkylation :

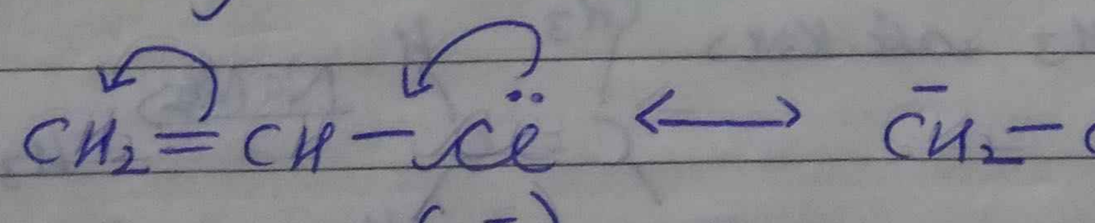


by Acylation :



- Reaction of vinyl halides and allyl halides :

- Vinyl halides normally do not undergo nucleophilic substitution reactions.



- Allyl halides undergo nucleophilic substitution by SN1 as well as SN2

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$CH_2=CH-CH_2-Cl + AqKOH \rightarrow CH_2=CH-CH_2-OH$

- Reaction of polyhalogen compounds :

– Vicinal halides

° $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2Cl + AqKOH \rightarrow CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

Vicinal diol

– Gem dihalides

• $CH_3-CH_2-CHCl_2 + AqKOH \rightarrow CH_3CH_2-CHO$

° $CH_3-CCl_2-CH_3 + AqKOH \rightarrow CH_3-CO-CH_3$

☆ ° $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}} \xrightarrow{alc.KOH} \underset{(E_2)}{} \overset{CH_3}{\underset{H}{C}}=\overset{Cl}{\underset{H}{C}} \xrightarrow{NaNH_2} CH_3-C\equiv CH$

☆ ° $CH_3-CCl_2-CH_3 \xrightarrow{alc.KOH} \overset{CH_3}{\underset{Cl}{C}}=\overset{H}{\underset{H}{C}} \xrightarrow{NaNH_2} CH_3-C\equiv CH$

• $2CHCl_3 + 6Ag \rightarrow HC\equiv CH + 6AgCl$

☆ $CHCl_3 + HNO_3 \rightarrow O_2N-CCl_3$

Chloropicrin

Tear gas

- $2CHCl_3 + O_2 \xrightarrow{hv} 2COCl_2 + 2HCl$
  Phosgene

- $CHCl_3 + R-NH_2 \text{ (or } Ar-NH_2\text{)} + 3KOH \longrightarrow R-NC \text{ (or } Ar-NC\text{)} + 3KCl + 3H_2O$
  aromatic