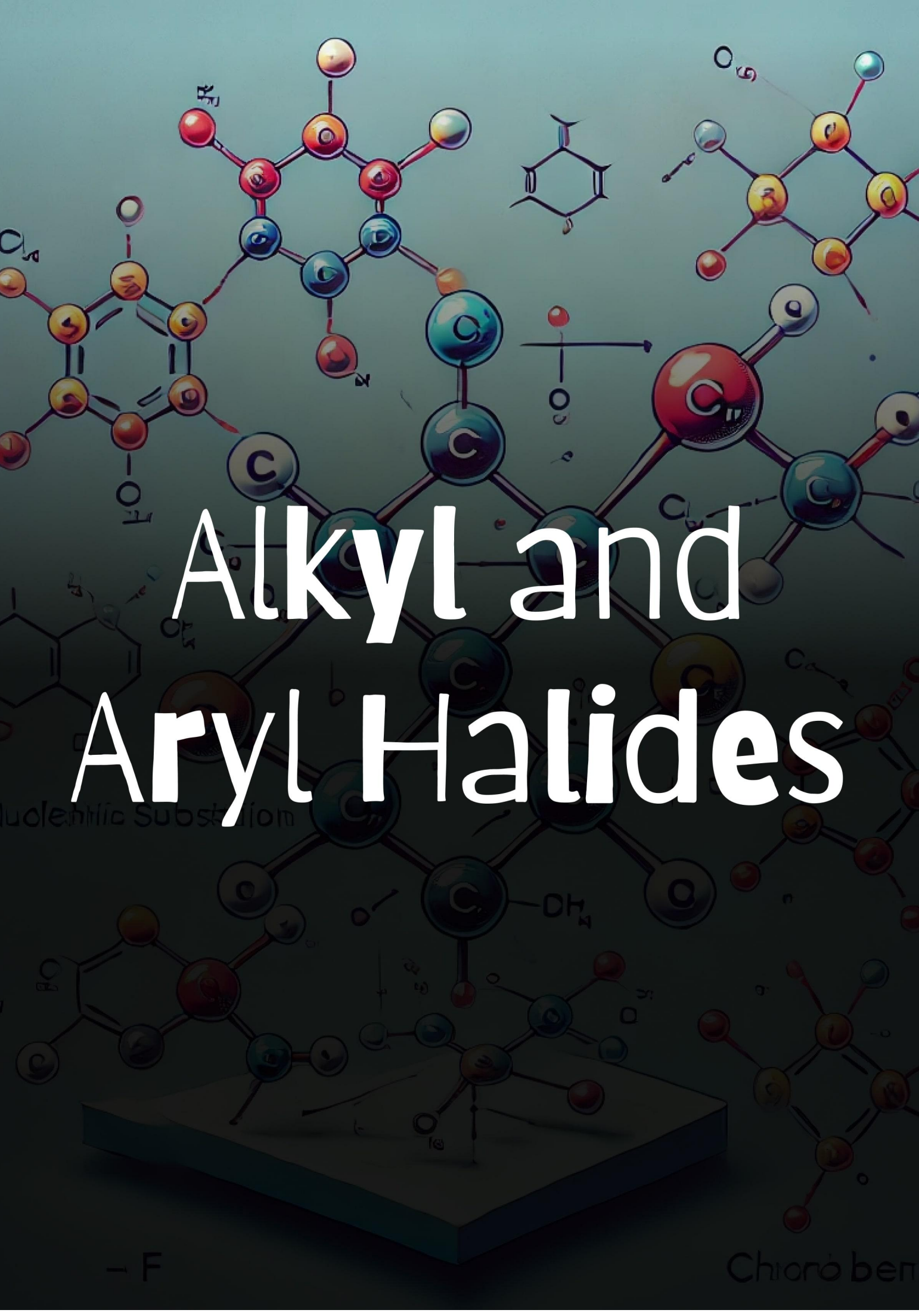


ALKYL HALIDES

PREPARATION

1. By halogenation of alkanes

$$R-H + X_2 \longrightarrow R-X + HX$$

$$X_2 \longrightarrow 2X$$

$$R-H + X \longrightarrow R + HX$$

$$R + X-X \longrightarrow R-X + X$$

$F_2 > Cl_2 > Br_2 > I_2$

↓ reversible

2. By hydrohalogenation of alkenes

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

3. By hydrobromination of alkenes in presence of peroxide

$$R-CH=CH_2 + HBr/H_2O_2 \longrightarrow R-CH_2CH_2Br$$

4. By halogenation of alkenes

$$-\overset{|}{C}=\overset{|}{C}- + Br_2/CCl_4 \longrightarrow -\underset{\underset{Br}{|}}{\overset{|}{C}}-\overset{Br}{\overset{|}{C}}-$$

5. By reaction with HOX

$$R-CH=CH_2 + HOX \longrightarrow R-\underset{\underset{OH}{||}}{CH}-\underset{\underset{X}{|}}{CH_2}$$

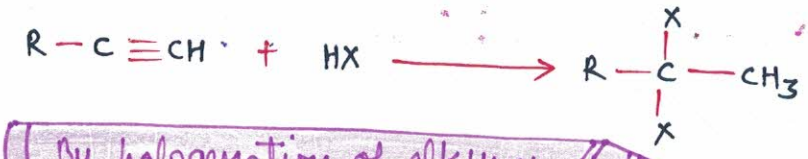
6. By reaction of $X_2/h\nu$

$$CH_2=CH-CH_3 + X_2/h\nu \longrightarrow CH_2=CH-CH_2-X$$

7. By NBS

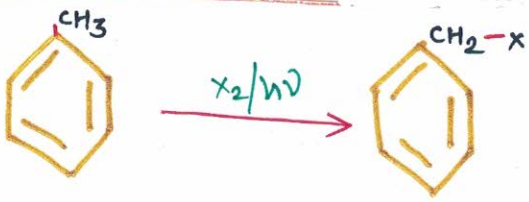
$$CH_2=CH-CH_3 + NBS \xrightarrow{h\nu} CH_2=CH-CH_2-Br$$

8. **By hydrohalogenation of alkynes**

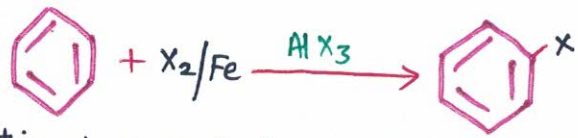


9. **By halogenation of alkynes**

10. **By halogenation of al**

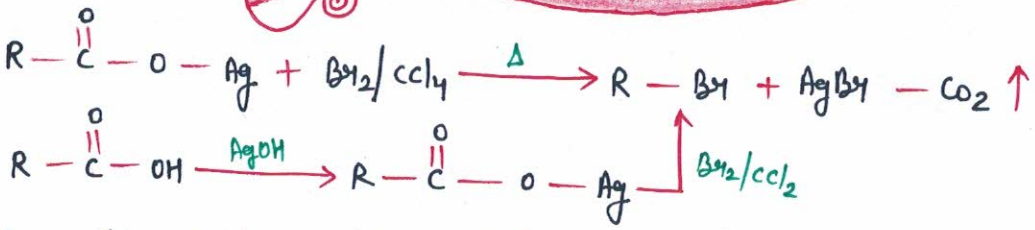


11. **By halogenation of aromatic hydrocarbons**



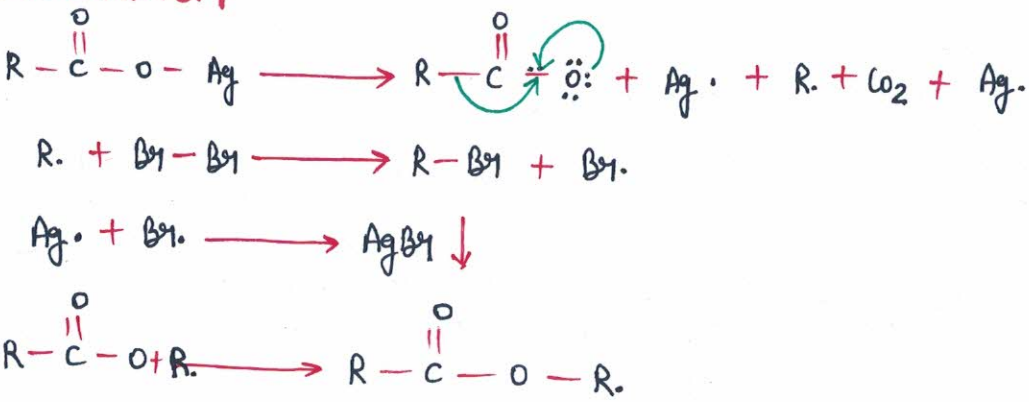
Halogenation show β hydrogen isotopic effect. $CH_4 > CD_4$ (Rate)

HUNS DICKER REACTION



Preparation of only alkyl bromide fomcarbonylic acids by reaction with AgOH & further with Br_2/CCl_4.

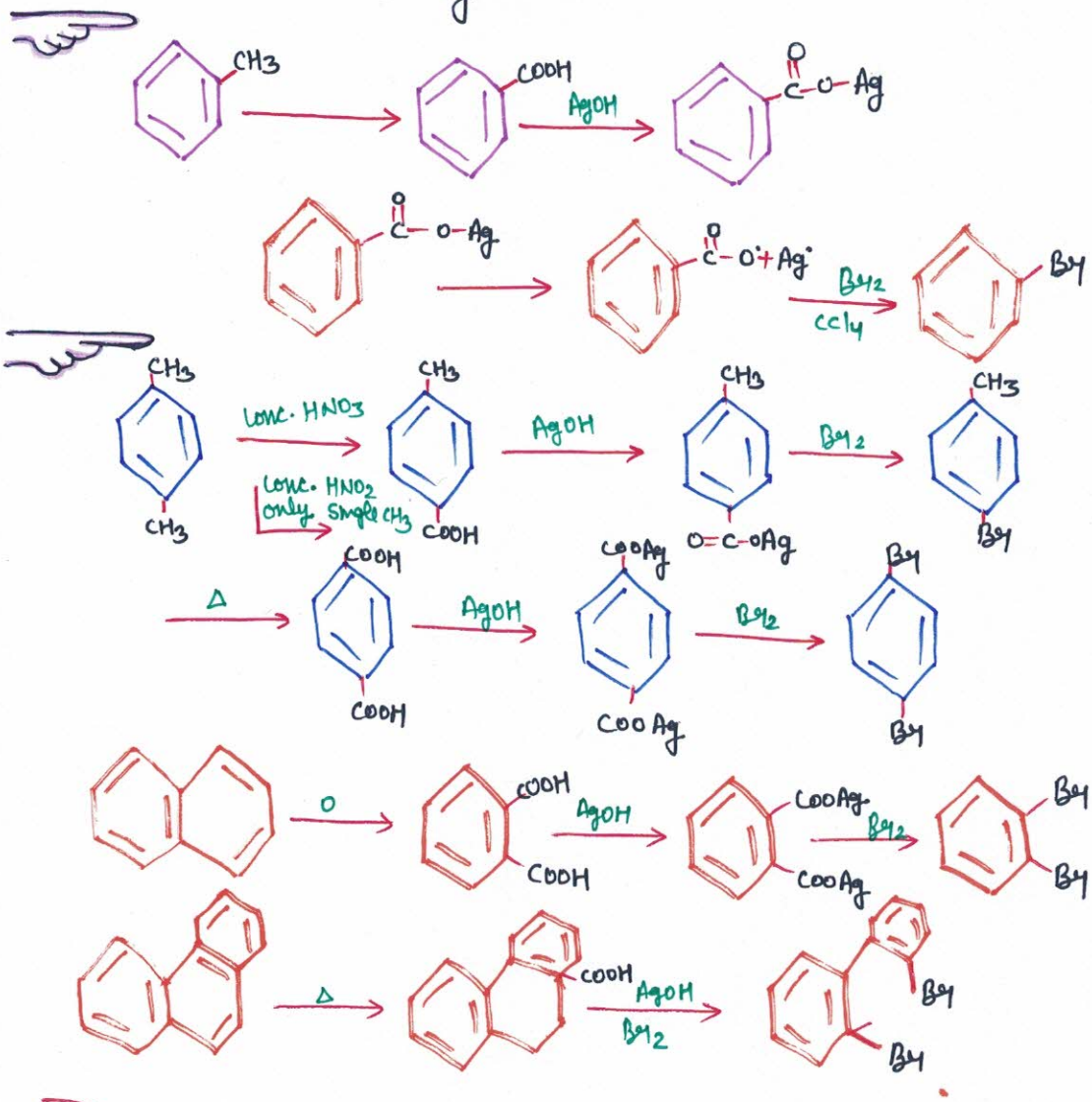
MECHANISM



In this reactions, ester may be formed as by product.

In Nail Polish Butyl Acetate is solvent.

Esters Fruity smell



Imp....

$$R-COOH + AgOH \longrightarrow RCOOAg \xrightarrow{Cl_2} R\,Cl + AgCl + CO_2\uparrow$$

$$R-(Cl)_x$$

chlorine becomes so reactive at the reaction conditions, that it undergoes poly chlorination

$$R-COOAg \longrightarrow R-I + CO_2 + AgI$$

$$R-I \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-R$$

with iodine, as I is good leaving group RI again reacts with silver salt to form ester.

Ester is major product.

BY HALIDE EXCHANGE REACTION

a. Finkel stein Reaction

$R-F + NaI/\text{Acetone} \longrightarrow R-I + NaF$

$R-Cl + NaI/\text{Acetone} \longrightarrow R-I + NaCl$

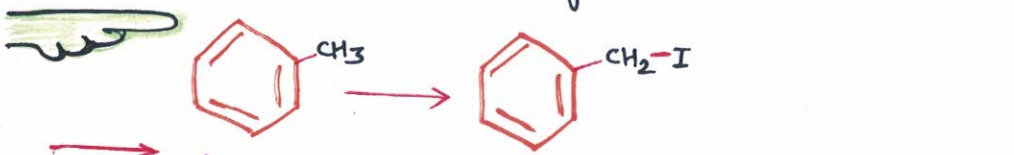
$R-Br + NaI/\text{Acetone} \longrightarrow R-I + NaBr$

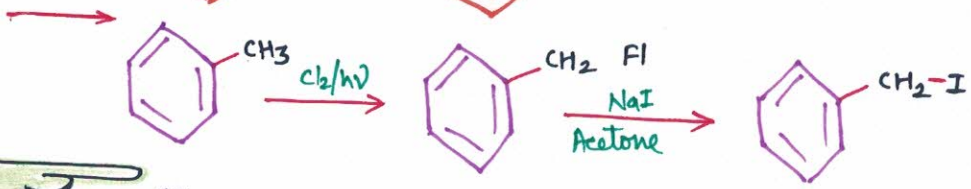
$NaF > NaCl > NaBr > NaI$

Ionic nature

only NaI is soluble in acetone because it is covalent. All others are ionic and not soluble.

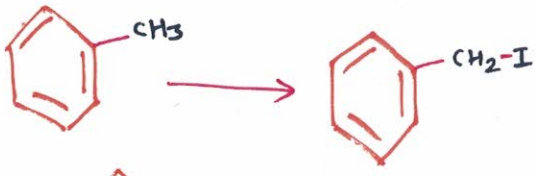
only covalent are soluble in organic solvent. i.e - acetone

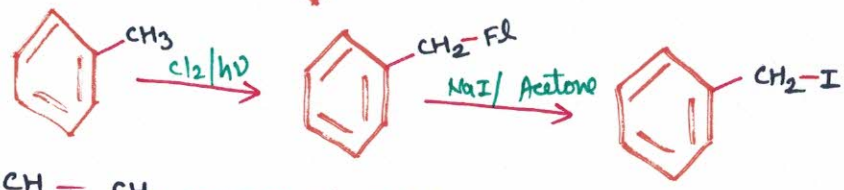




$CH_2=CH-CH_3 \longrightarrow CH_2=CH-CH_2-I$

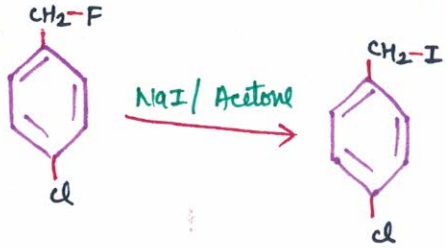
$CH_2=CH-CH_3 \longrightarrow CH_2=CH-CH_2-Cl \xrightarrow{NaI/\text{Acetone}} CH_2=CH-CH_2-I$





$CH_2=CH-CH_3 \longrightarrow CH_2=CH-CH_2-I$

$CH_2=CH-CH_3 \xrightarrow{Cl_2/h\nu} CH_2=CH-CH_2-Cl \xrightarrow{NaI/\text{Acetone}} CH_2=CH-CH_2-I$



$Cl-CH=CH-CH_2-Cl + NaI/\text{Acetone} \longrightarrow Cl-CH=CH_2-CH_2-I$

$Br-CH=CH-CH_2-F + NaI/\text{Acetone} \longrightarrow Br-CH=CH_2-CH_2-I$

This reaction is used because as iodonation is reversible, it is difficult to prepare iodine products.

b. By SWARTS Reaction

$R\text{-}Cl + AgF \xrightarrow{\text{aqueous medium}} RF + AgCl$

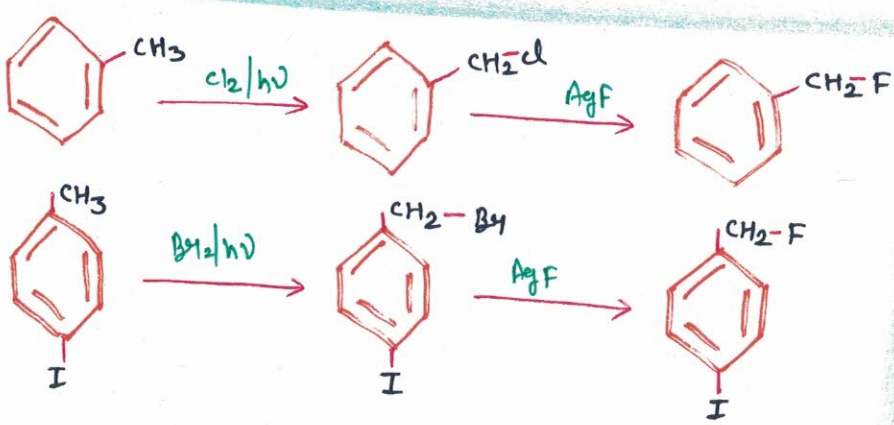
$R\text{-}Br + AgF \xrightarrow{"} RF + AgCl$

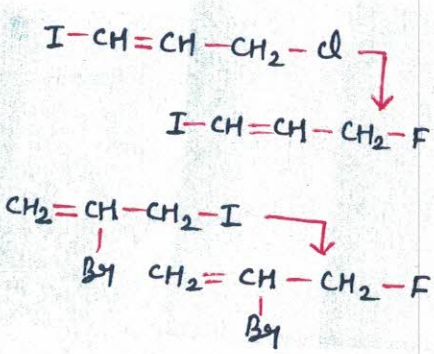
$R\text{-}I + AgF \xrightarrow{"} RF + AgCl$

$AgCl$ ↓ Precipitate

only silver fluoride is soluble in water and others are precipitated. so only AgF is formed.

The use of these reactions is that fluorination is highly exothermic and we use it to form fluro products.



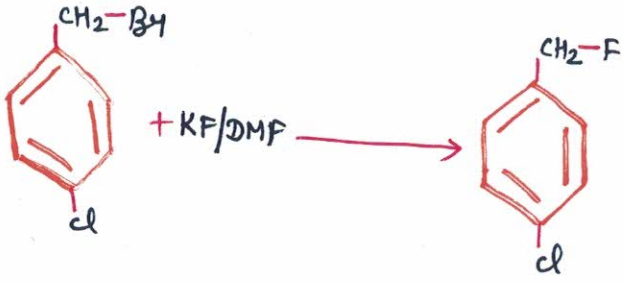


Nucleophilicity in protic – $F^- < Cl^- < Br^- < I^-$

In Aprotic – $F^- > Cl^- > Br^- > I^-$

So, we use following reaction → $R\text{-}Cl + KF/DMF \xrightarrow[\text{Aprotic}]{} RF + KCl$

F^- is more nucleophilic than Cl^-

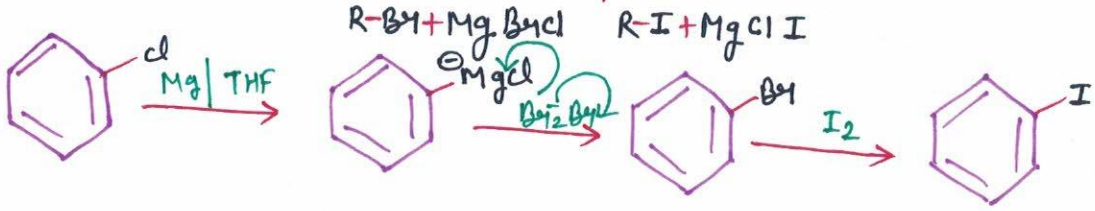


we can also use KCl/DMF to replace Br & I similarly KBr/DMF for I but there is no meaning of KI/DMF.

c. By using Grignard reagent

$$R-Cl + Mg/Et_2O \longrightarrow R^{\oplus}MgCl$$

$R-Br + Mg, BrCl$ (Br2) $\quad R-I + MgClI$ (I_2)

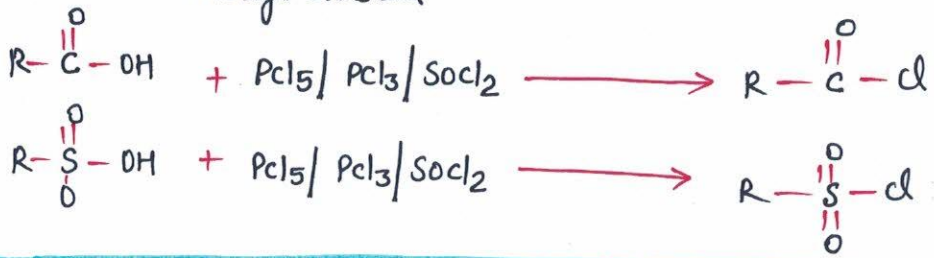


BY REACTION WITH ALCOHOLS

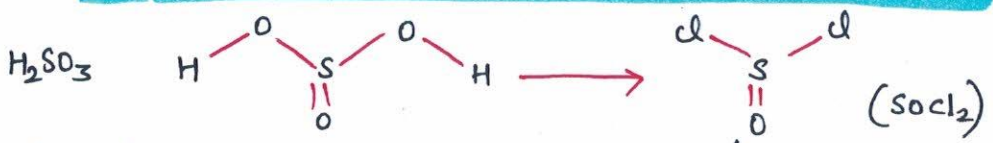
a. WITH PCl_5 / PCl_3 / $SOCl_2$

R OH	PCl_5	R Cl	$POCl_3$	HCL	
3R OH	PCl_3	R Cl	H_3PO_3		
R OH	$SOCl_2$	R Cl	SO_2	HCL	

Thionyl chloride



It is method to convert –OH into –Cl.

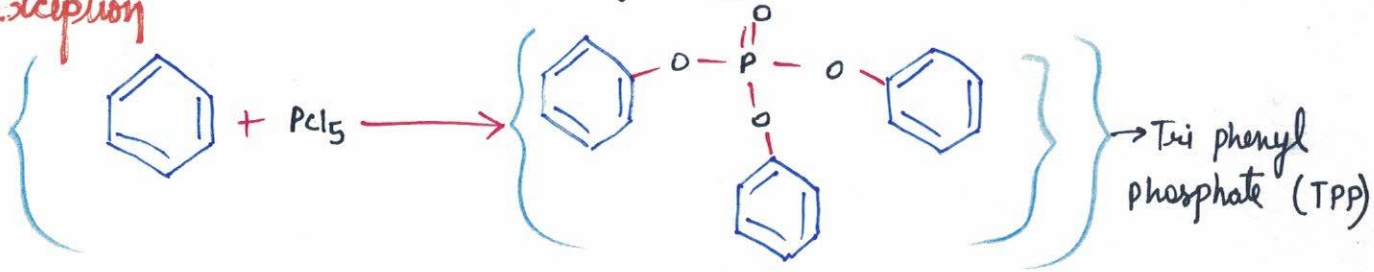


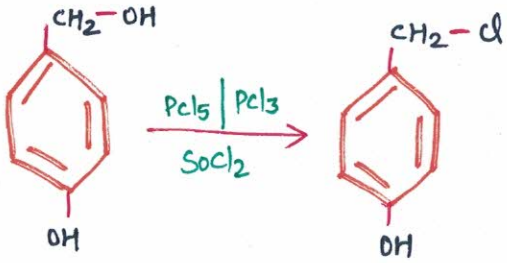
Glycerol + PCl_5 / PCl_3 / $SOCl_2$ → $Cl-CH_2-\underset{Cl}{CH}-CH_2-Cl$

In PCl_5, $POCl_3$ is liquid & in PCl_3, H_3PO_3 is liquid so we have to separate alkyle halide from mixture.

But in $SOCl_2$, SO_2 & HCL both are gases and hence there is no need of separation. Hence $SOCl_2$, is generally prefferred.

Exception





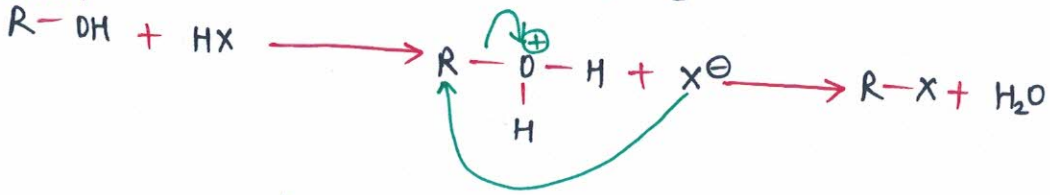
$$P + I_2 \longrightarrow PI_3$$

$$R\text{–}OH + PI_3 \longrightarrow R\text{–}I + H_3PO_3$$

BY REACTION WITH HX

$$R\text{–}OH + HX \longrightarrow R\text{–}X + H_2O$$

MECHANISM



$$R\text{–}OH + KX \longrightarrow N.R.$$

with HX, leaving group is H_2O i.e neutral hence good leaving group. with KX, leaving group is OH^- which is not good. Rather OH^- again reacts with RX to reverse the reactions, no forward reaction occurs. Hence nucleophilic substitution reactions of alcohol occurs only in acidic medium. It does not occur in basic or neutral medium acids catalyse nucleophilic substitution reaction.

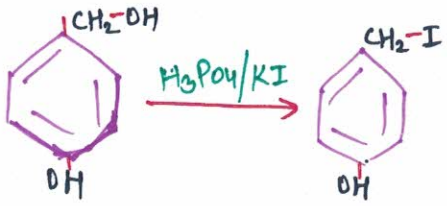
$$KI + H_3PO_4 \rightleftharpoons HI$$

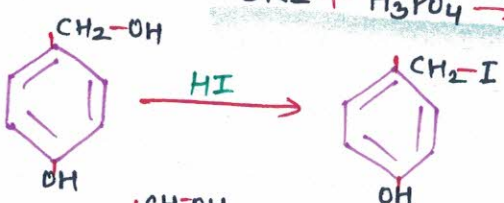
$$3KI + H_3PO_4 \longrightarrow K_3PO_4 + 3HI$$

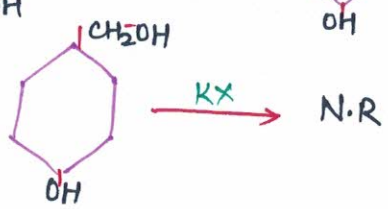
$$R\text{–}OH \xrightarrow{H\cdot I} R\text{–}I$$

$$R\text{–}OH \xrightarrow{KX} N.R$$

$$R\text{–}OH \xrightarrow{KI + H_3PO_4} R\text{–}I$$

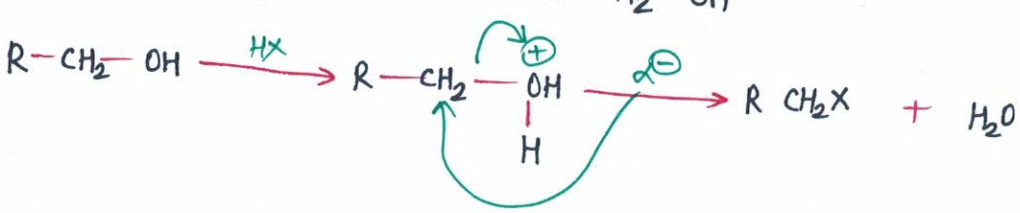


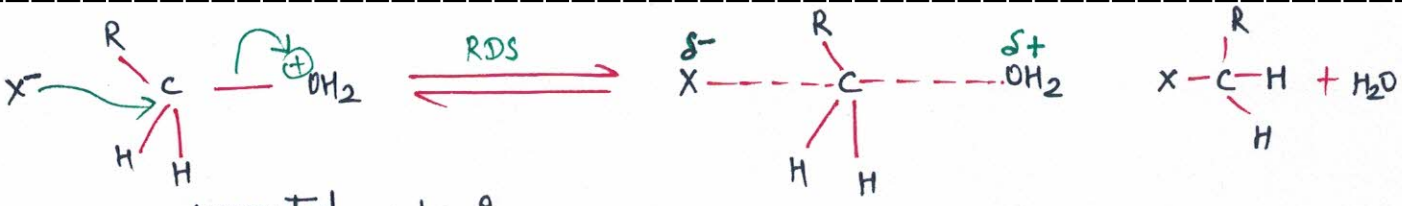




MECHANISM FOR PRIMARY ALCOHOLS

General formula : $R\text{–}CH_2\text{–}OH$





Concerted mechanism

Rate $\propto$ [ROH][HX] It is substitution nucleophilic bimolecular (SN_2)

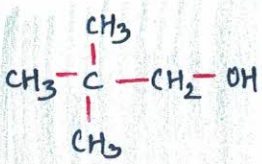
All primary alcohols undergo nucleophilic substitution by SN_2 mechanism.

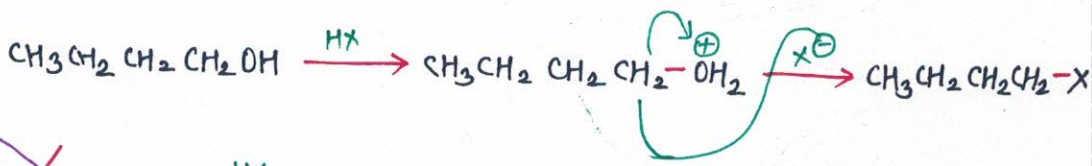
TS is intermediate, no rearrangement.

Rate is directly proportional to crowding of T.S. More crowded difficult to form. Hence, methyl alcohol undergo this reaction at the fastest rate.

Secondary & Tertiary alcohols do not undergo this mechanism only primary undergo due to less crowding.

As branching in β carbon ↑, crowding in TS ↑ Hence rate ↓.
So neopentyl alcohol appears to be primary but does not undergo this mechanism.





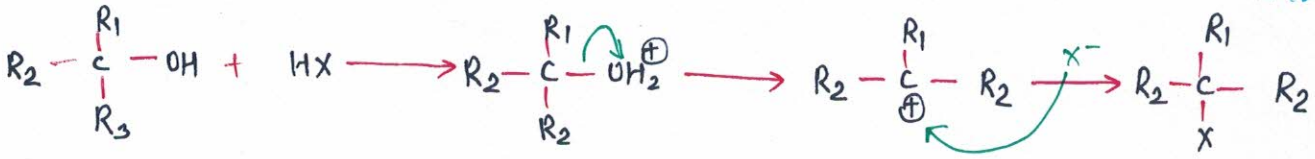
$CH_2-OH \xrightarrow{HX}$ Does not undergo SN_2 mechanism

In Protic solvent

HI > H-Br > HCl > HF

Because HI is strongest acid & $I^{\ominus}$ formed is strongest nucleophilic in protic solvent.

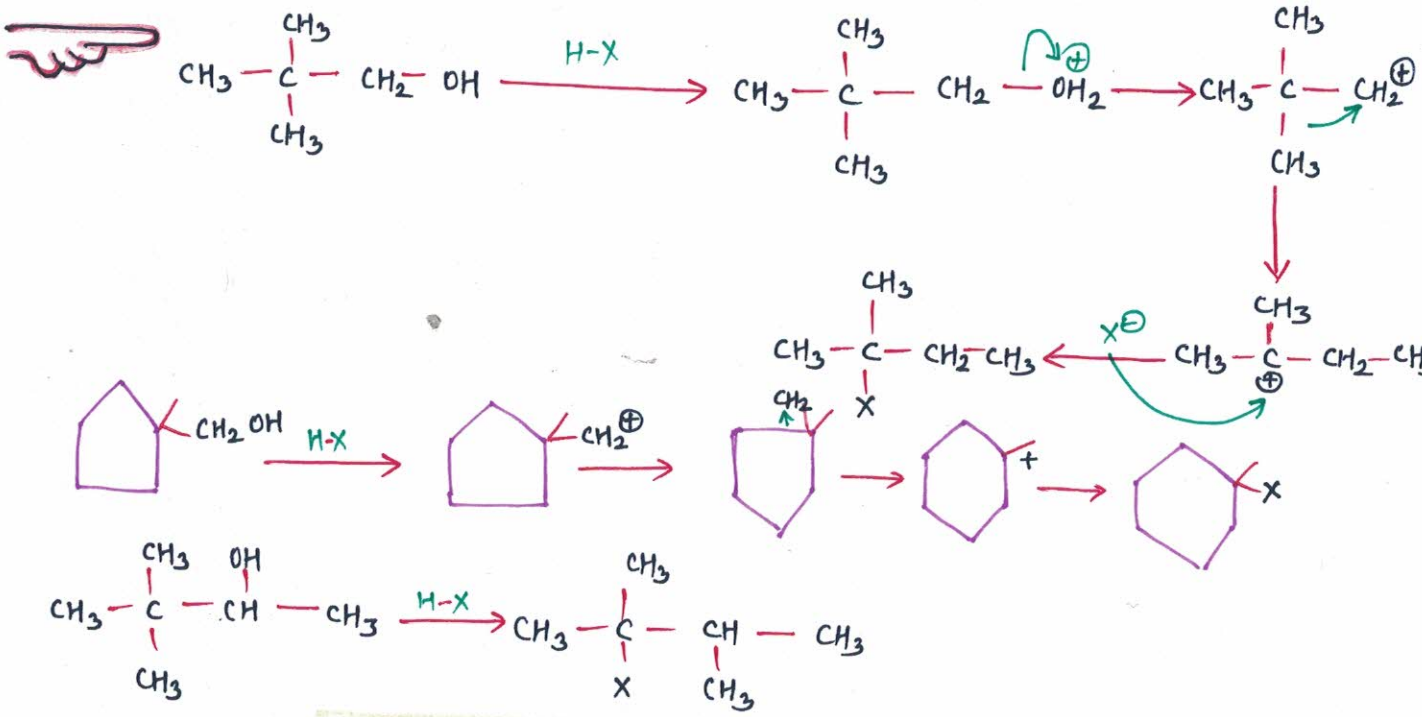
MECHANISM FOR 2 & 3 ALCOHOLS



They undergo by SN_1 mechanism because carbocation is more stable in 2 & 3 alcohol overall order.

Tertiary > Secondary > Primary

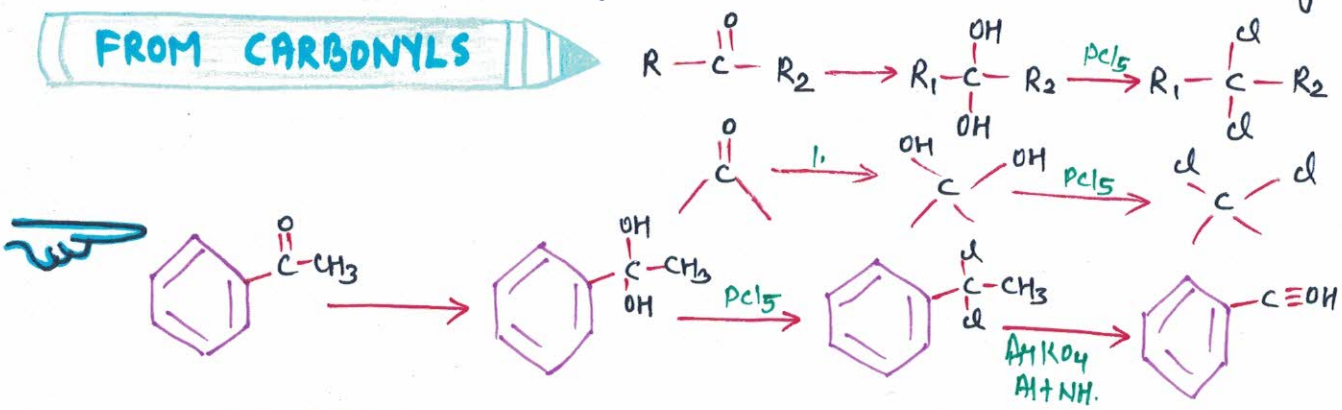
HI > HBr > HCl HF is practically not used.



$$R-CH_2-OH + HCl \longrightarrow R-CH_2-Cl$$

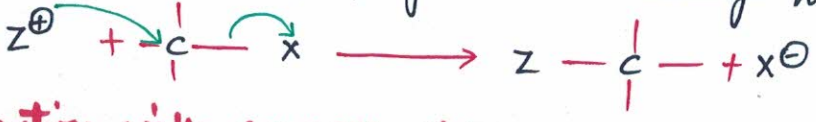
Zinc chloride is used as catalyst as this reaction is slowest among all others.

FROM CARBONYLS



PROPERTIES OF ALKYL HALIDES

1. The most important property is that it undergo nucleophilic substitution.



Reaction with aqueous NaOH

$$R-CH_2-X + NaOH \longrightarrow R-CH_2-OH + NaX \text{ (substitution)}$$

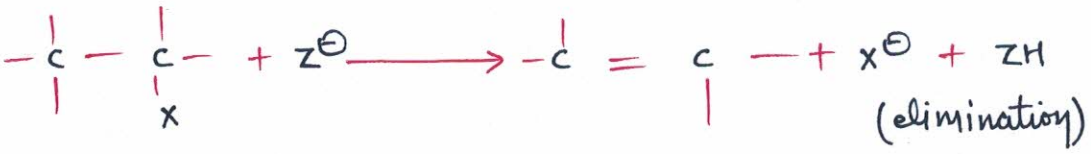
$$1 + 1 = 1 + 1$$

$$\Delta S = 0$$

$$\Delta G = \Delta H + T\Delta S$$

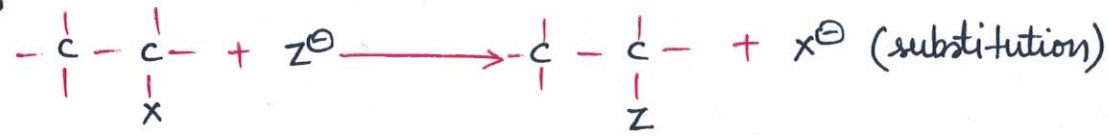
$$\Delta G = \Delta H$$

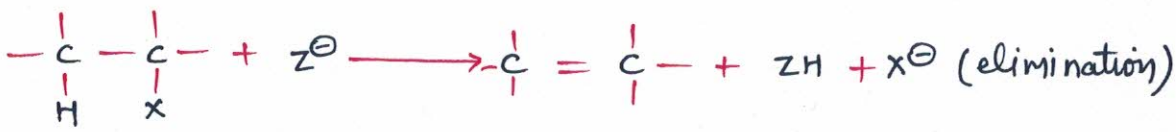
No dependence on temperature can occur at any temperature.



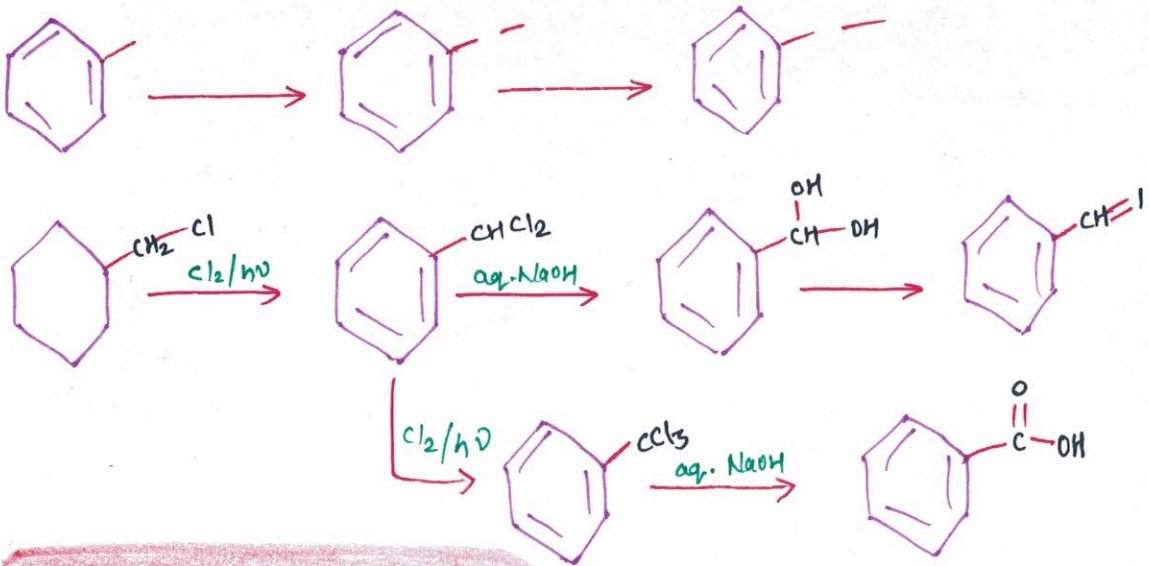
Elimination occurs at high temperature
Addition occurs at low temperature
substitution occurs at any temperature

$\Delta G = \Delta H - T\Delta S$ (+) (+y) At high temp, $\Delta G < \Delta$, so spontaneous



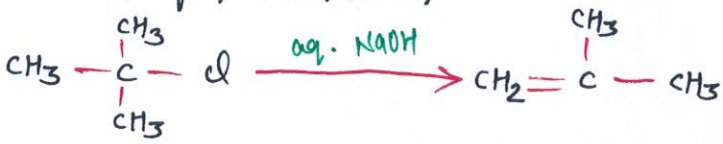


NaOH is weak base than KOH, strongest base alcKOH
aq. NaOH is weak base than aq.KOH, weak base aq. NaOH
alc NaOH is weak base than alc KOH.
In alcohal $OH^{\ominus}$ is destabilised but in aq OH^- is stabilised by H^+
so alc NaOH > aq. NaOH (basic nature). similar for aq.KOH or KOH.



Mono halide	alcohal
Di halide	aldehyde
tri halide	carboxylic acid

But in tertiary halides even aq. NaOH is for elimination



WURTZ REACTION

IR X Na R R

(1) $R-X + e^- \longrightarrow R^{\ominus} + X^{\ominus}$ (reduction)

(2) $R^{\ominus} + R-X \longrightarrow R-R + X^{\ominus}$ (substitution) Read from alkanes.

Coupling with Grignard Reagent

$R^{\ominus}MgX + R_1-X \longrightarrow R-R_1 + MgX_2$

(R_1 ↓ Primary)

Carey Housie Reaction

$R_2CuLi + R_1-X \longrightarrow R-R_1$

ALKYLATION OF ALKYNS

$CH\equiv CH \longrightarrow$ Propyne $\quad CH\equiv CH + NaNH_2 \longrightarrow CH\equiv C^{\ominus}Na^{+} \xrightarrow{CH_3-Cl} CH\equiv C-CH_3 + Cl^-$

$CH\equiv C^- Na^+ + CH_3CHCl \longrightarrow CH\equiv C-CH_2-CH_3$

$Na^{+}\,{}^{\ominus}C\equiv C^{\ominus}Na^+ + 2CH_3Cl \longrightarrow CH_3-C\equiv C-CH_3$

REACTION WITH NaCN/KCN

$R-CH_2-X + NaCN \longrightarrow R-CH_2-CN \qquad CH_3CH_2X + NaCN \longrightarrow CH_3CH_2CN$

$R-C\equiv N \xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH$

MECHANISM

$R-C\equiv N \longrightarrow R-\overset{O-H}{C}=NH \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH$

☞ $CH_3CH_3 \longrightarrow$ succinic acid $\qquad HOOC-CH_2-CH_2-COOH$

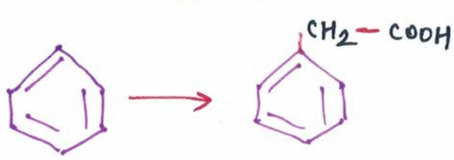
$\longrightarrow CH_3CH_3 \xrightarrow[\text{alc KOH}]{Br_2/h\nu} CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} Br-CH_2-CH_2-Br \xrightarrow{2NaCN} CN-CH_2-CH_2-CN$

$\downarrow H_3O^+$

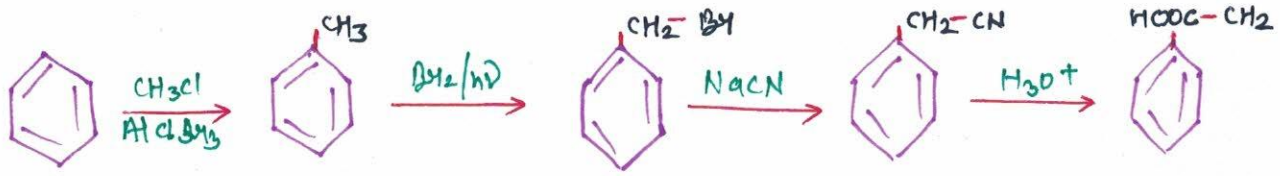
$HOOC-CH_2-CH_2-COOH$

☞ $CH_3CH_3 \longrightarrow H_2N-CH_2CH_2CH_2CH_2-NH_2$

$NC-CH_2CH_2-CN \xrightarrow{H_2/Ni-C} H_2N-CH_2CH_2-NH_2$



Phenyl acetic acid



REACTION WITH AgCN

$R-CH_2-X + AgCN \longrightarrow R-CH_2-N^{\oplus}\equiv C^{\ominus}$

(covalent)

NaCN/KCN ionic

(NC) → isocyanide

(CN) → cyanide

$R-CH_2-N^{\oplus}\equiv C^{\ominus} + H_3O^+ \longrightarrow R-CH_2-NH_2 + HCOOH$

In ionic Na^+ $C^{\ominus}\equiv N$ $X-R-CH_2 \longrightarrow R-CH_2-CN$

$C^{\ominus}$ is better nucleophilic than N:

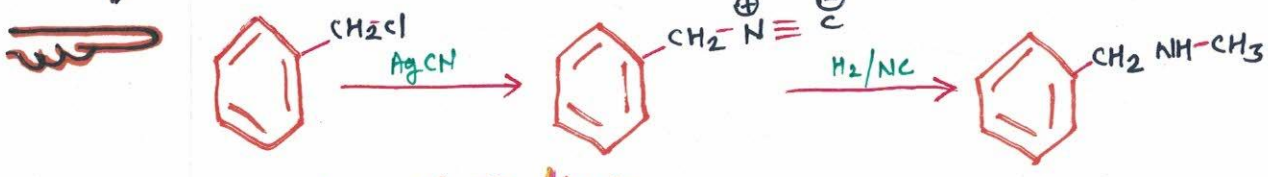
In covalent $R-CH_2-X$ $:N\equiv C-Ag \longrightarrow R-CH_2-N^{\oplus}\equiv C^{\ominus}$

$R-CH_2-N^{\oplus}\equiv C^{\ominus} \xrightarrow{H_2} R-CH_2-NH-CH_3$

$R-C\equiv N \xrightarrow{H_2} R-CH_2-NH_2$

$R-N^{+}\equiv C^{\ominus} \xrightarrow{H_2} R-NH-CH_3$

$CH_3-CH_3 \xrightarrow[Alc.KOH]{Br_2/h\nu} CH_2=CH_2 \xrightarrow{Br_2/CCl_4} CH_2(Br)-CH_2(Br) \xrightarrow{AgCN} CH_2(CN)-CH_2-N^{+}\equiv C^{\ominus} \xrightarrow{H_2/Pd-C} CH_3-NH-CH_2CH_2-NH-CH_3$



REACTION WITH $NaNO_2/KNO_2$

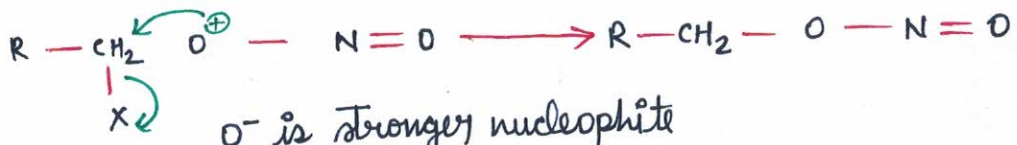
$R-CH_2-X + NaNO_2 \longrightarrow R-CH_2-O-N=O$

(Alkyl nitrite)

$Na^+ O^{\ominus}-N=O$ → sodium nitrite

$R-O-N=O$ → alkyl nitrite

MECHANISM

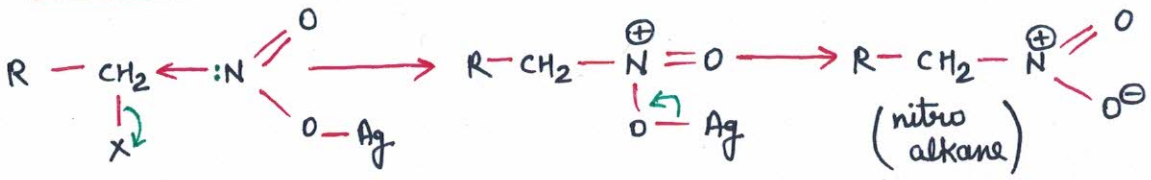


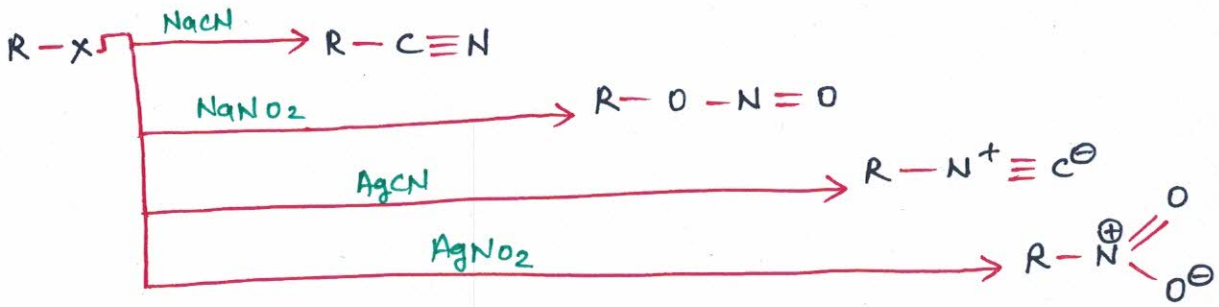
O^- is stronger nucleophile

$CH_3CH_2-Br + NaNO_2 \longrightarrow CH_3CH_2ONO$ (ethyl nitrite)

(benzyl nitrite)

REACTION WITH $AgNO_2$





Williamson's Synthesis

$R-O^-Na^+ + R_1-CH_2-X \longrightarrow R-O-CH_2-R_1$

The preparation of ethers from sodium alkoxide by reaction with primary alkyl halide is called williamson's synthesis.

$CH_3-O-CH_2-CH_3$

(i) $CH_3O^-Na^+ + CH_3CH_2Cl \longrightarrow CH_3OCH_2CH_3 + \underbrace{CH_2=CH_2 + CH_3OH}_{\text{(by product)}}$

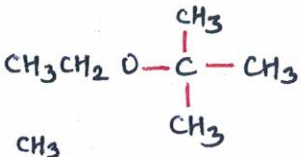
(ii) $CH_3CH_2O^-Na^+ + CH_3Cl \longrightarrow CH_3CH_2OCH_3$ (only products)

Hence, second method should be used.

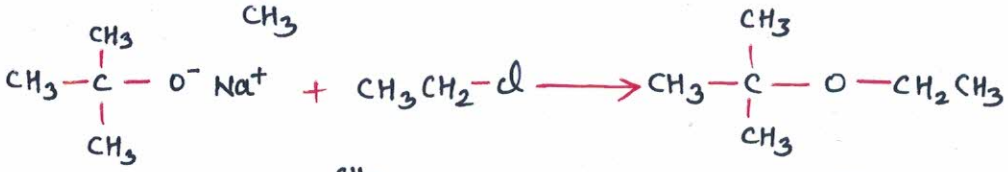
$CH_3CH_2O\,CH_2\,CH_2\,CH_3$

(i) $CH_3CH_2O^-Na + CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2O\,CH_2\,CH_2OH + \underbrace{CH_3CH_2OH + CH_2=CH-CH_3}_{\text{minor}}$

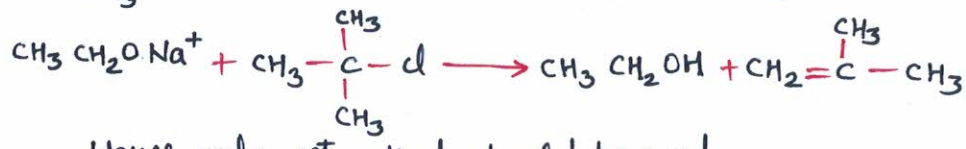
(ii) $CH_3CH_2CH_2O^-Na^+ + CH_3CH_2Cl \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + \underbrace{CH_3CH_2CH_2OH + CH_2=CH_2}_{\text{minor}}$



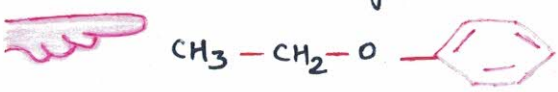
(i)



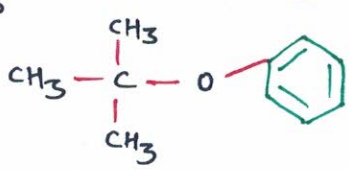
(ii)

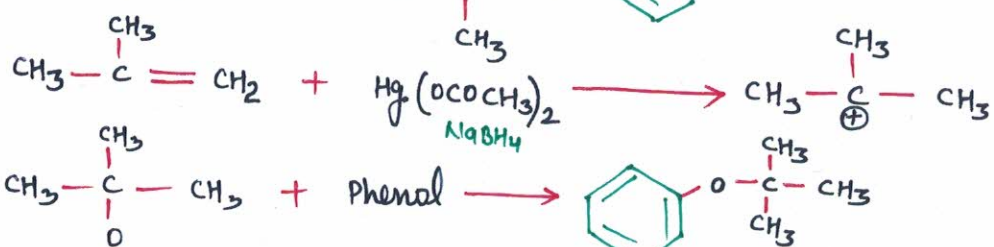


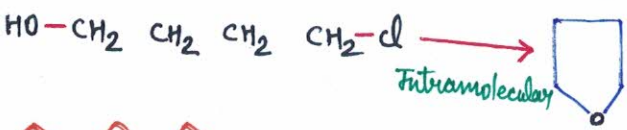
Hence, only 1st method should be used.

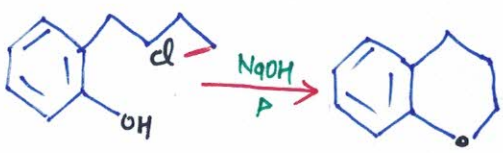


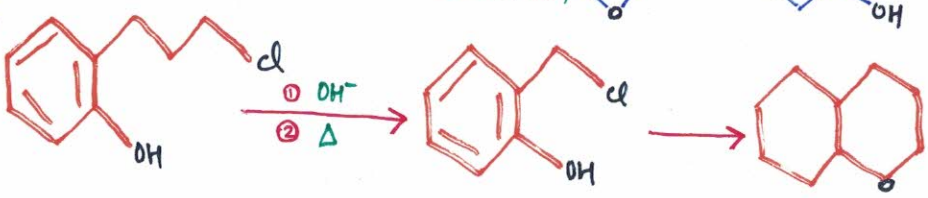
How to prepare











REACTION WITH KSH

$R-CH_2-X + KSH \longrightarrow R-CH_2-SH + KX$

(mercaptan)

$CH_3CH_2SH \xrightarrow{HgCl_2} (CH_3-CH_2-S)_2Hg \downarrow$ (Black ppt)

$R-SH + HgCl_2 \longrightarrow (R-S)_2Hg \downarrow$ (Black)

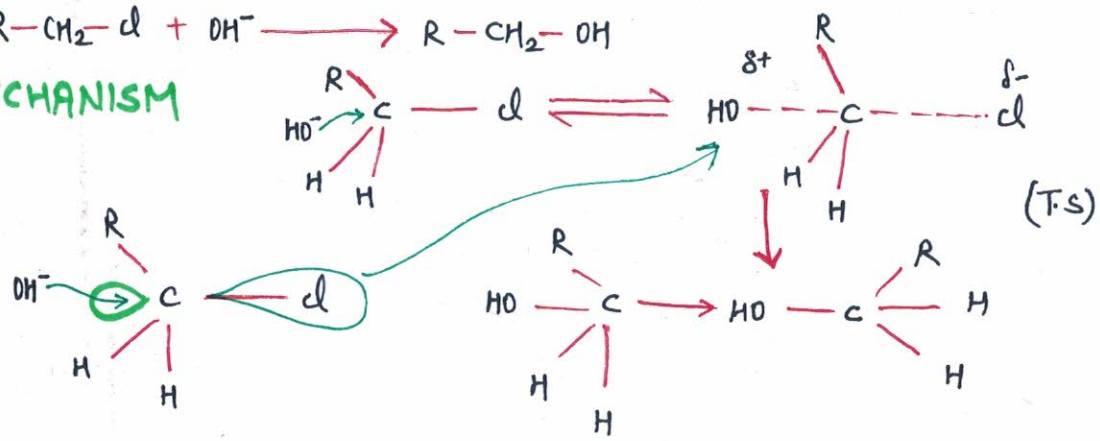
Mercury catching → mercapton

$2R-X + Na_2S^{-2} \longrightarrow 2(RS)^{\ominus} \xrightarrow{R-X} R-S-R$

SUBSTITUTION NUCLEOPHILIC - BIMOLECULAR (SN_2)

$R-CH_2-Cl + OH^- \longrightarrow R-CH_2-OH$

MECHANISM



Rate $\propto [RX][Z^-]$, It's substitution nucleophilic (SN_2)

Rate depends on how fast Ts is formed. It depends on how many collisions occur b/w the reactants and that depends on conc^n of reactants.

It is concerted mechanism. T.S is intermediate. No rearrangement occurs. It shows elemental effect. shows walden Inversion.

Most reactive halide in SN_2 is methyl halide because as size increase T.S becomes difficult to form due to crowding. only in CH_3X T.S is easy to form.

$CH_3-X > CH_3CH_2-X > CH_3CH_2CH_2-X > R-CH_2-X$

As branching increase at β carbonn rate of reaction decreases as T.S is unstable due to crowding and becomes difficult to form.

CH_3-X > CH_3-CH_2-X > $CH_3-CH(CH_3)-CH_2-X$ > $CH_3-C(CH_3)_2-CH_2-X$

MeX > 1 > 2 > 3 Rate of reaction

I II III

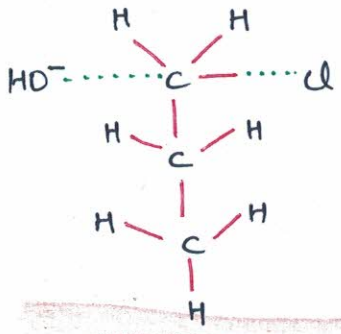
$CH\equiv C \leftarrow CH_2-Cl$ > $CH_2=CH \leftarrow CH_2-Cl$ > $CH_3-CH_2 \rightarrow CH_2-Cl$

Rate of SN_2 is more in I because $C\equiv C$ is withdrawing group and hence the carbon is most e^- deficient so Z^- attacks the most e^- deficient carbon. Hence rate of SN_2 reaction ↑.

2nd reason In $CH_3CH_2CH_2Cl$

(Like a tree)

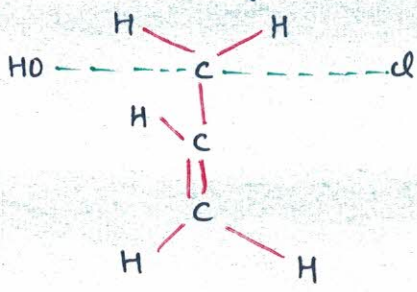
More crowding T.S unstable



(crowded)

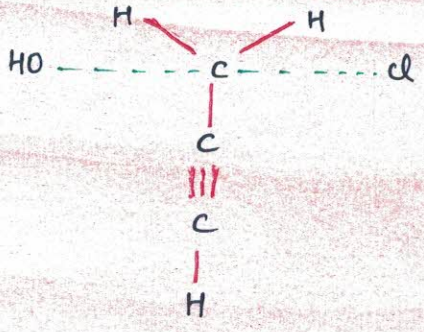
$CH_2=CH-CH_2-Cl$

(Wall) Less crowding T.S relatively stable



CH C CH_2 Cl

(Pole) T.S very stable, No crowding



3rd Another explanation

$CH_3CH_2CH_2-\overset{a}{-}Cl$ $CH_2=CH-CH_2-\overset{b}{-}Cl$ $CH\equiv C-CH_2-CH$

bond strength a > b > c, weak bond breaks easily. so rate of reactions

→ c > b > a

4th If there is a pie bond adjacent to carbon undergoing nucleophilic substitution and P orbital of carbon undergoing SN_2 reaction and p orbital of π bond interact (delocalise) which stabilise the T.S formed.

So, { $CH\equiv CCH_2Cl$ (Propargyl chloride) > $CH_2=CH-CH_2-Cl$ (Allyl chloride) > $CH_3CH_2CH_2Cl$ (Alkyl chloride) }

i. Z^- attacks on e^- deficient

ii. Bond strength : b > a ⇒ a is weak than b, a is easy to break.

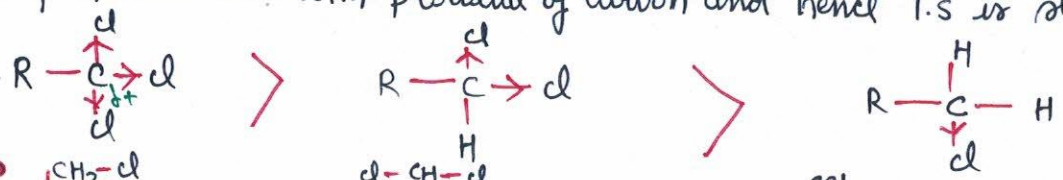
iii. II has 3D structure but I is planar. so more crowding in II.

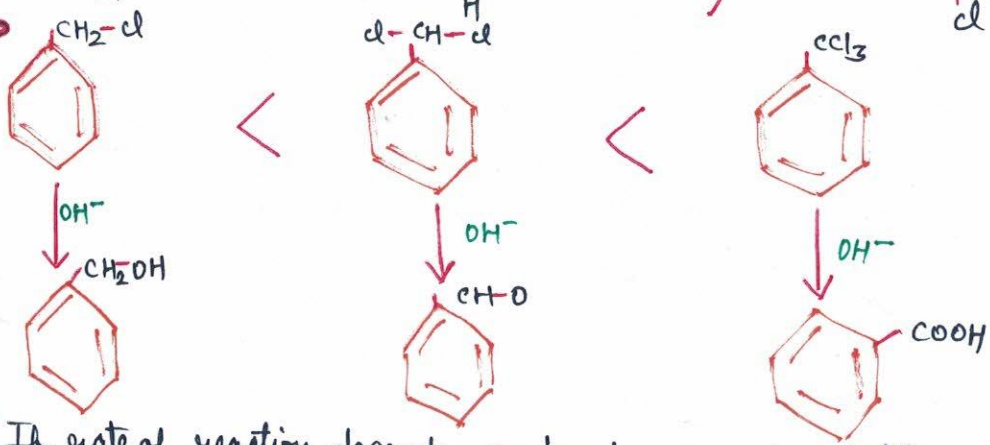
iv. Adjacent double bond to carbon undergoing SN_2 reaction Hence rate more as T.S is stable. 5000 times more than it.

$CH_2CH_2-O \leftarrow CH_2-Cl$ > $CH_3\ CH_2 \rightarrow CH_2-Cl$

when not in resonance. CH_3CH_2O shows -I effect.

If an atom with a lone pair is adjacent of carbon undergoing SN_2 reaction then lone pair delocalises with p orbital of carbon and hence T.S is stablised.

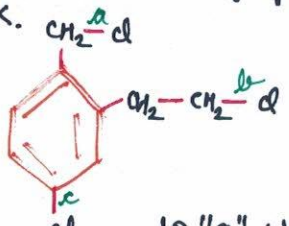




If rate of reaction depends on leaving group stability then it shows elemental effect. All SN_2 reaction show elemental effect.

$R-I > R-Br > R-Cl > R-F$

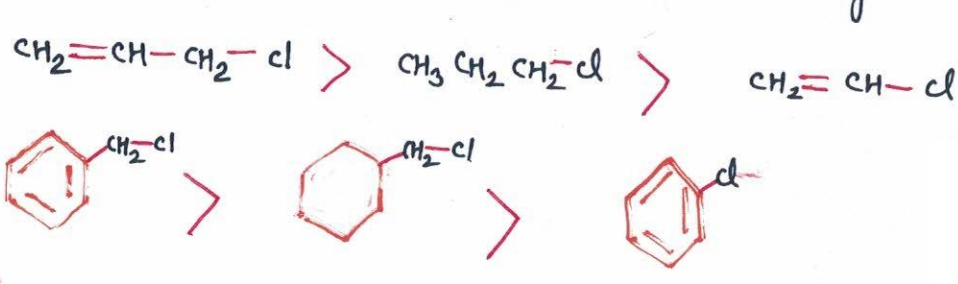
I^- is better leaving group and C-F bond is strongest and hence difficult to break.



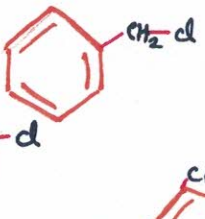
a < b < c (bond strength)

so "a" will break first when attacked by Z^-

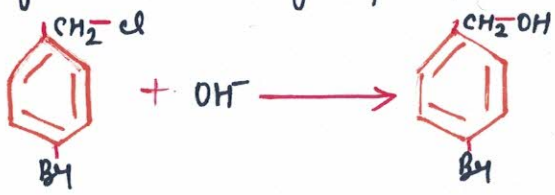
Rate

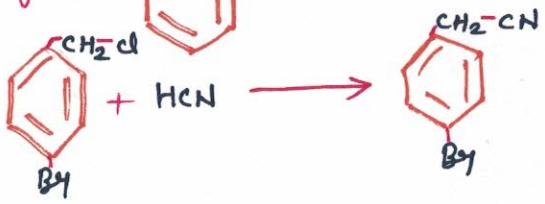


Allyl halide gives precipitate with $AgNO_3$. eg.



Aryl halide do not give precipitate with $AgNO_3$





SOLVENT EFFECT

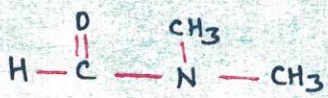
If the nucleophilicity of nuclephile increases in SN_2, rate of reaction increases as rate of $[Z^-]$.

So, any solvent which ↑ the nucleophilicity will increase rate of reaction.

So, as in protic, solvation occurs nucleophilicity ↓ But in aprotic, no solvation nucleophilicity ↑ due to destabilisation of nucleophilic.

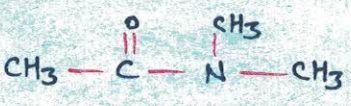
E.g. **APROTIC SOLVENTS**

DMF



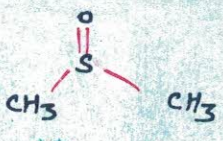
(di methyl formation)

DMAC



(di methyl acetamide)

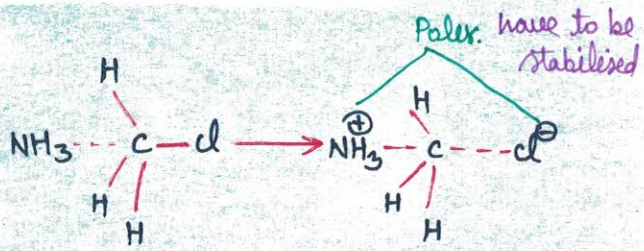
DMSO



(di methyl sulphoxide)

Protic solvents stabilise both cation & anion aprotic " " only cation.

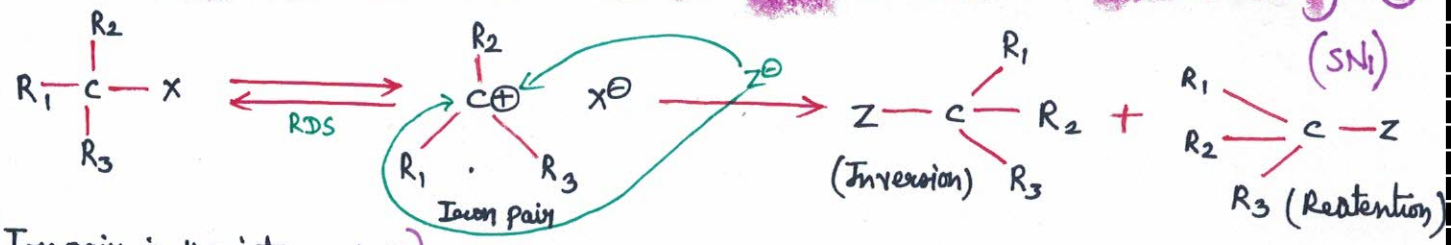
But with neutral nucleophilic, protic should be used because TS is ionic. so both ⊕ & ⊖ poles must be stabilised. so as protic stabilises both, protic is used instead of aprotic which stabilises only ⊕ pole of T.S.



In SN_2 reaction, complete inversion occurs 100%. The configuration of carbon undergoing SN_2 is totally changed.

This inversion of SN_2 carbon is called "Walden Inversion."

SUBSTITUTION NUCLEOPHILIC UNIMOLECULAR



{Ion pair is the intermediate}

If $Z^{\ominus}$ attacks on same side from where $X^{\ominus}$ leaves, then it is called "Retantion".
If $Z^{\ominus}$ attacks on the opposite site from where $X^{\ominus}$ leaves, it is called "Inversion".
The rate of formation of intermediate is independent of conc^{n} of nucleophilic and depends only on conc^{n} of reactants. $\therefore$ Rate $\propto$ [Rx]

It is substitution nucleophilic unimolecular. In this rearrangement occurs. Ion pair is the intermediate. It shows elemental effects.

Partial Recimization occurs

SN1 Rate

Heat of ionisation increase

$CH_3-X \longrightarrow CH_3^{\oplus} + X^{\ominus}$

$CH_3CH_2-X \longrightarrow CH_3CH_2^{\oplus} + X^{\ominus}$

$CH_3-\underset{CH_3}{\overset{|}{CH}}-X \longrightarrow CH_3-\underset{CH_3}{\overset{|}{CH^{\oplus}}} + X^{\ominus}$

$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-X \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C^{\oplus}}}}} + X^{\ominus}$

Rate of reaction ↑
as more stable carbocation is formed.

Stable the intermediate, lesser the heat of ionisation required.

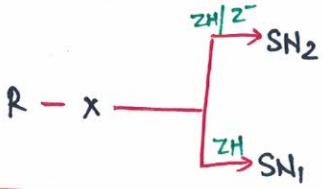
$CH_3-CH=CH-Cl$ > $CH_3-CH_2-CH_2-Cl$ > $CH_2=CH-CH_2-Cl$ 3>2>1 >Me-X

(Heat of ionisation) Rate

Allyl can undergo SN_2 & SN_1 reaction as the rate is equally stable for both the reaction.

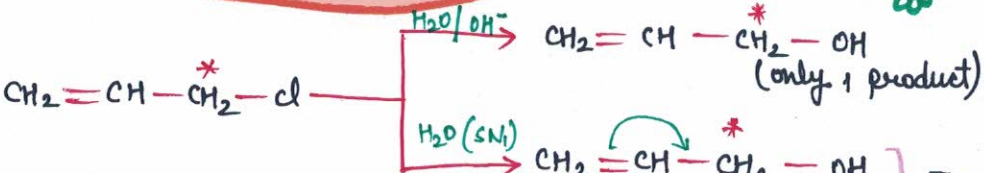
To differentiate b/w SN_2 & SN_1, we learn the concept that stronger the nucleophile, the mechanism moves towards SN_2 as it is very hungry it will not wait for leaving group to go). weaker the nucleophile, the mechanism towards SN_1, as it is not as much hungry as the stronger nucleophile.

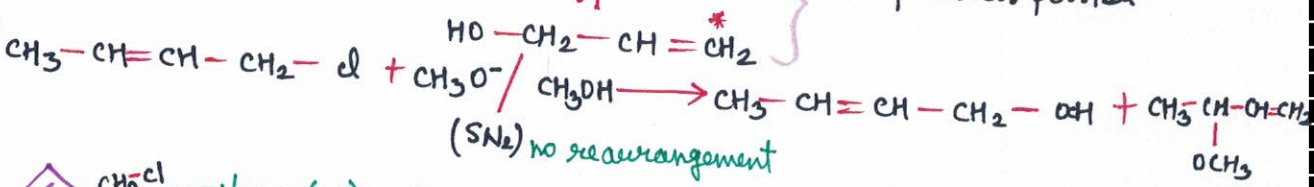
To increase rate of reaction, the nucleophile is taken with its conjugate and hence is involved in RDS. Hence reaction proceeds towards SN_2.

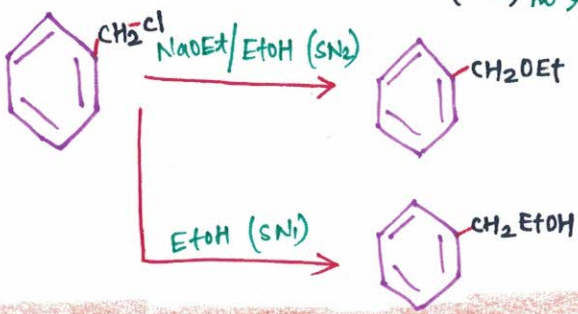


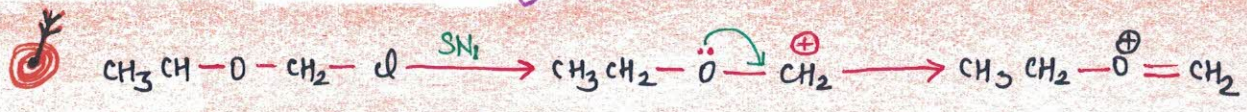
If solvent acts as a nucleophile it is called solvolysis and as they are neutral they are weak nucleophiles and hence reaction is SN.

Solvolysis by pure solvent is always SN_1.
Solvolysis catalysed by the conjugate pair of pure solvent is always SN_2.

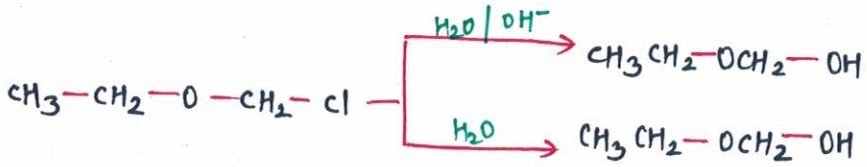


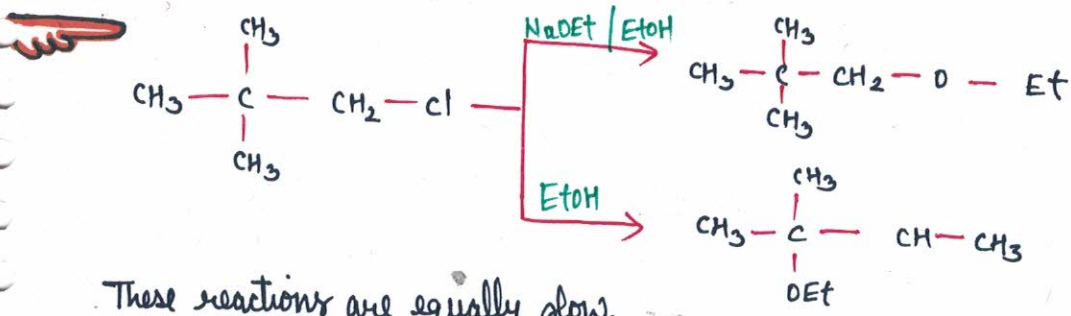




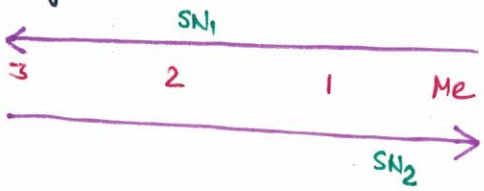


Hence it is equally fast as SN_2.





These reactions are equally slow.



SOLVENT EFFECT (S_N1)

Solvated ion pairs are highly unstable. S_N1 reaction do not occur in gas phase as they unsolvated in gas phase.

Most of the energy to break the bonds comes from heat of solvation.

Stabilisation of nucleophile does not form a part of rate of reaction. Rate depends on how fast ion pair is formed.

In Aprotic solvent, anion is destabilised hence leaving group stability ↓, Hence rate ↓

But in protic solvents, both are stabilised Hence rate ↑.

Hence, S_N1 reactions are carried out in protic solvents.

E.g. - CH_3COOH, CF_3COOH, $HCOOH$, $EtOH$, CH_3OH, H_2O.

Element Effect

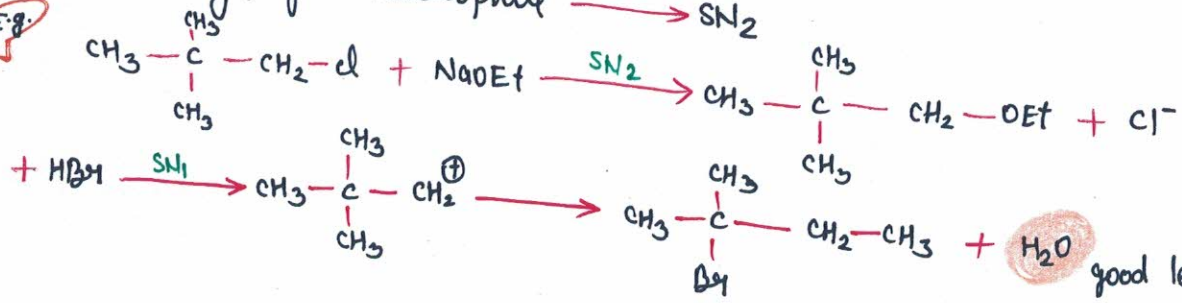
S_N1 reactions require highly stabilised leaving group.

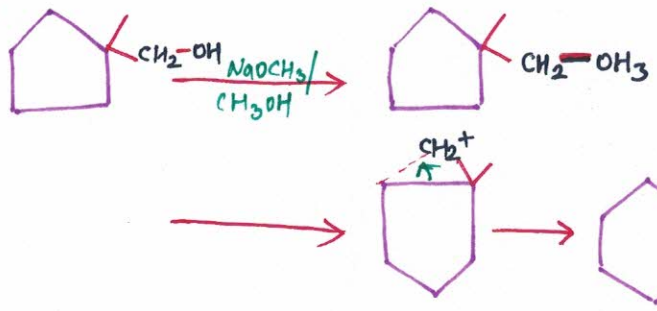
R-I > R-Br > R-Cl > R-F

Good leaving, weak nucleophile ⟶ S_N1

Poor leaving, good nucleophile ⟶ S_N2

E.g.





S_N1 reaction - stereochemistry

If both retention & inversion are equal, then recimization occurs.
But in retention there is repulsion b/w leaving group & nucleophile, hence retention less, inversion more.
So, there is {partial recimization}
In S_N2, there is complete inversion no retention. If the nucleophile is weak, then S_N1 is followed and moreover the ions get time to solvate and hence get separated with no attraction. Hence complete reconization occurs.

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

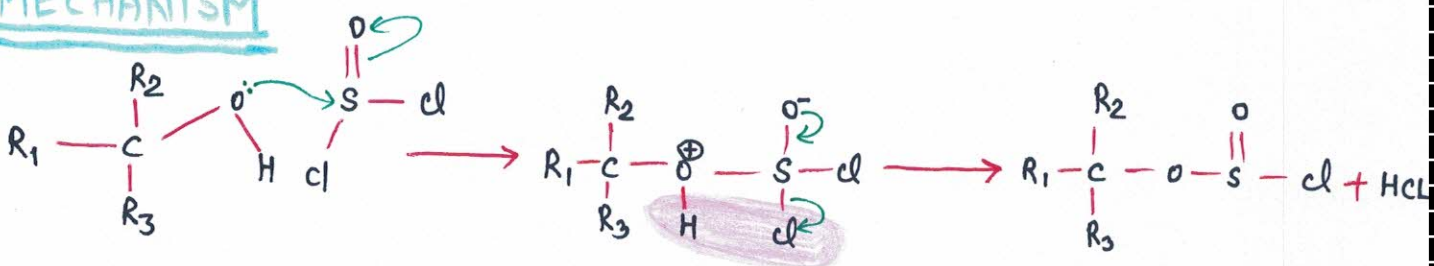
(R^+ completely alone (retention = inversion))

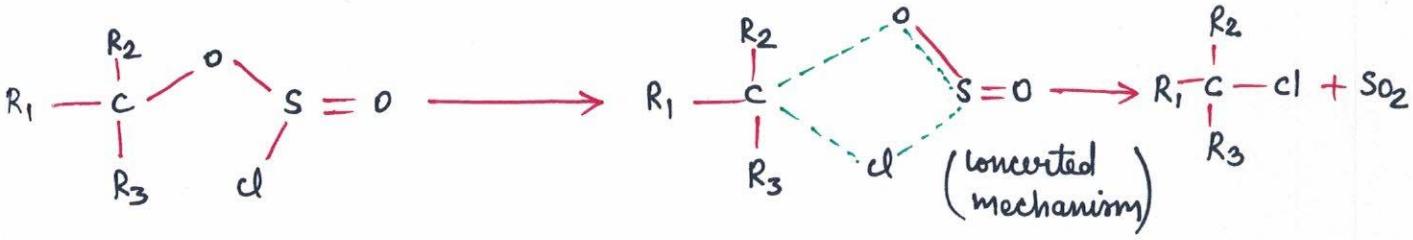
But if nucleophile is strong, inversion is more than retention (as S_N2) hence extent of reanization increases.
Also if the ion pair is stabilised then they are separated easily, hence extent of recimization ↑. Also if leaving group stability ↑ extent of recimization ↑.

More and more S_N1, more extent of recimization.

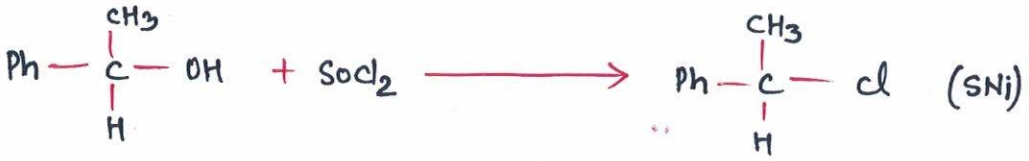
Subs. Nucleophilic Internal (S_Ni)

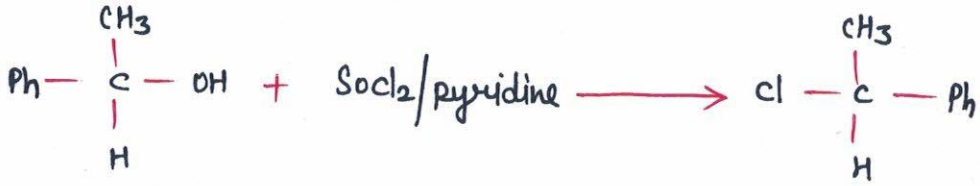
MECHANISM



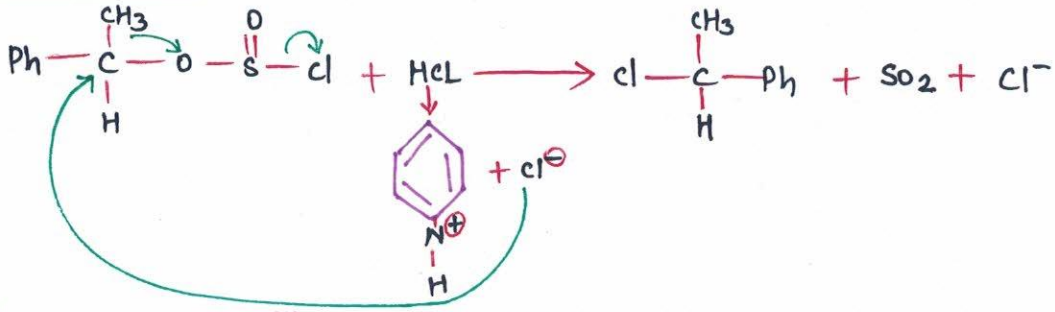


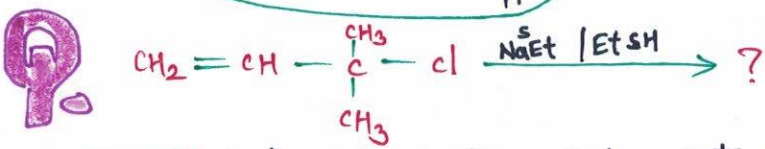
Cl is formed on same side as OH.



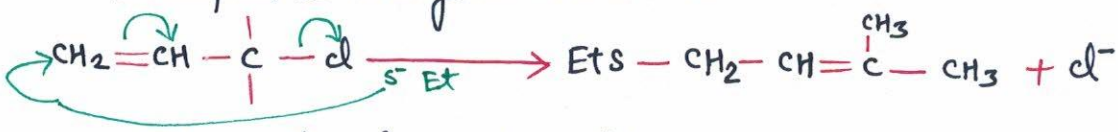


MECHANISM

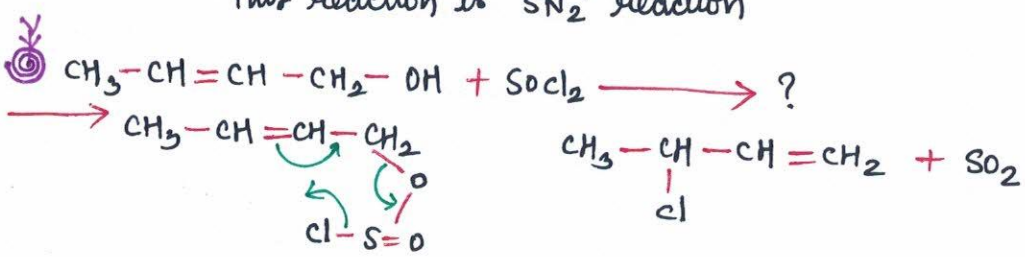




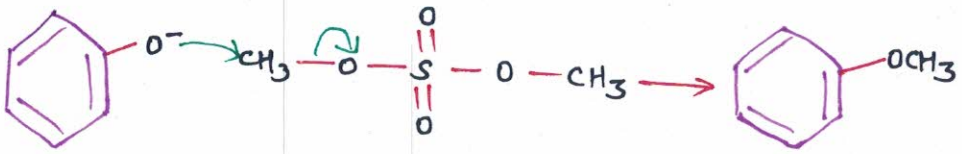
→ Nucleophile is strong but substrate is crowded.

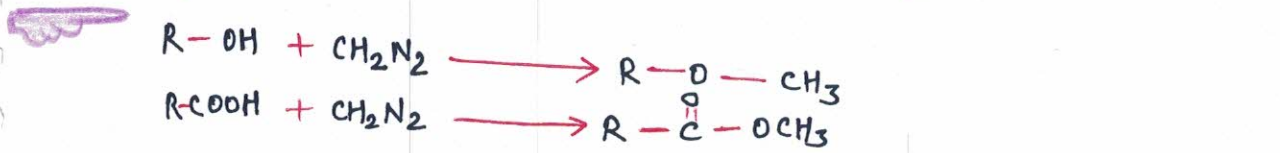


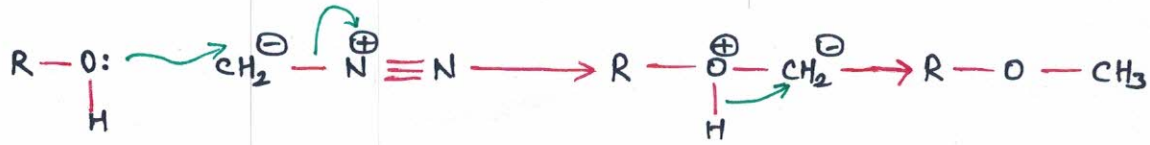
This reaction is SN_2' reaction

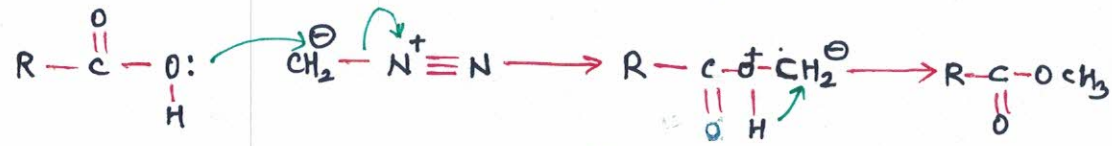


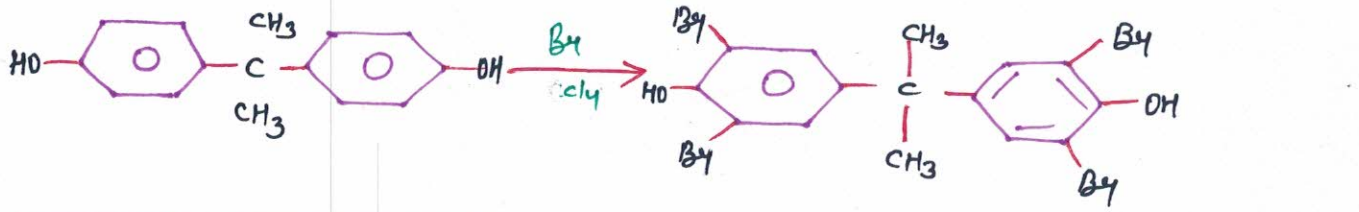
PHENOLS REACTION



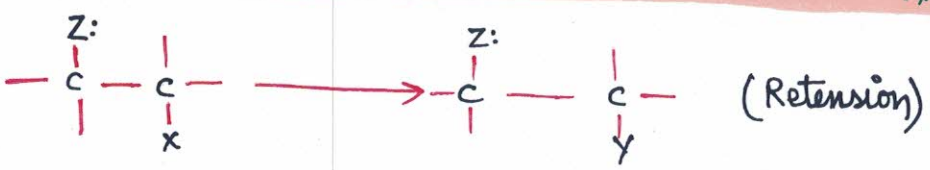


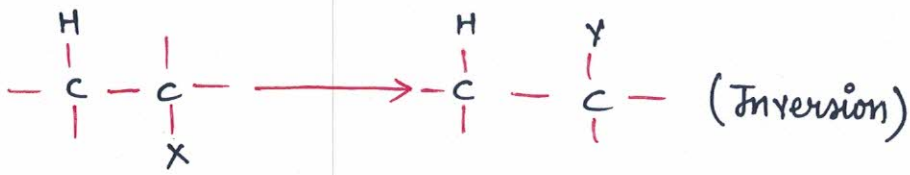




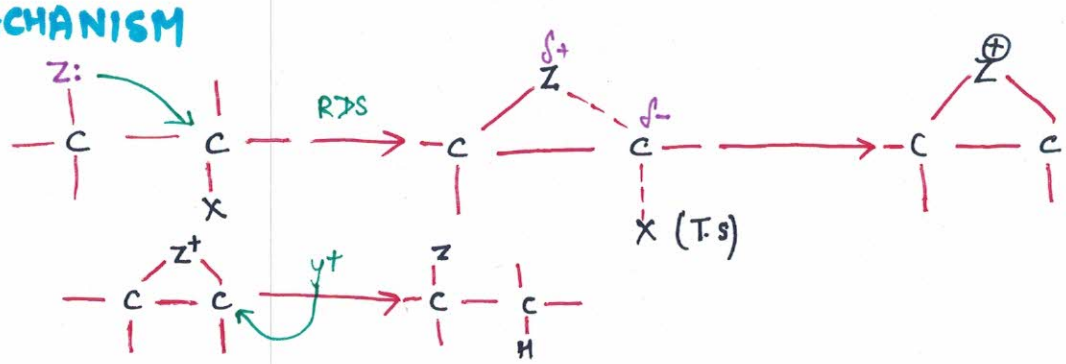


NUCLEOPHILIC SUBSTITUTION BY NEIGHBOURING GROUP PARTICIPATION → Anchimeric Assitance.....





MECHANISM



If there is a group with a lone pair on β carbon, two subsequent S_N2 reaction take place & configuration is retained. Hence retention takes place.
The group takes part in S_N2 reaction. This mechanism is also known "NGP" mechanism in short.

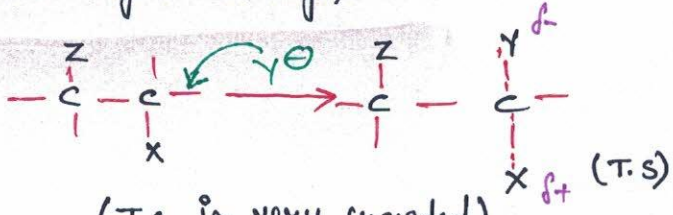
{ Anchimeric in Latin means neighbour } 2 inversions → 1 retention

Internal nucleophile enjoys the benefit of better rate of reaction because –

i. T.S. formed is less crowded

iii. Frequency of collisions is very much high.

Had the reaction been –

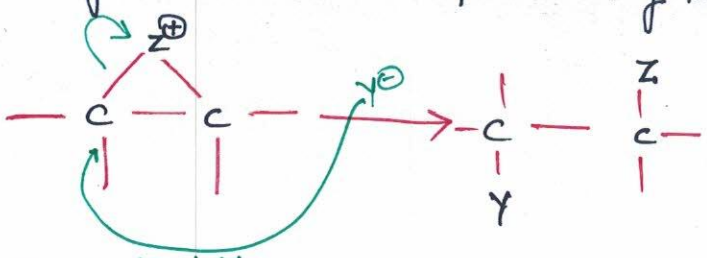


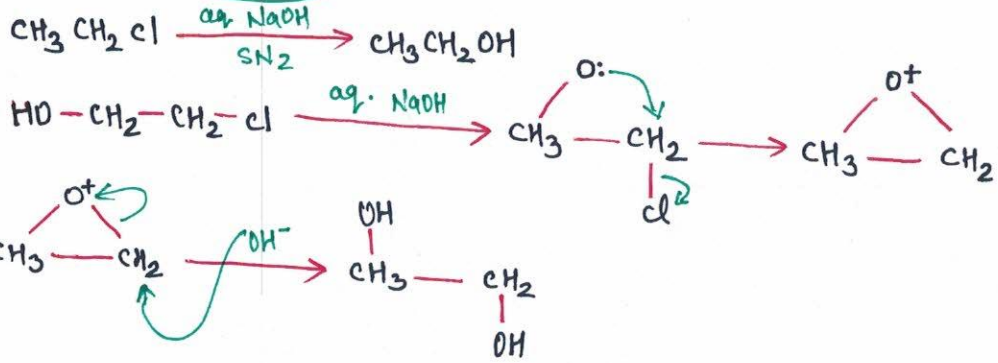
(T.S is very crowded)

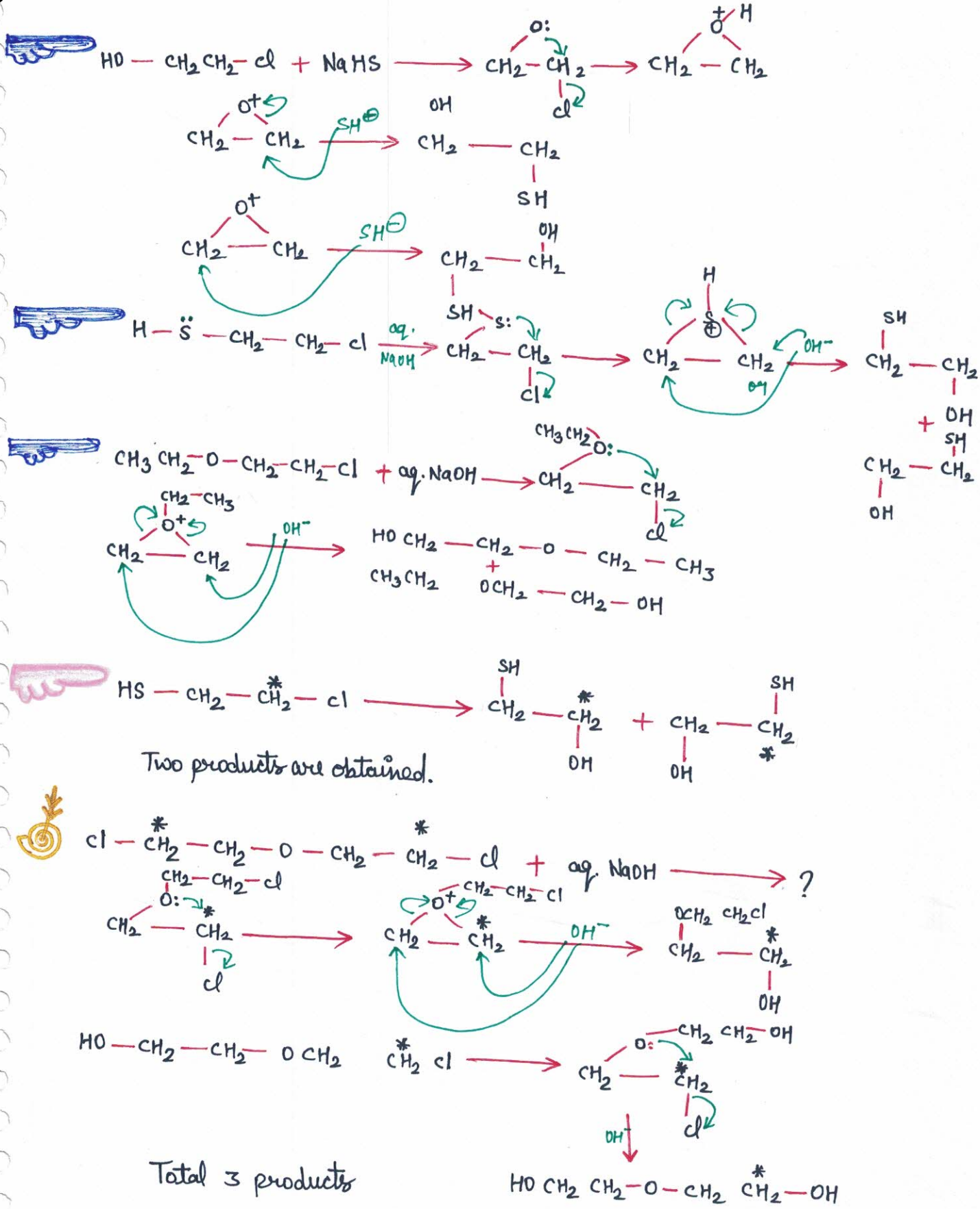
Hence, it has very less frequency of collision as compared to collisions b/w internal nucleophile and the reagent.

Enhancement of rate of nucleophilic substitution with participitation of internal nucleophilic is called Anchimeric assistance.

Rearrangement can also take place during the reaction.

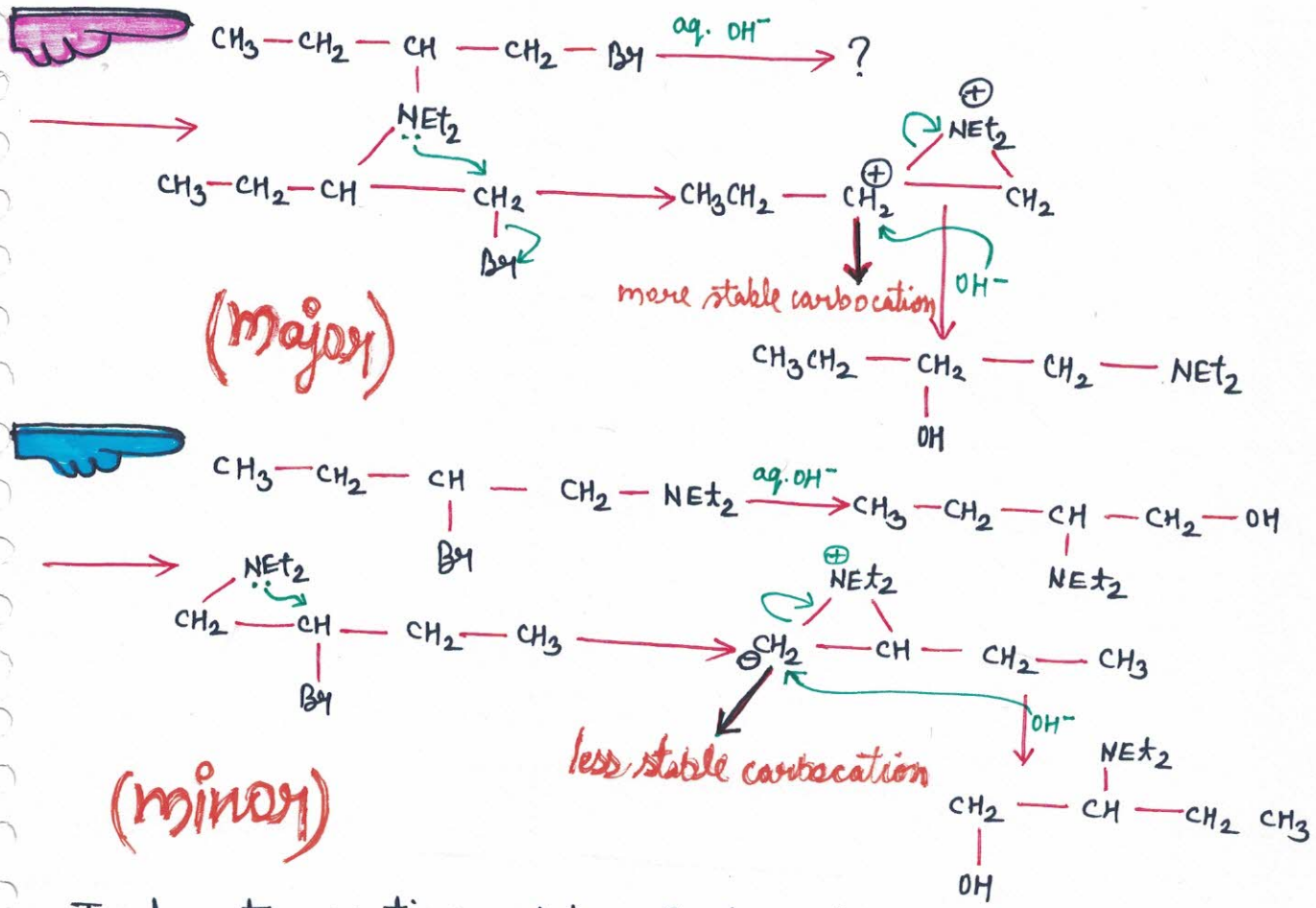




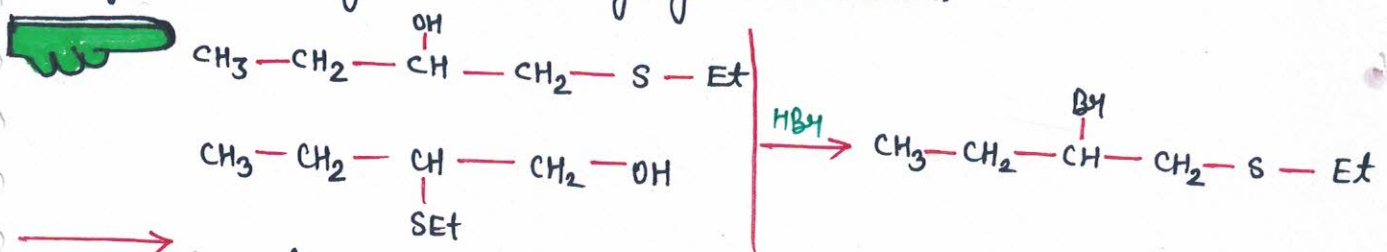


Two products are obtained.

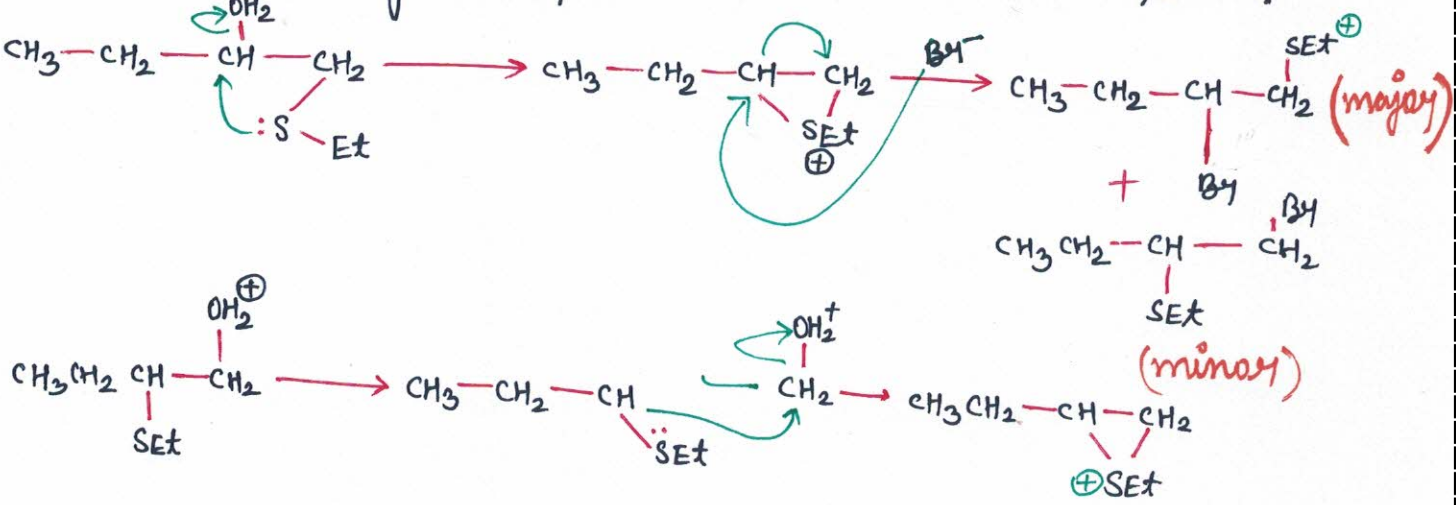
Total 3 products

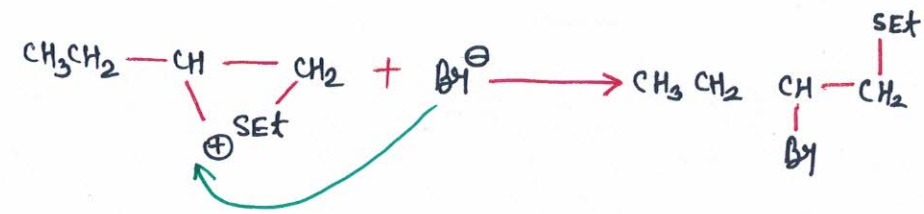


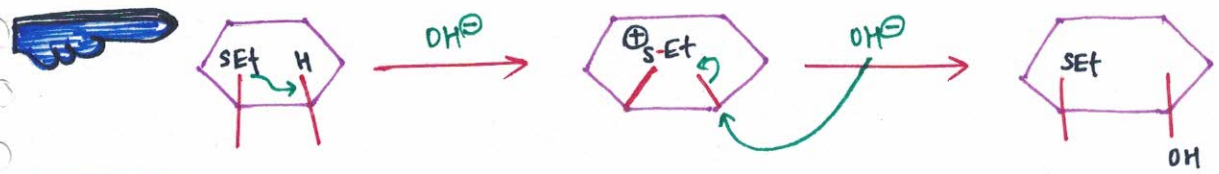
In above two reactions, mixture is formed of two products but I is majoy because of more stability of carbocations.

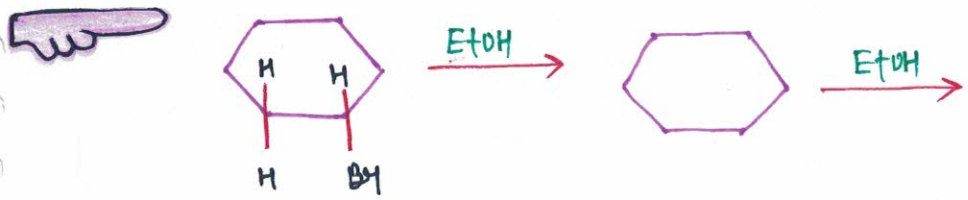


Alcohol undergo nucleophilic substitution in acidic medium

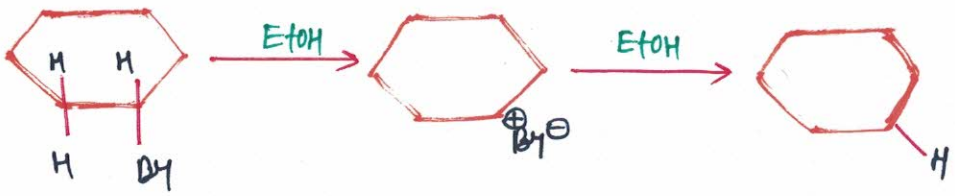




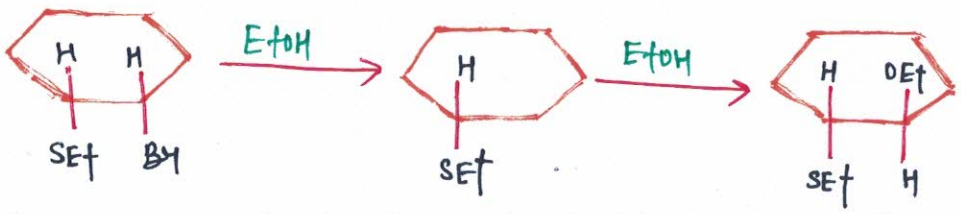




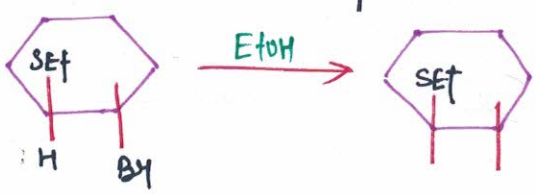
Rate-1



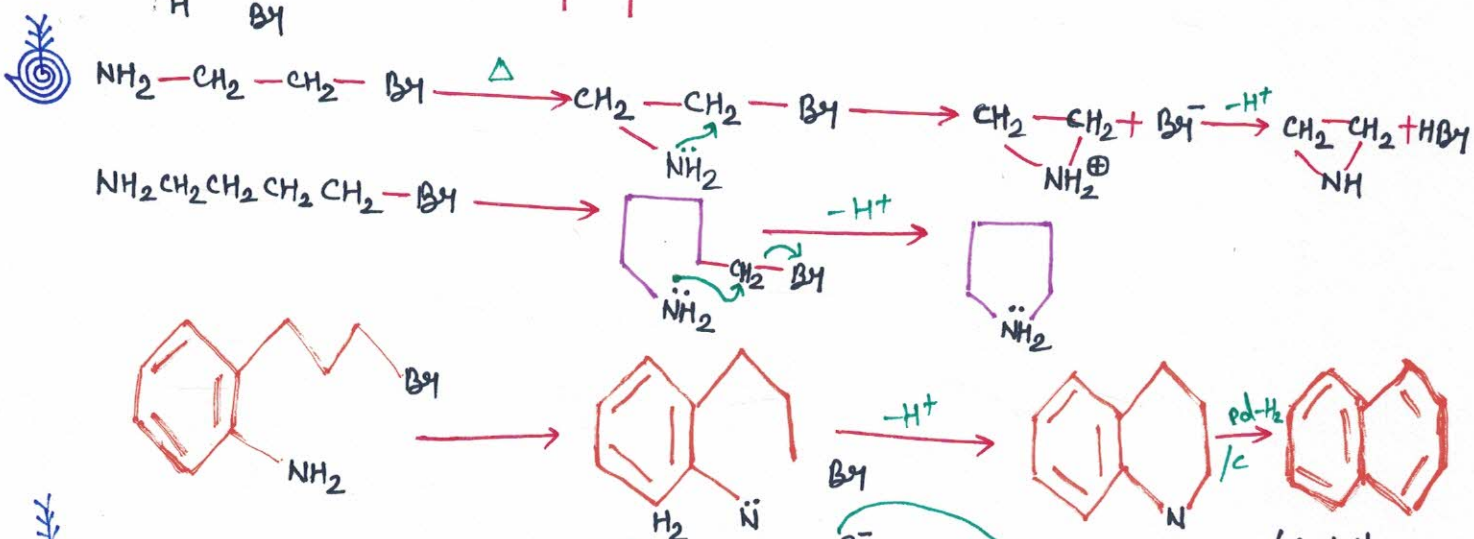
Rate-1 (b)

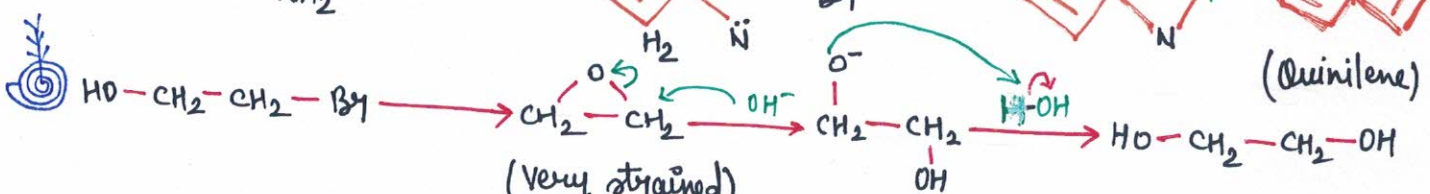


The neighbouring group having lone pair should be on opposite side of leaving group. If on same side, then simple S_N1 or S_N2 takes place.



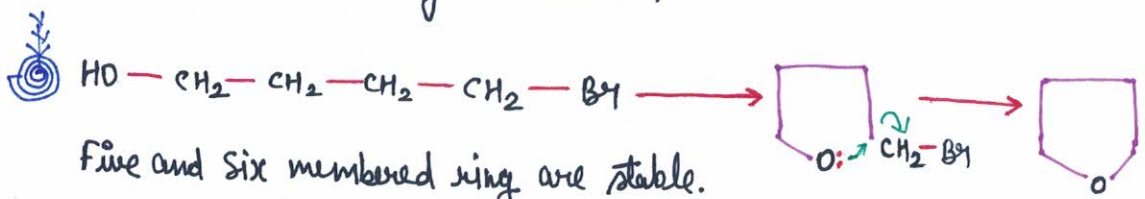
Rate = 70,000 (Anchimeric effect)



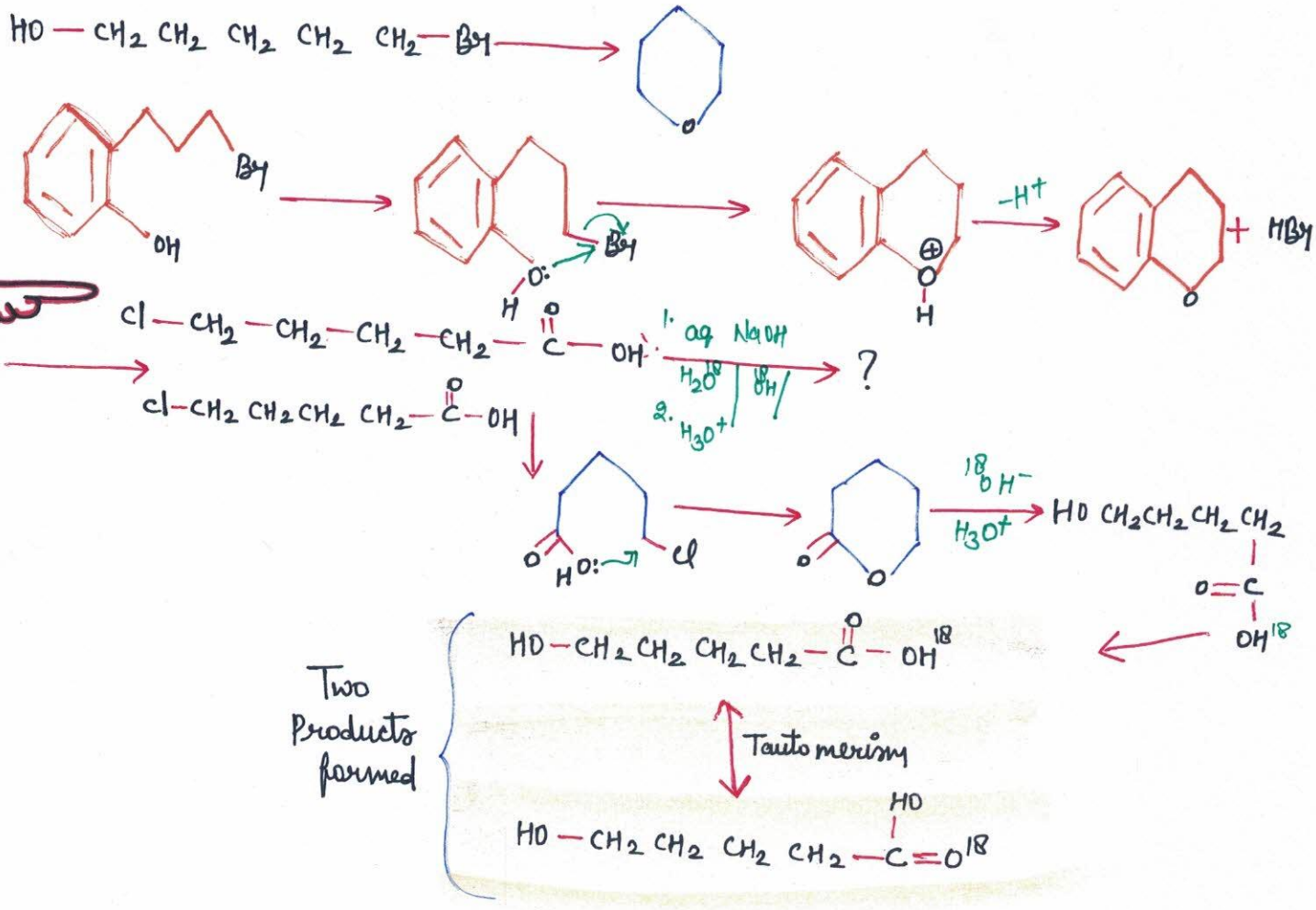


(Very strained)

Three membered ring is strained.

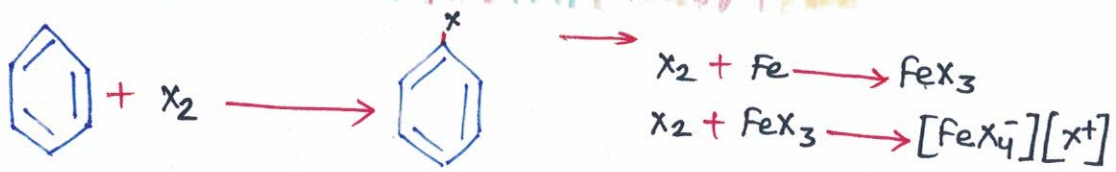


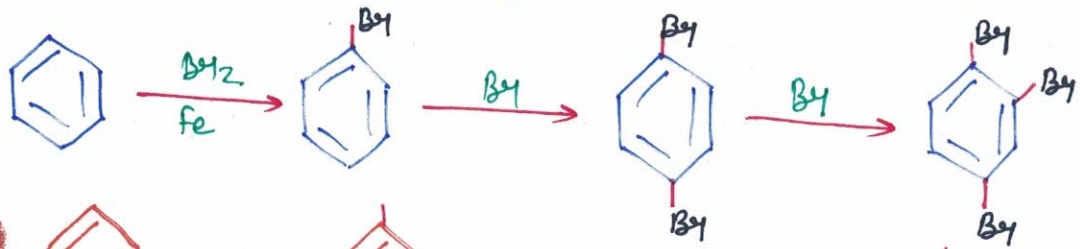
Five and Six membered ring are stable.

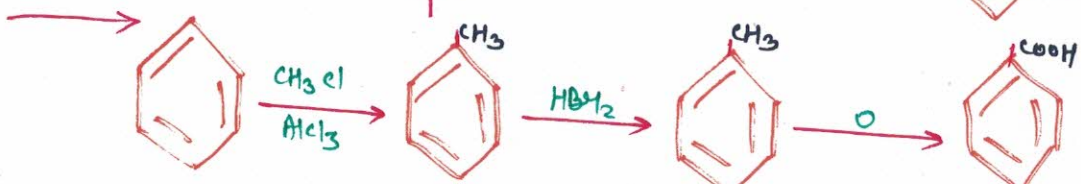


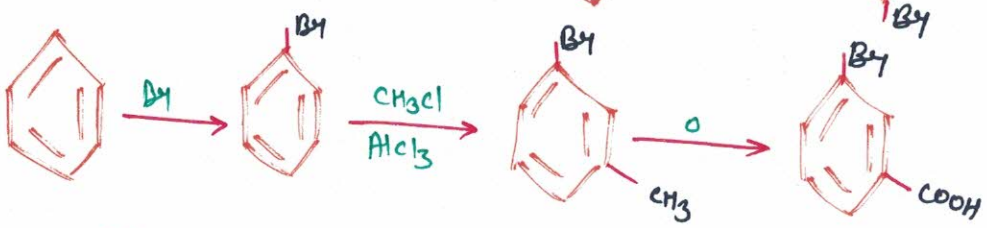
ARYL HALIDES

PREPARATION



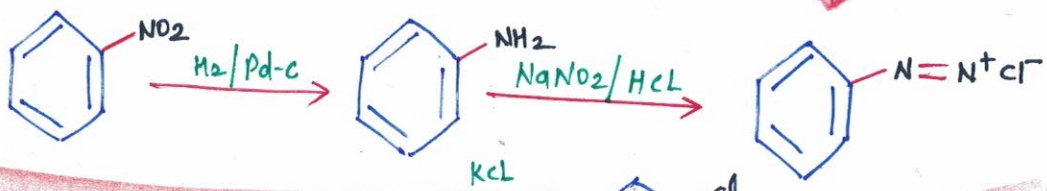


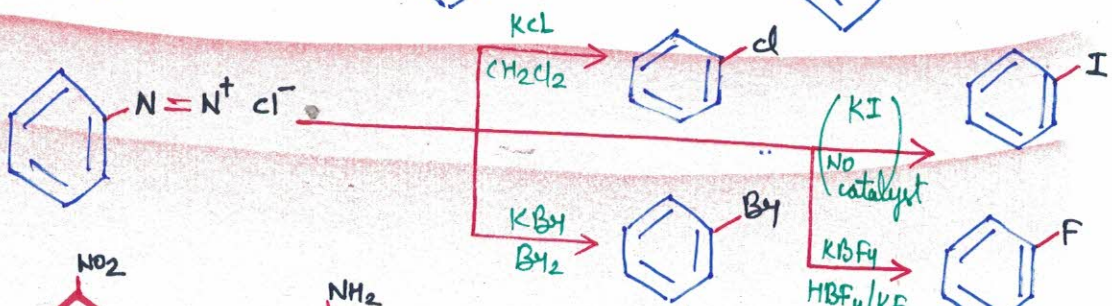


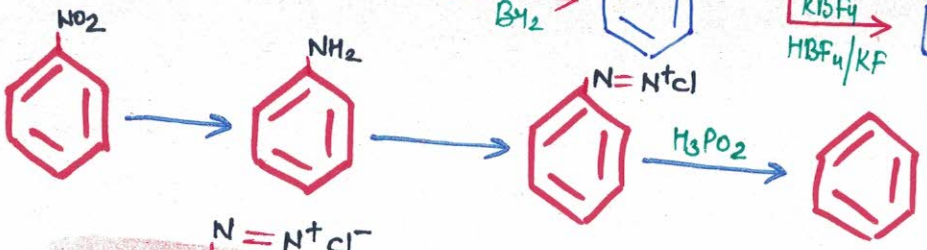


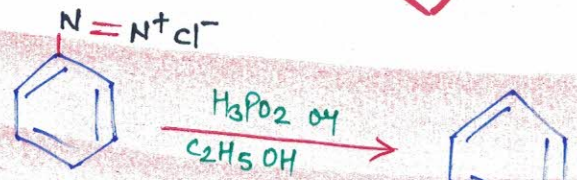
HUNS DICKER REACTION

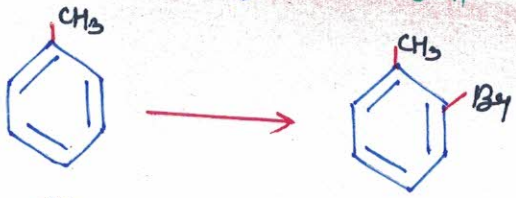
SANDMAYER'S REACTION

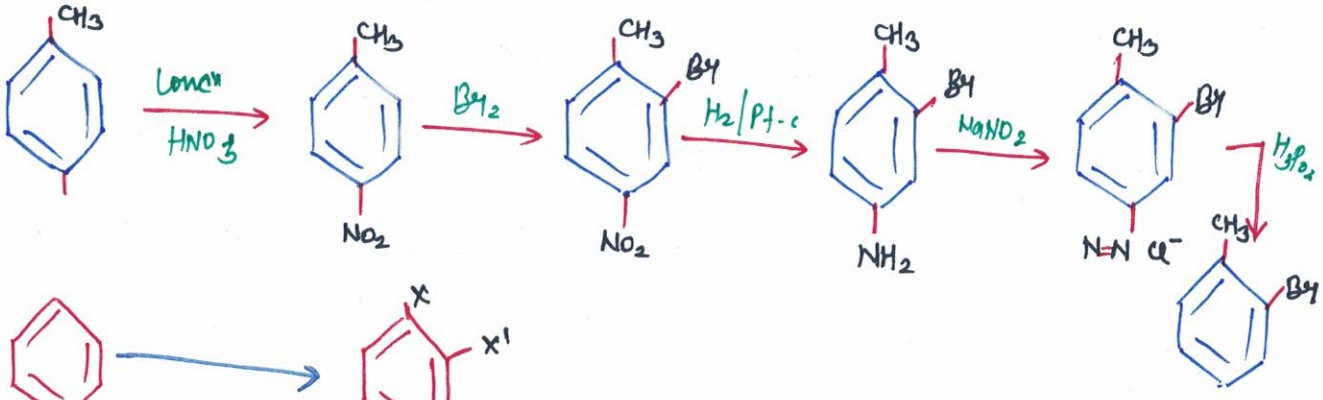


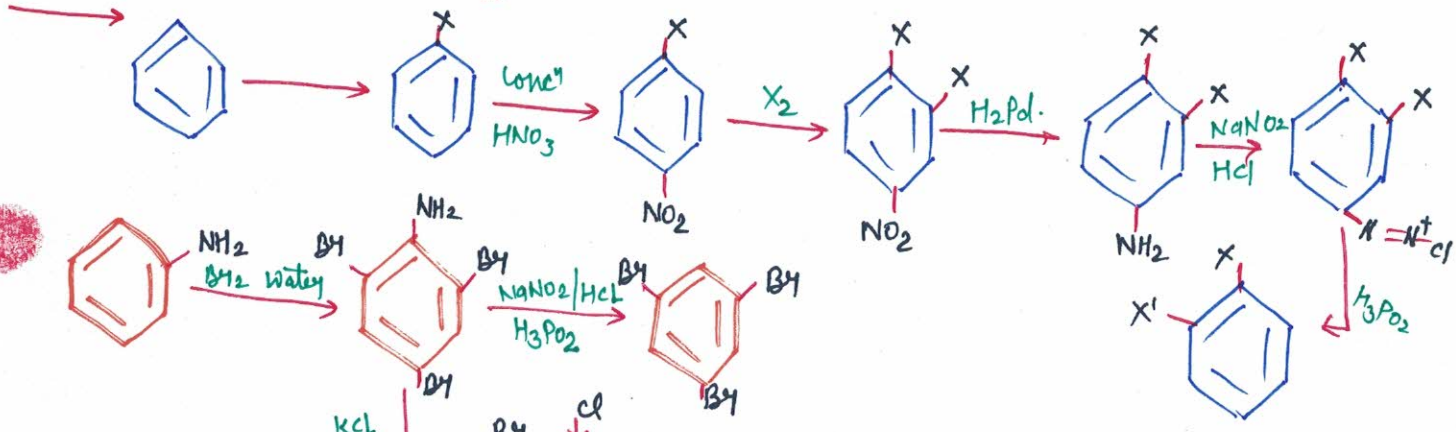


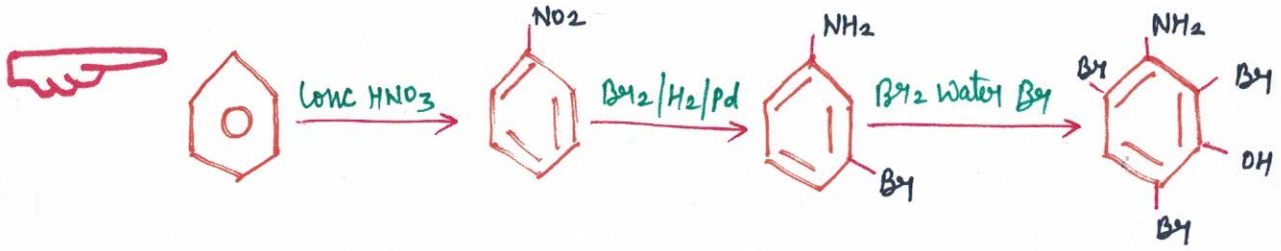






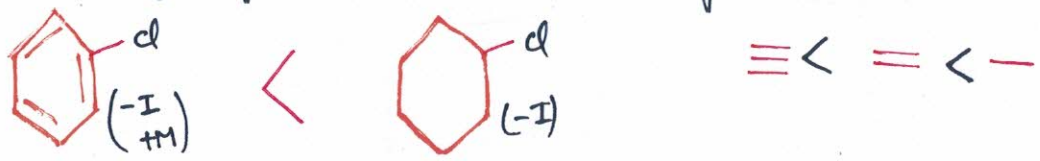






PROPERTIES OF ARYL HALIDES

Dipole moment of alkyl halides is more than aryl halides.



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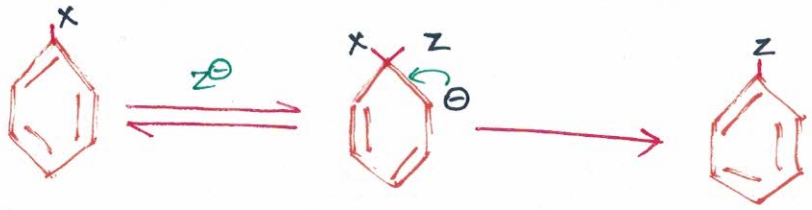
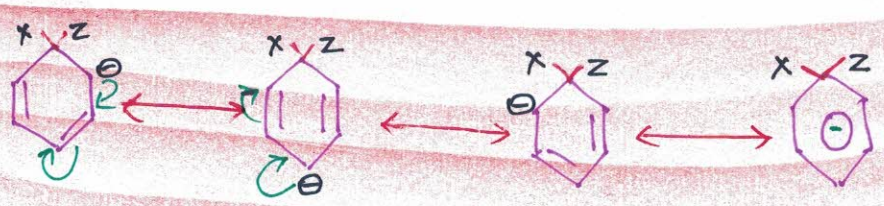
NUCLEOPHILIC SUBSTITUTION

— There are two methods of substitutio

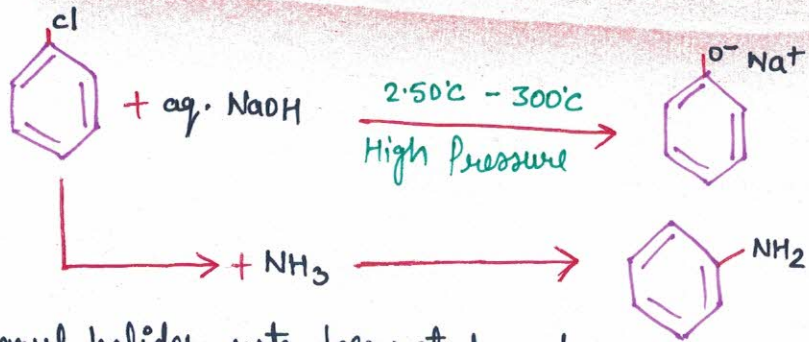
1. By substitution bimolecular (S_N2)

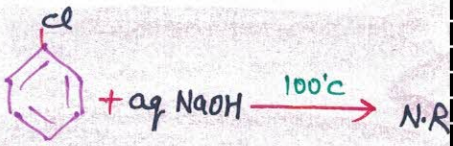
MECHANISM



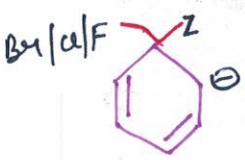


Resonating structures

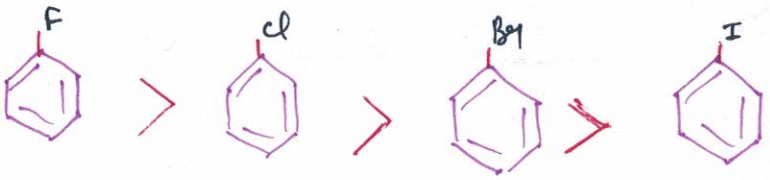




In aryl halides rate does not depend on the bond strength but depends on stabilisati of intermediate carbocation as in RDS –X bond is not broken.

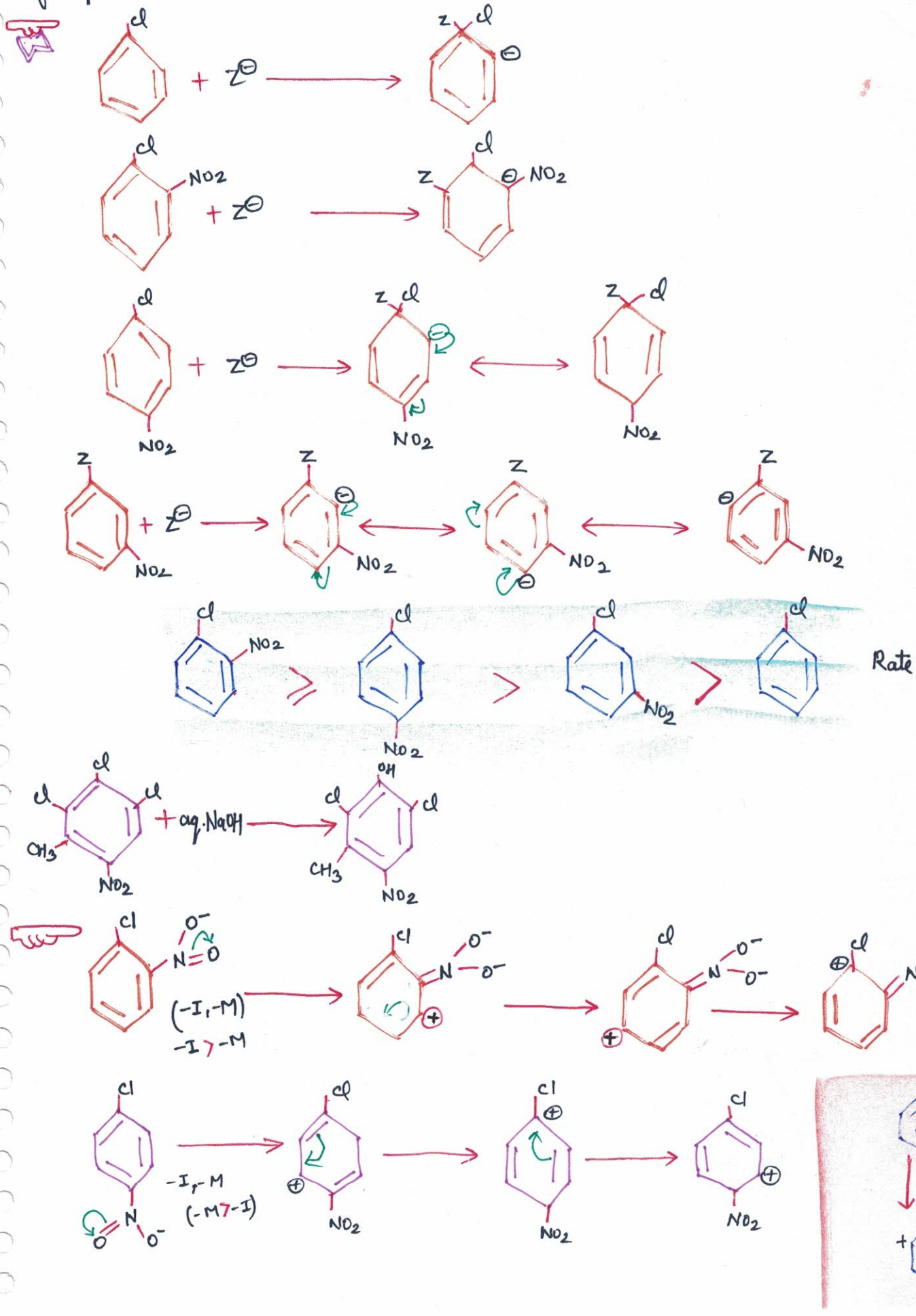


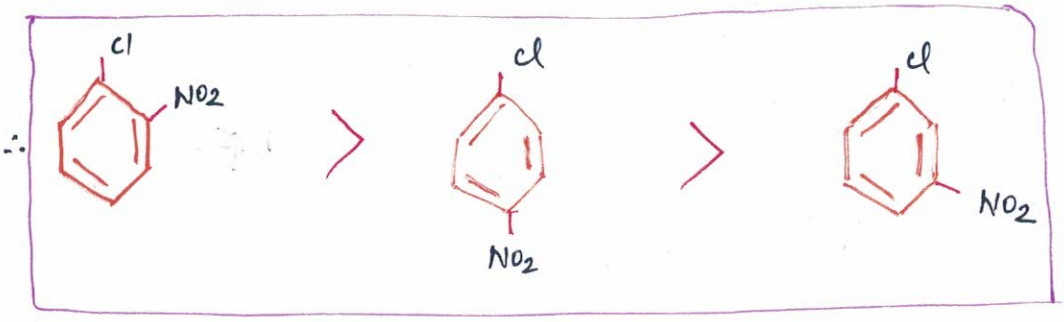
→ most stable when F is attached.

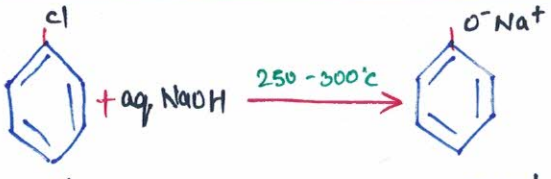


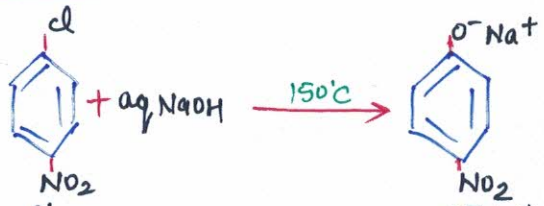
{ Rate of nucleophilic substitution }

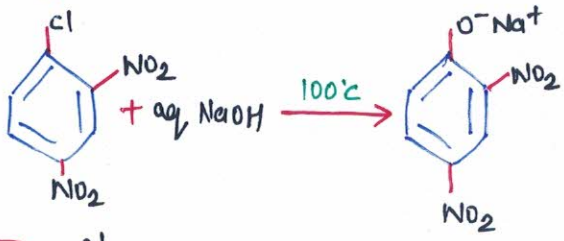
Therefore, they do not show elemental effect. so, if a with drawing group is attached to aryl halide. rate ↑ due to stabilisation of intermediate but if releasing group is attached rate ↓

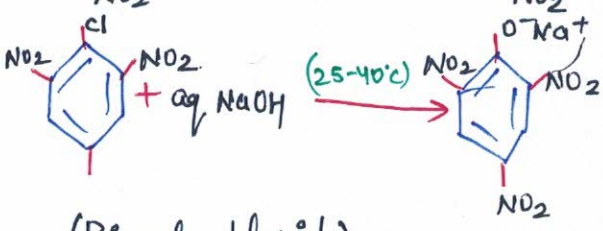




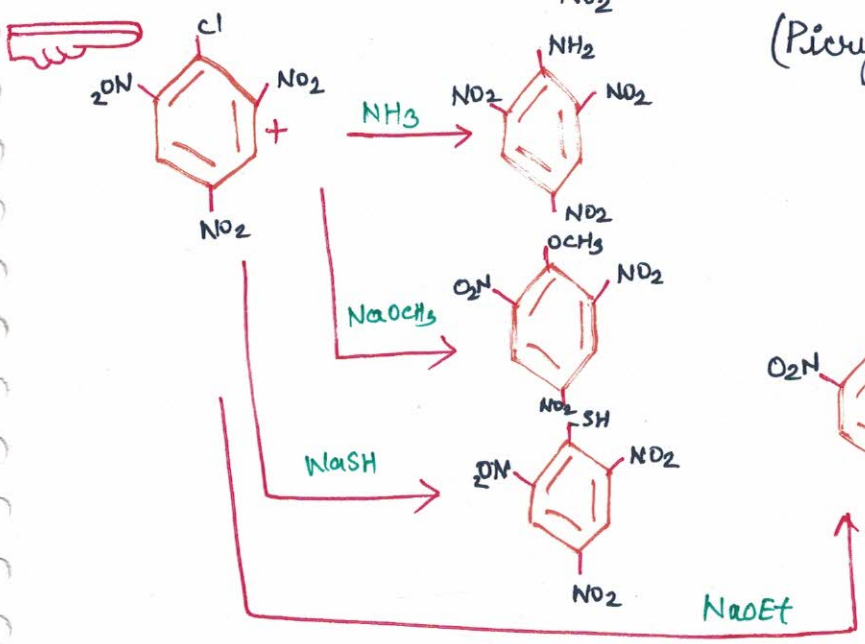


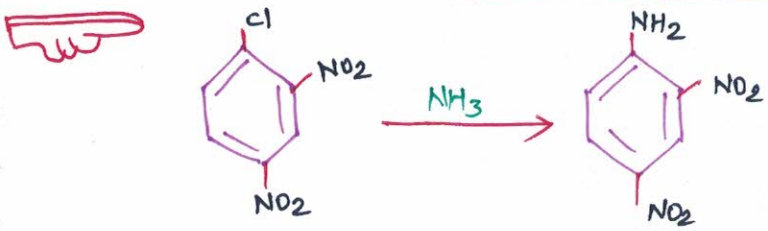






(Picryl chloride)

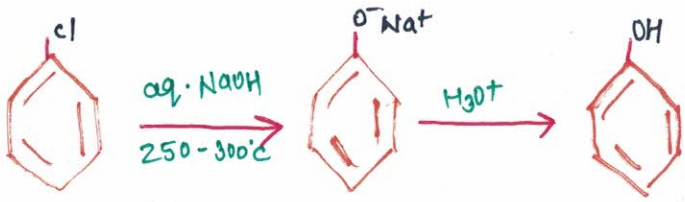


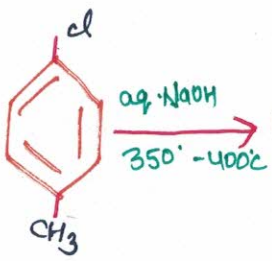


Picryl chloride can undergo nucleophilic substitution even at room temperature.

2. Elimination - Addition

MECHANISM

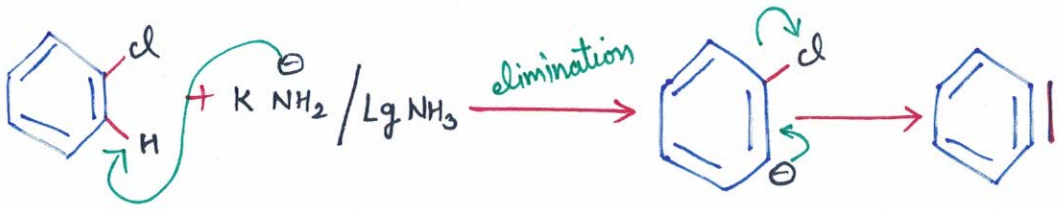




Not reaction by S_N2

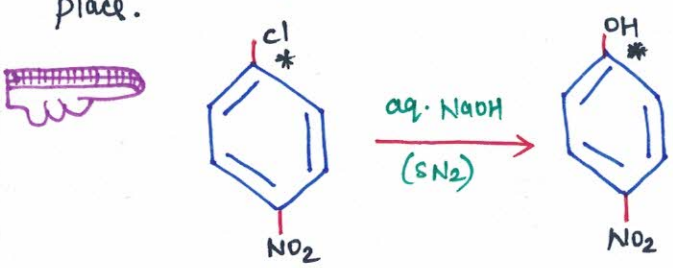
Aryl halides having releasing groups undergo substitution by elimination addition mechanism.

MECHANISM

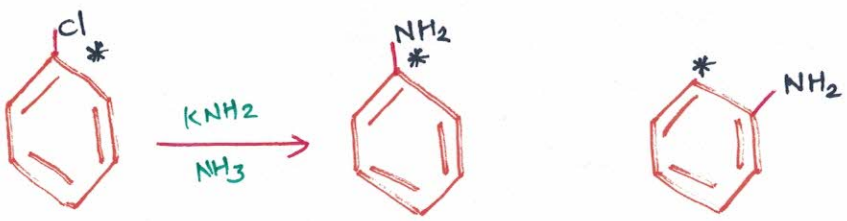


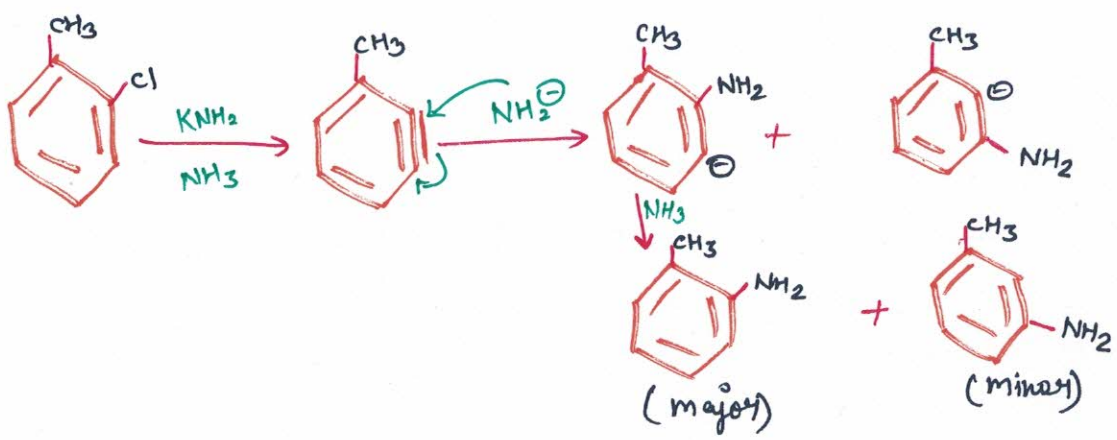
In elimination addition, two products can be obtained but in S_N2 only one product is obtained.

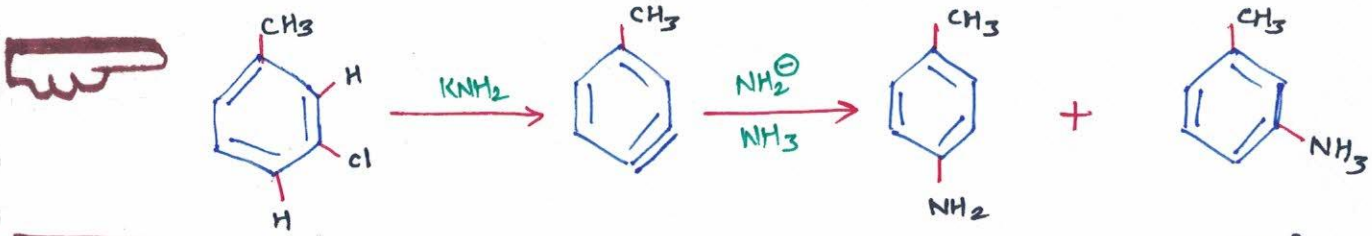
Hence, if aryl halide is reacted with strong base elimination is prone to take place.

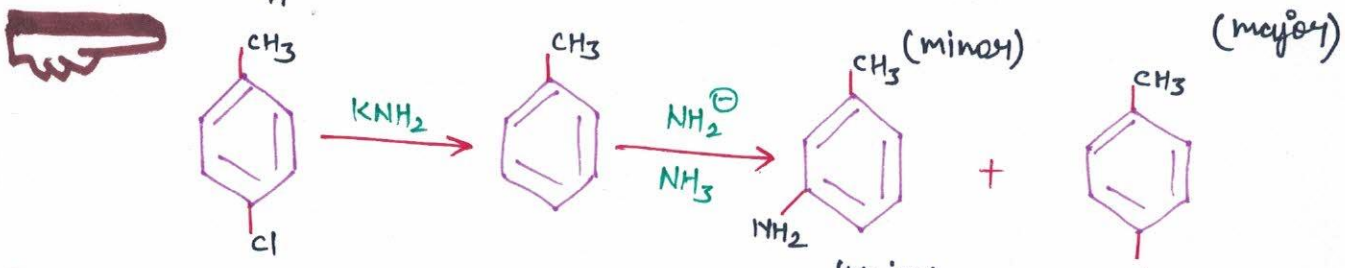


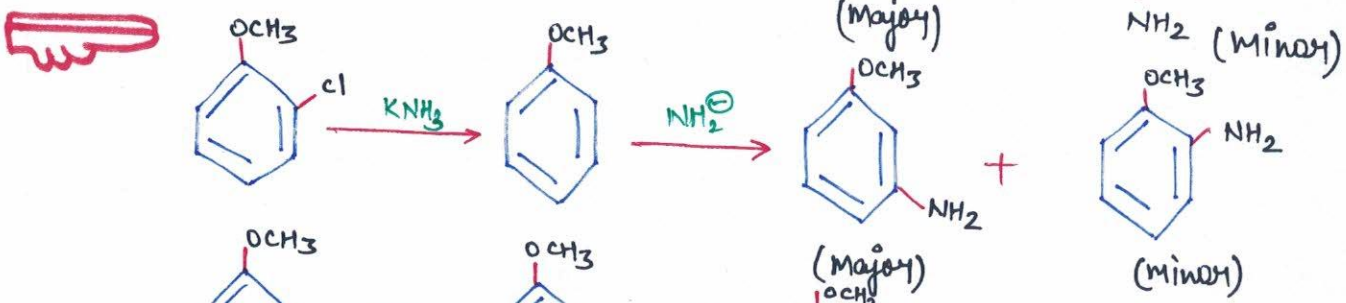
More acidic – H is removed and then the prod. is formed at adjacent of most stable carboanion.

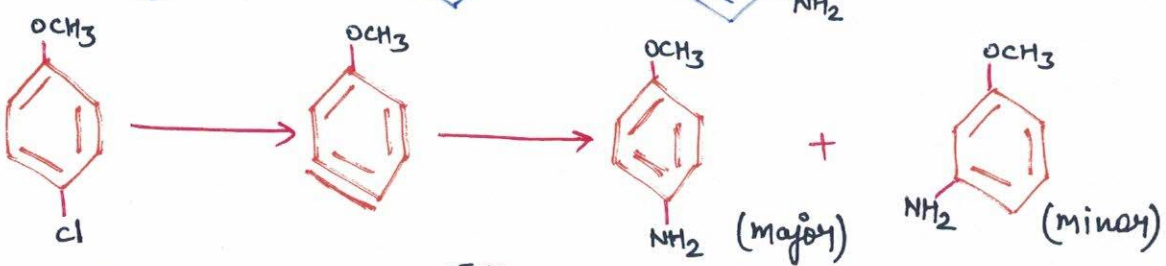


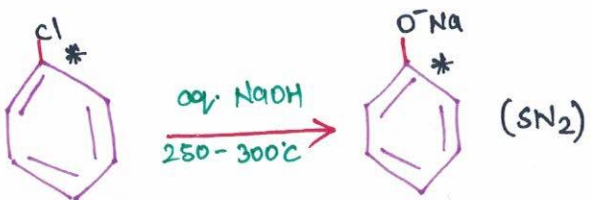






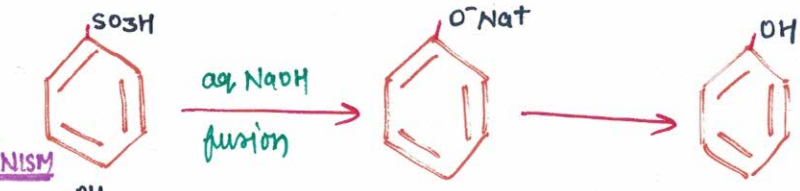


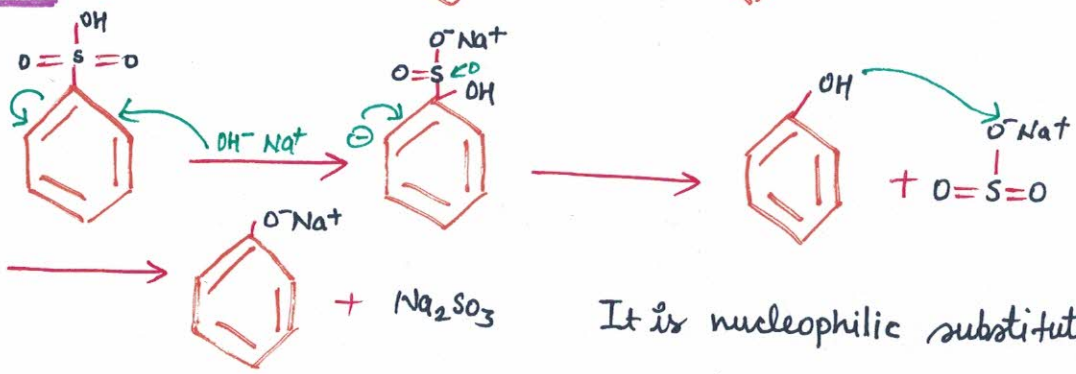




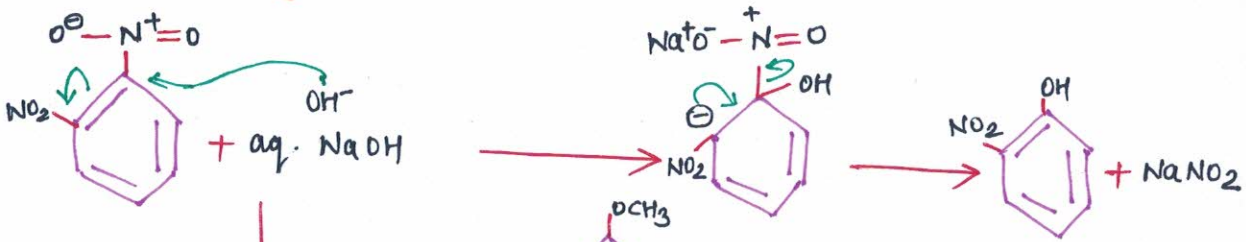
In elimination - addition, benzyne is intermediate

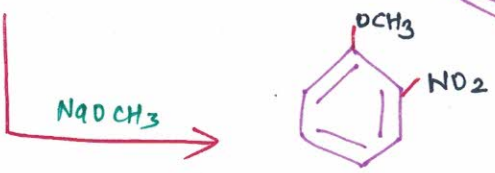
MECHANISM

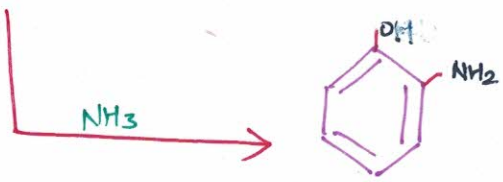


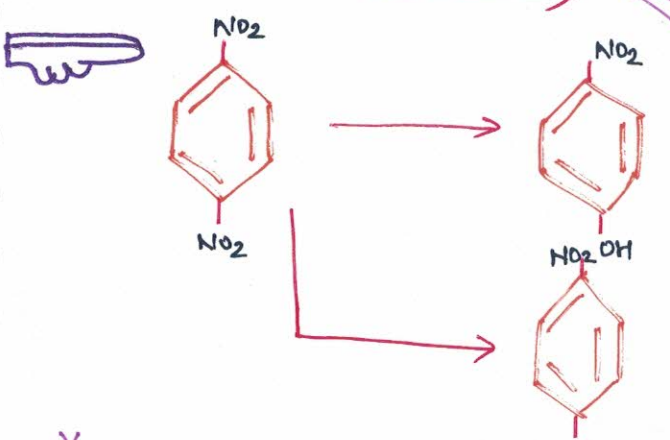


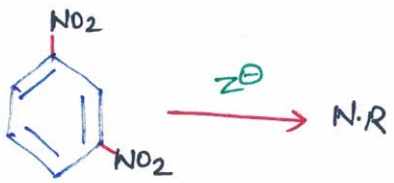
It is nucleophilic substitution reaction.



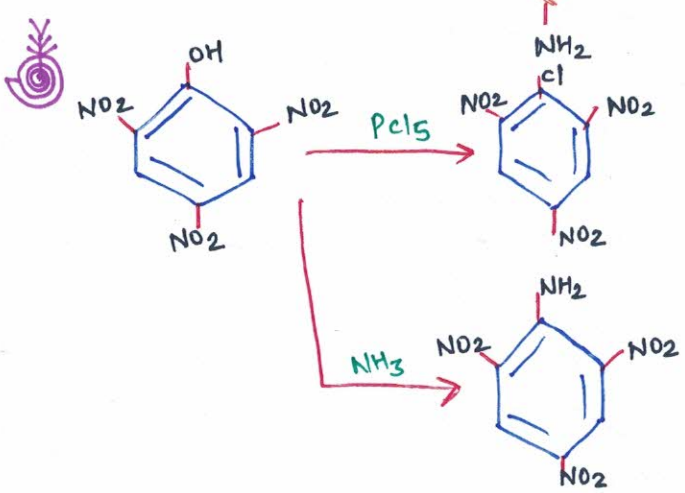


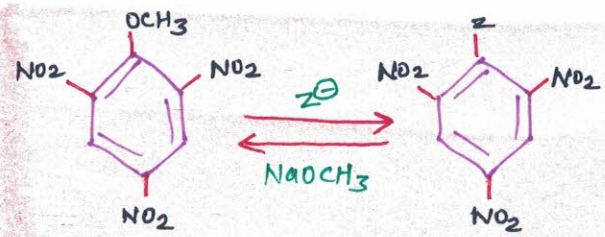






A nitro group can undergo nucleophilic substitution provided there is another $-NO_2$ group at ortho or para positions.

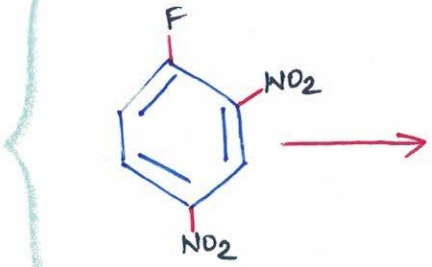




It is in equilibrium.

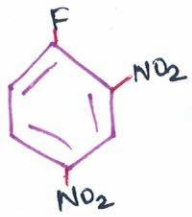
If excess of Z^- is taken forward reaction.

If excess of $NaOCH_3$ is taken backward reaction.

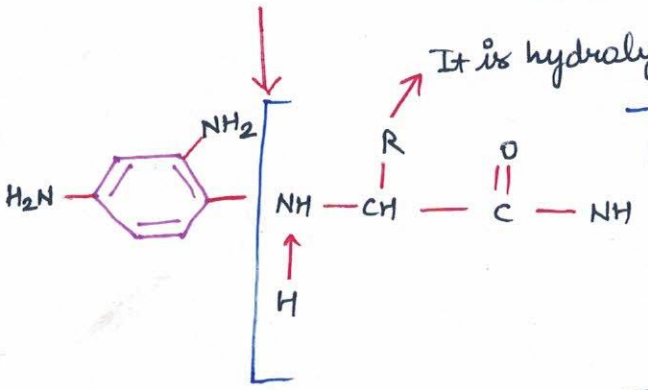


→ Songer's Reagent

The use of Songer's Reagent is to identify the terminal amino acid group in a Protein.



+ $NH_2 - CH - CO - NH$ - - - - - -



It is hydrolysed and separated & then its molar mass can be calculated.
It is used to determine molar mass of terminal group.

This reaction is also nucleophilic substitution reaction.