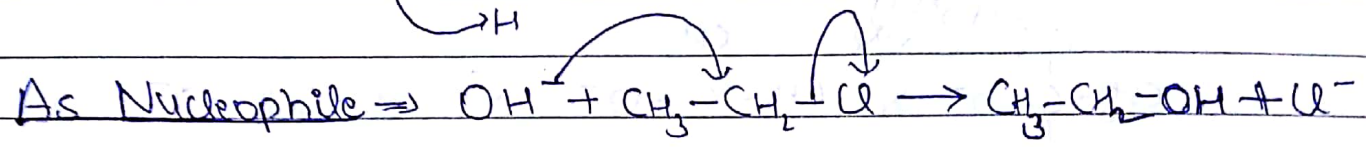
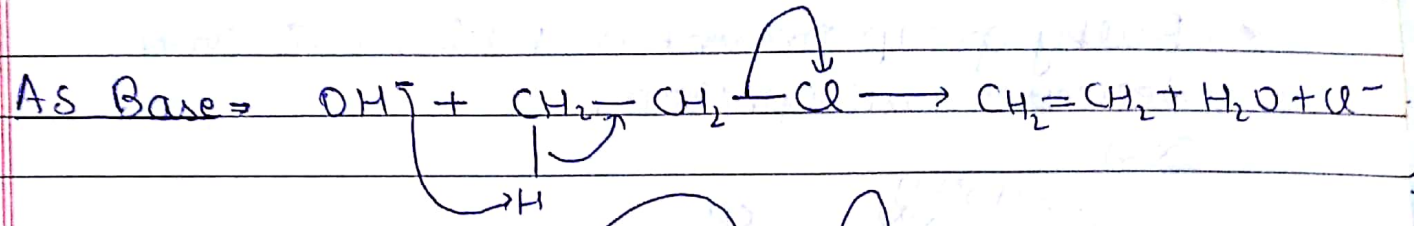


ORGANIC CHEMISTRY

Basicity - Tendency of an atom, ion or molecule to donate electron pair to H⁺ ion is known as basicity.

Nucleophilicity - Tendency of an atom, ion or molecule to give electron pair to an electron deficient atom is defined as nucleophilicity.



Criteria for Nucleophilicity -

Any

- Factor which increase the electron density at donor atom, increase nucleophilicity. Ex $\rightarrow \text{R-O}^- > \text{R-OH}$
- More polarisable donor atom is better nucleophile. Therefore larger size donor atom increases nucleophilicity. Ex $\text{R-S}^- > \text{R-O}^-$

Rules to decide Nucleophilicity -

- Species with -ve charge is stronger nucleophile than similar neutral species. Ex $\rightarrow \text{OH}^- > \text{H}_2\text{O}$
 $\text{RO}^- > \text{ROH}$, $\text{RS}^- > \text{RSH}$, $\text{SH}^- > \text{H}_2\text{S}$, $\text{NH}_2^- > \text{NH}_3$
- Electronegativity of donor atom increases, nucleophilicity decreases or on moving left to right in a period, nucleophilicity decreases.

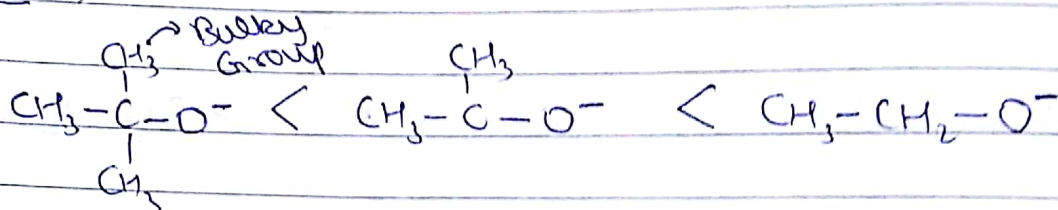
Ex $\rightarrow \bar{O}H > F^-$, $\ddot{N}H_3 > H_2O$, $R_3P \cdot > R_3S$, $\bar{N}H_2 > \bar{O}H$,
 $\bar{C}H_3 > \bar{N}H_2$

- As size of donor atom increases, nucleophilicity increases. Or on moving down the group nucleophilicity increases.

Ex $\rightarrow I^- > Br^- > O^- > F^-$; $SeH^- > SH^- > OH^-$, $R_3P \cdot > R_3N \cdot$,
 $\ddot{P}H_3 > \ddot{N}H_3$

- Bulky group present on nucleophilic centre decreases nucleophilicity.

Ex \rightarrow



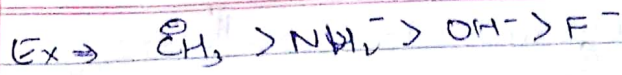
~~Exception~~ Nucleophilicity vs Basicity

\rightarrow Generally strong base are strong nucleophilic & weak base are weak nucleophile

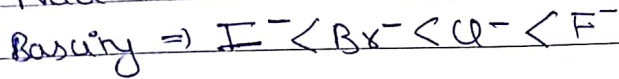
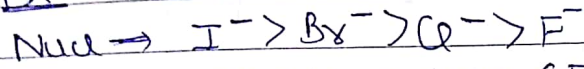
\rightarrow If nucleophilic centre is same, then, 'basicity & nucleophilicity' order is same.
 Eg. $\text{CH}_3\text{COO}^- < \text{OH}^- < \text{RO}^- \Rightarrow$ Basic strength order & Nucleophilic Order.

- As the steric hindrance increases, nucleophilicity decreases, \therefore tertiary but-oxide ion is strong base but weak nucleophile.

- Along a period basicity & Nucleophilicity or as the electronegativity of donating atom increases basicity & nucleophilicity decreases.

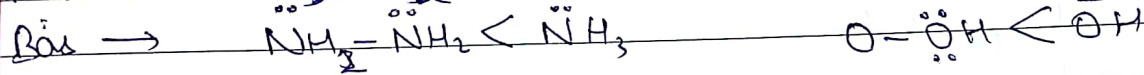
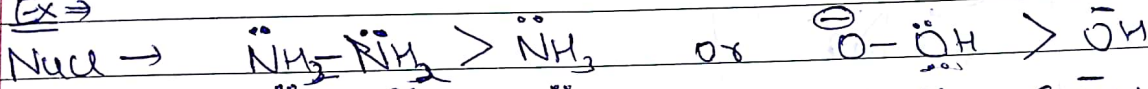


- On moving down the group, basicity is inversely proportional to nucleophilicity. Or as size increases nucleophilicity increases but basicity decreases



- When the atom bonded to nucleophilic centre also have a lone pair of electron, then nucleophilicity & basicity

Ex \Rightarrow



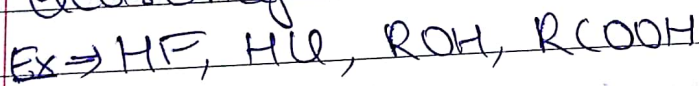
Effect of Solvent on Nucleophilicity -

Solvent are of 2 types -

- Polar Protic Solvent
- Polar Aprotic Solvent

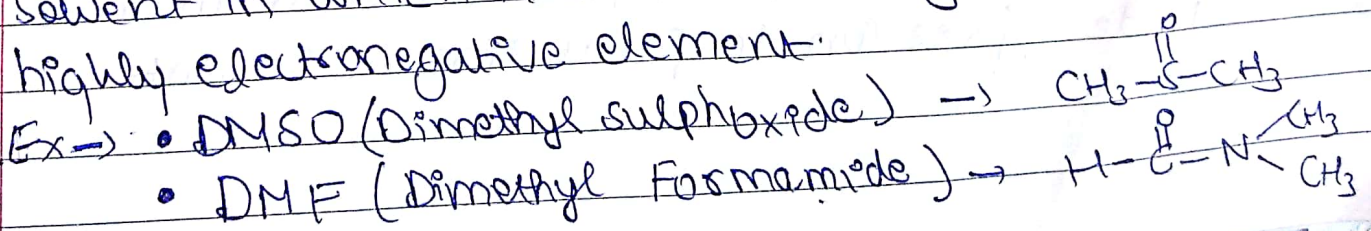
Polar Protic Solvent -

Solvent in which H is directly attached with an electronegative element is known as polar protic solvent

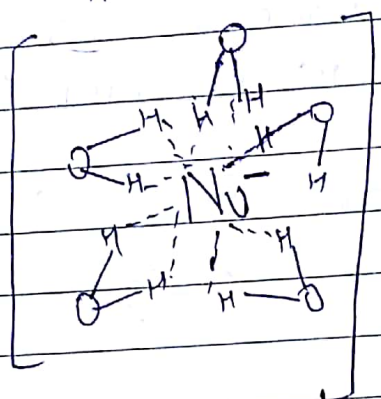
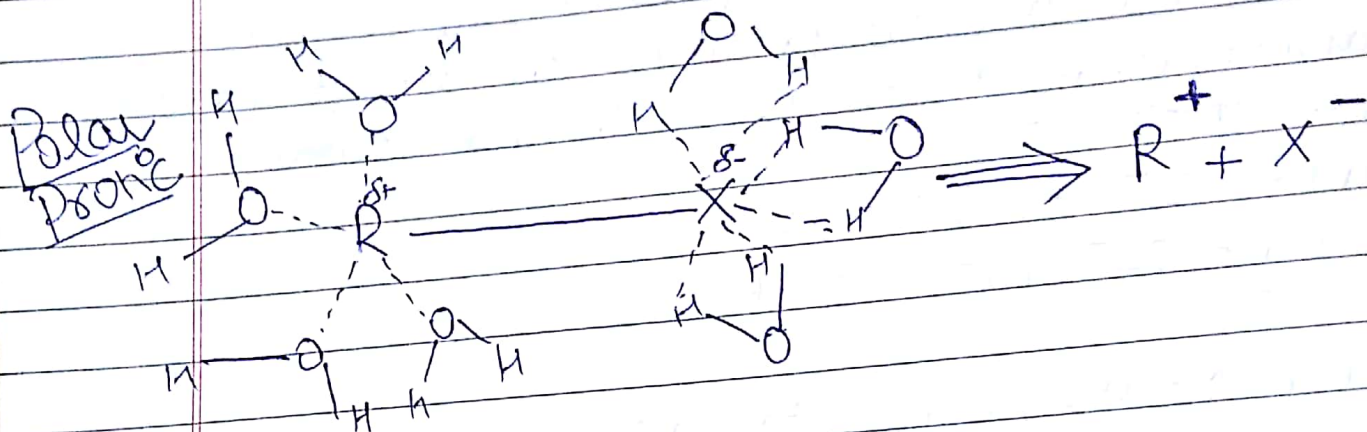


Polar Aprotic Solvent -

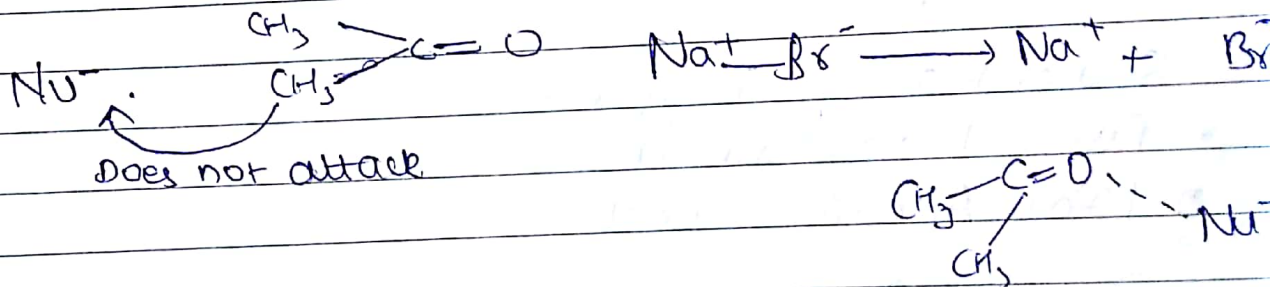
Solvent in which H is not directly attached with highly electronegative element.



- DNA (Dimethyl acetamide) - $\text{CH}_3\text{-C}(=\text{O})\text{-N}(\text{CH}_3)_2$
- Acetone $\rightarrow \text{CH}_3\text{-C}(=\text{O})\text{-CH}_3$



Polar Aprotic



- In polar protic solvent, anion can be solvated by ion dipole interaction hence it will decrease nucleophilicity of that anion
- Polar Aprotic can only solvate cation. Cations are solvated by ion dipole interaction while anion are not solvated because of hindrance so anion is made a free ion in polar aprotic solvent.

Reaction Mechanisms -

Reactions are basically different types

- Substitution
- Elimination
- Addition

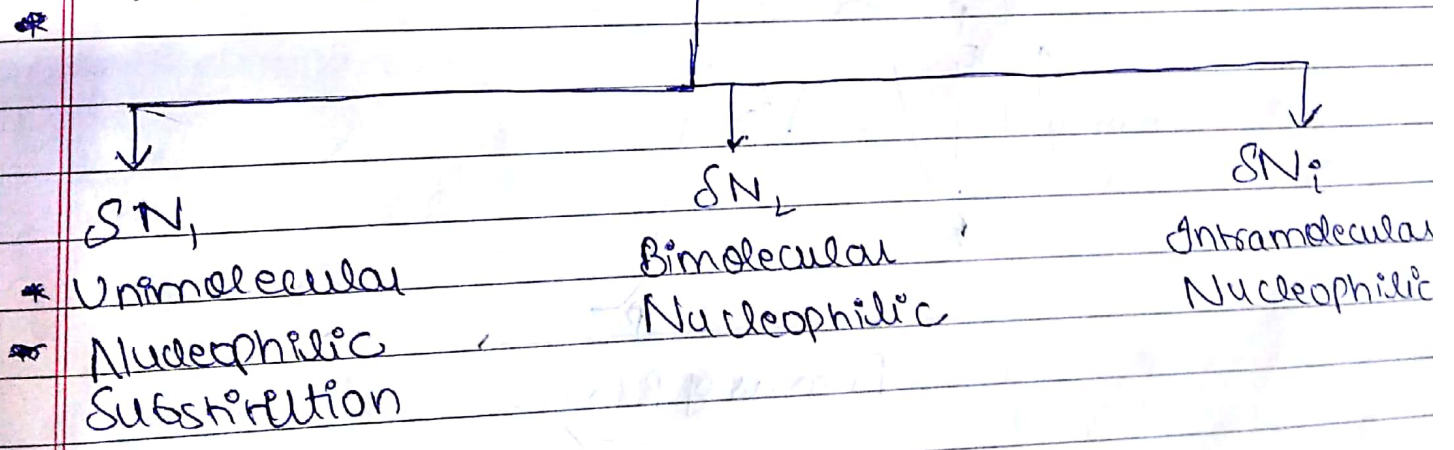
Substitution Reactions -

There are 3 types of substitution rxn -

- Free Radical
- Electrophilic Substitution
- Nucleophilic "

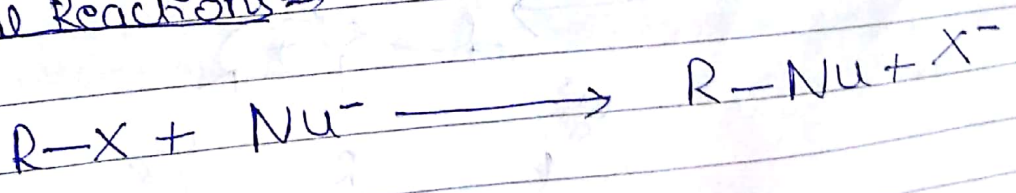
⇒ Nucleophilic Substitution Rxn -

They are of 3 types -

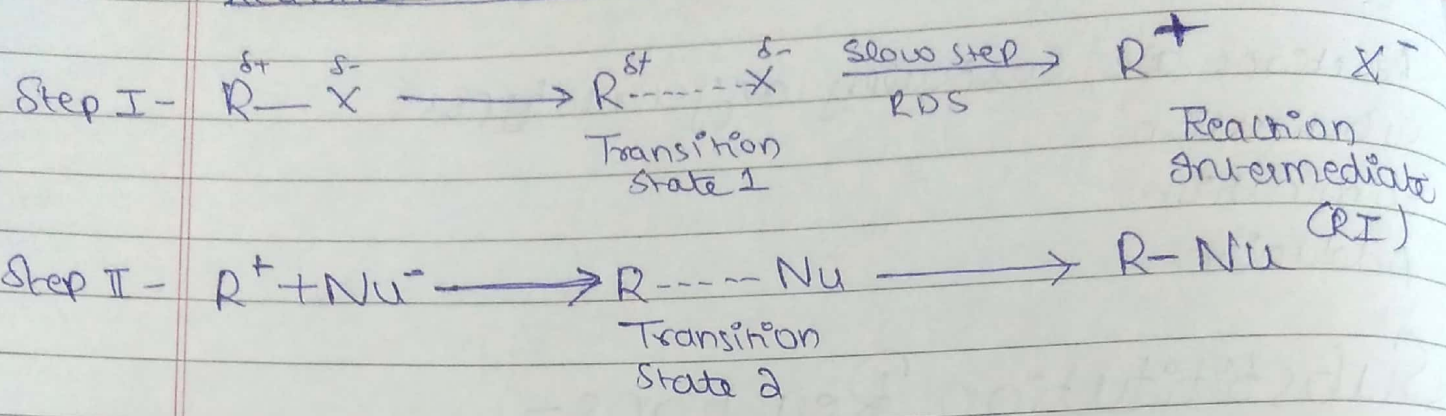


SN1 ⇒

* General Reactions ⇒



* Reaction Mechanism \Rightarrow

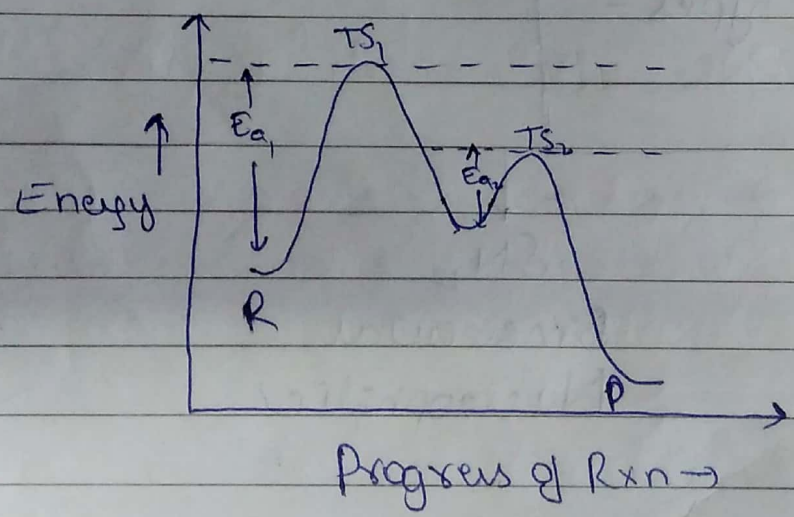


* Kinetics of Reaction \Rightarrow

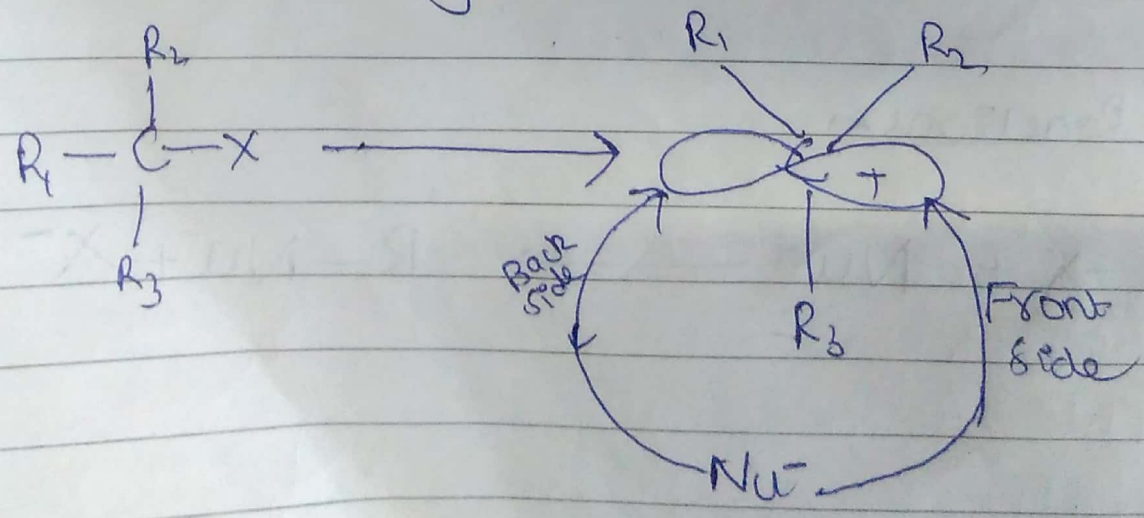
$R \propto [R-X]$

$R = k [R-X]^1 \rightarrow$ 1st Order Reaction

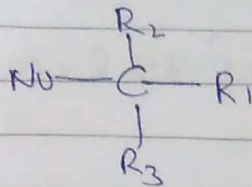
* Energy Diagram \Rightarrow (Exothermic Rxn)



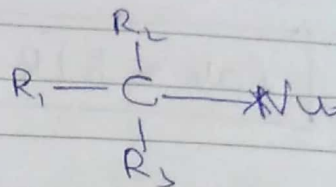
* Stereochemistry \Rightarrow



Back Side



Front Side



Inversion Product (50%)

Retention Product (50%)

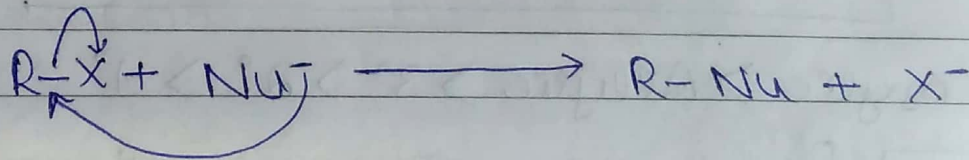
Racemic Mixture

→ % of Racemisation depends on 2 factors -

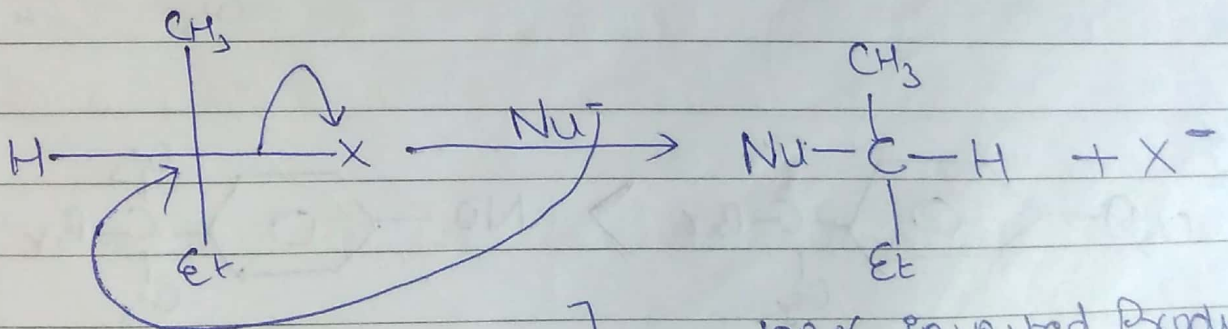
- Stability of Carbocation - Greater the stability of carbocation more is proportion of racemisation
- Concentration of Nucleophile - Higher the concⁿ of nucleophile inverted product will be formed more & less racemic mixture is formed

SN2 ⇒ (*Nucleophile always attacks from the back side. Always inversion)

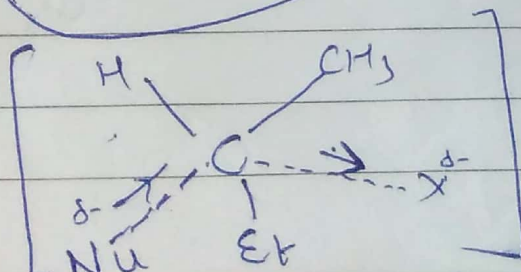
* General Rxn → * Exothermic Rxn



* Reaction Mechanism ⇒



Transition State ⇒

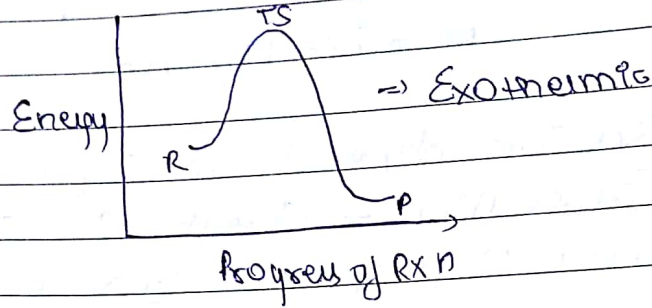


100% Inverted Product (Walden Inversion)

* Kinetics \rightarrow

$$\text{Rate} = k[R-X][Nu^-] \rightarrow \text{2nd Order Rxn}$$

* Energy Diagram \Rightarrow



* Stereochemistry \Rightarrow

- An S_N2 , 100% inversion will occur.

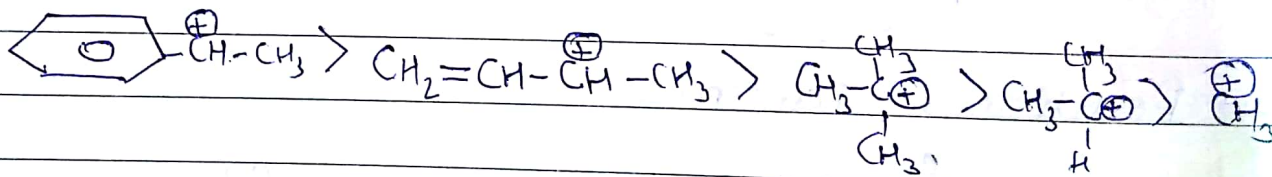
* Factors Affecting S_N1 & S_N2 \Rightarrow

Effect of substrate on S_N1 \Rightarrow

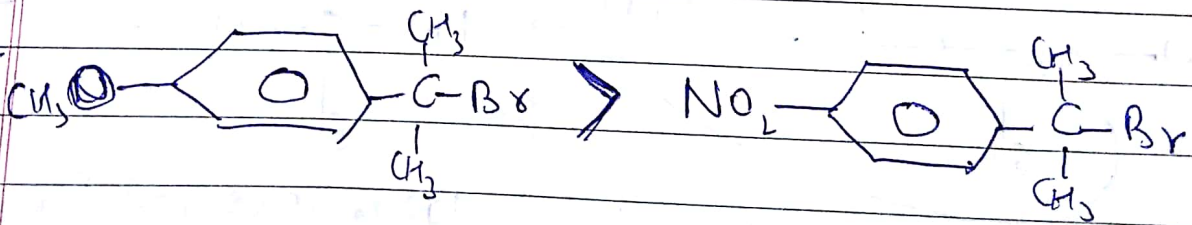
Carbocation stability will decide the reactivity.

Stability of Carbocation \propto Reactivity

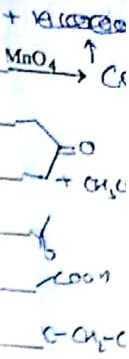
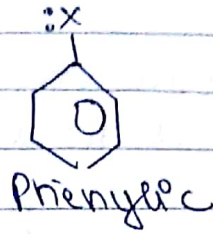
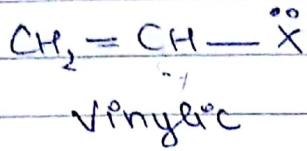
* Benzyllic $>$ Allylic $>$ $3^\circ >$ $2^\circ >$ 1°



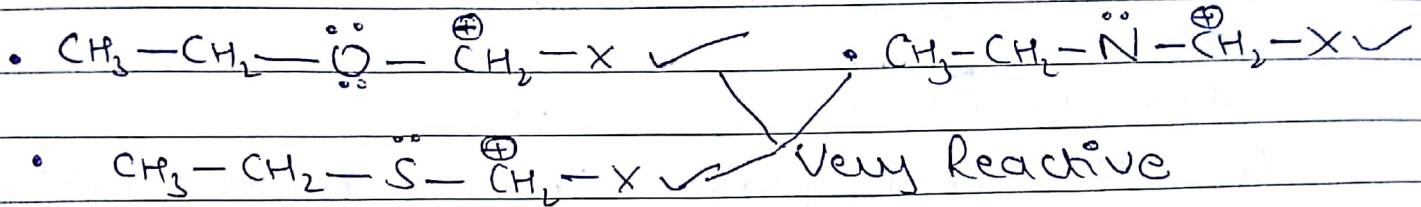
Ex



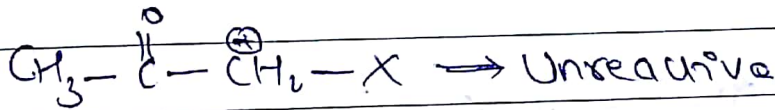
Vinyllic & Phenyllic do not give S_N1 rxn.



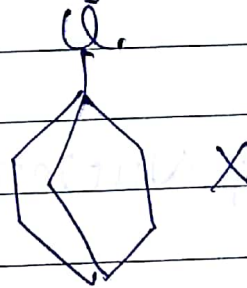
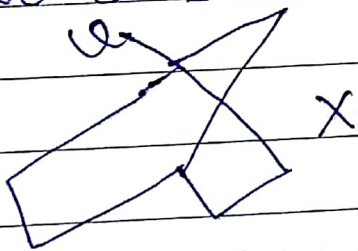
If any hetero atom are present in α -position, then they are highly reactive.



Presence of carbonyl group on α -~~position~~ ^{Carbon} is highly unfavourable bcoz carbonyl group has very strong $-I$ effect which destabilises the intermediate

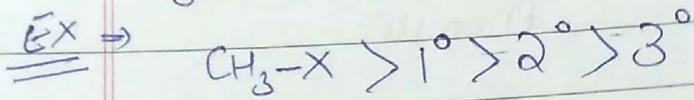


Bicyclo Bridge ~~gives~~ with 3° alkyl halide does not give S_N1 reaction.

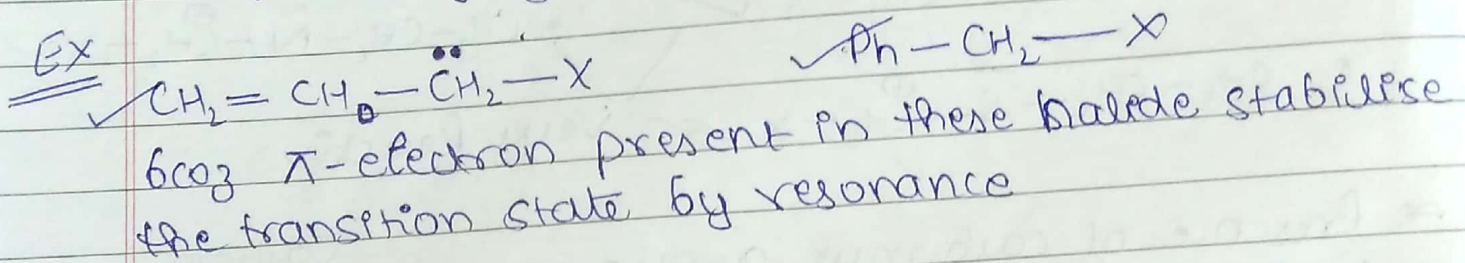


• Effect of Substrate on $S_N2 \Rightarrow$

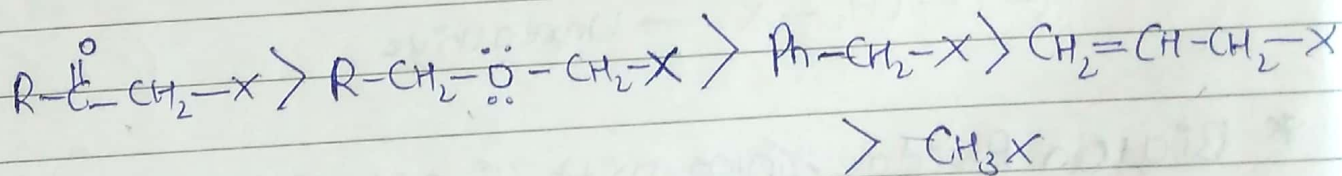
* As the steric strain on α -carbon increases, rate of S_N2 decreases



* The presence of unsaturation on β -carbon increase the reactivity of S_N2 reaction.



* Presence of hetero-atom on α -position also increase the reactivity & presence of carbonyl group on α -carbon is highly reactive for S_N2 rxn.

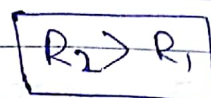
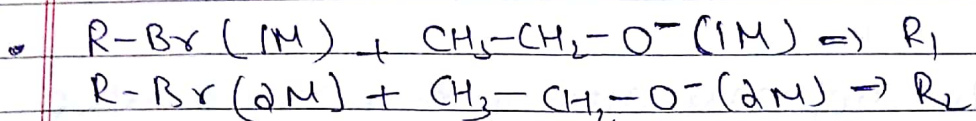
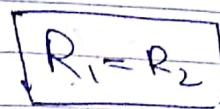
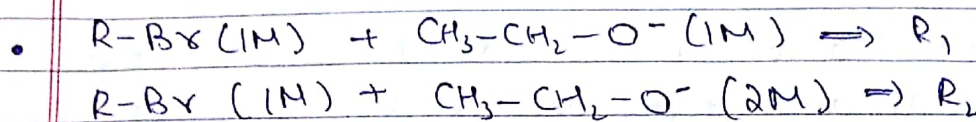


• Effect of Nucleophile on $S_N1 \Rightarrow$

* S_N1 ~~is~~ is not affected by nucleophilicity or concentration of nucleophile bcoz nucleophile is not present on rate determining step

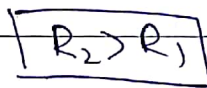
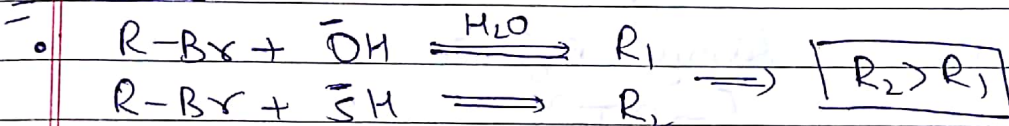
* Sometimes water ~~can~~ (solvent) can act as a nucleophile.

Q For S_N1



* Since S_N2 rxn involve substrate & nucleophile in RDS so it depends on conc. & nucleophilicity of nucleophile.

Q For S_N2



Effect of Solvent on $S_N1 \rightarrow$

* S_N1 rxn require polar protic solvent as polar protic solvent stabilises the intermediate.

Effect of Solvent on $S_N2 \rightarrow$

* Polar Aprotic solvent are required bcoz they solvate cation but they cannot solvate anion so unsolvated nucleophile has more nucleophilicity.

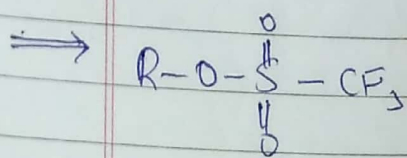
Effect of Leaving Group \Rightarrow

* A good leaving group is that which become a stable ion after its departure. So we can say weak base are better leaving group.

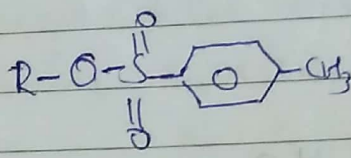
OR

* Stronger the conjugate acid of the leaving group better is its leaving ability.

Ex \rightarrow $I^- > Br^- > Cl^- > F^- \rightarrow$ Leaving Ability

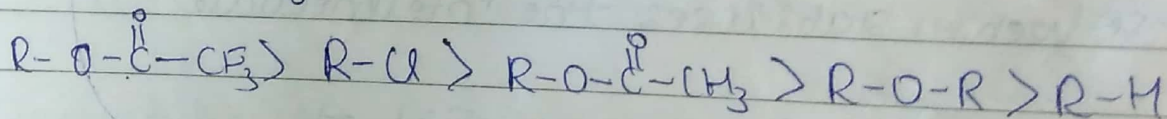
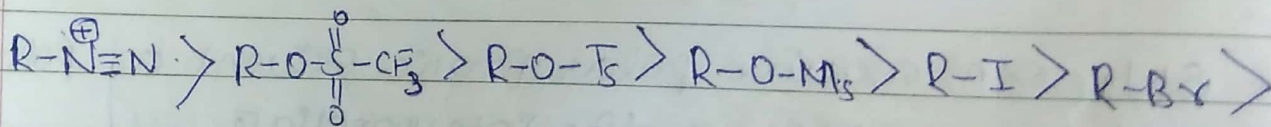


Alkyl Triflate
($-OTf$)



Alkyl Tosylate
($-OTs$)

\Rightarrow Leaving Ability Order \Rightarrow



* Both SN_1 & SN_2 require good leaving group

Difference b/w S_N1 & S_N2

S_N1	S_N2
It is one step mechanism	It is 2 step mechanism
Bimolecular Rxn	Unimolecular Rxn
Product formation takes place by Transition State	Product formation takes place by carbocation (Reaction Intermediate)
No rearrangement.	Carbocation can rearrange itself.
Favourable by polar aprotic solvent.	Favourable by polar protic solvent.
Order of Reactivity of RX bond $\Rightarrow CH_3X > 1^\circ > 2^\circ > 3^\circ$	Order of Reactivity of RX bond $\Rightarrow 3^\circ > 2^\circ > 1^\circ > CH_3X$
Favoured by high conc ⁿ of nucleophile.	Independent of conc ⁿ of nucleophile.
Inversion will occur.	Racemisation will occur.

Neighbouring Group Participation \Rightarrow (NGP)

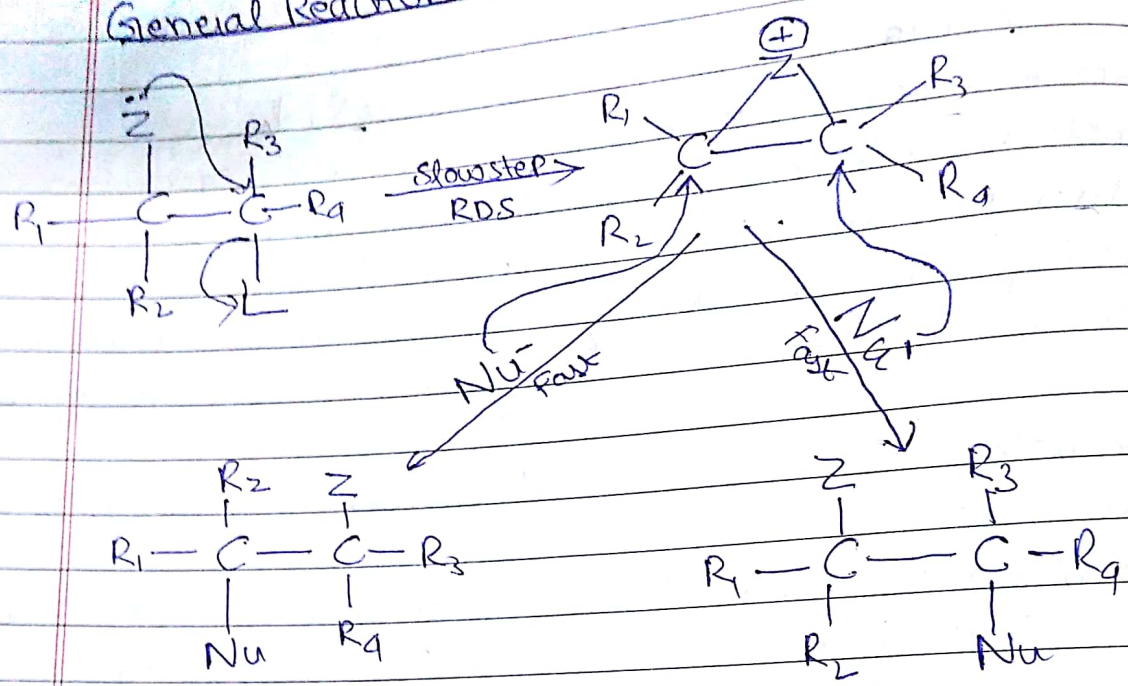
Hetero atom present at β -Carbon or π -bond present on γ -Carbon of leaving group, then neighbouring group participation rxn occurs

Common feature of all δ NGP Mechanism is the formation of highly reactive 3, 4, 5 or 6 membered cyclic rings

In this mechanism 2 step will occur via S_N2 mechanism but NGP rxn are faster than normal intramolecular S_N2 rxn bcoz of availability of nucleophile on adjacent position.

NGP > SN2

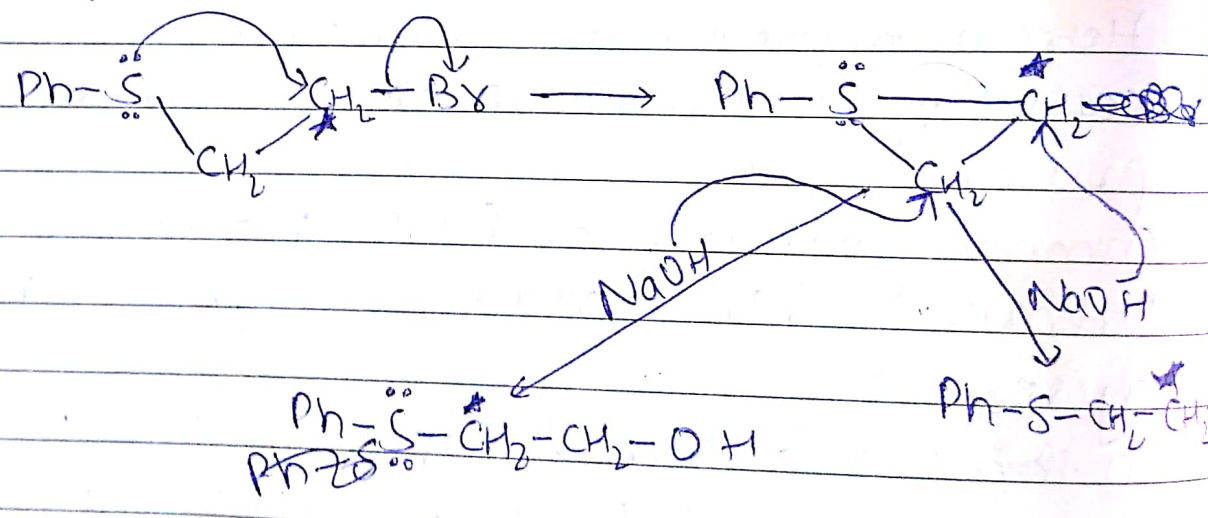
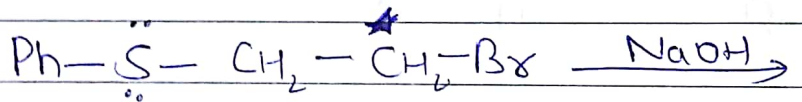
General Reaction \Rightarrow $Z-OH$ \Rightarrow $Z \& L$ should be at \ast trans position



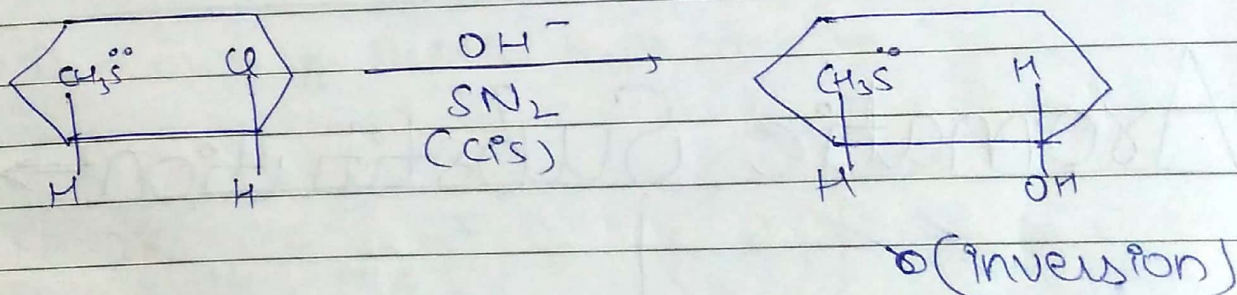
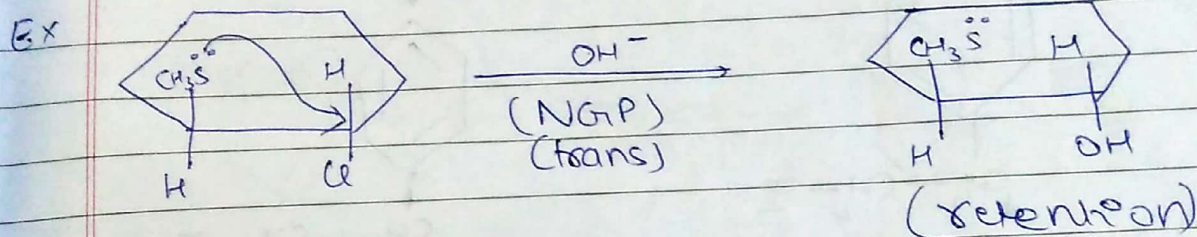
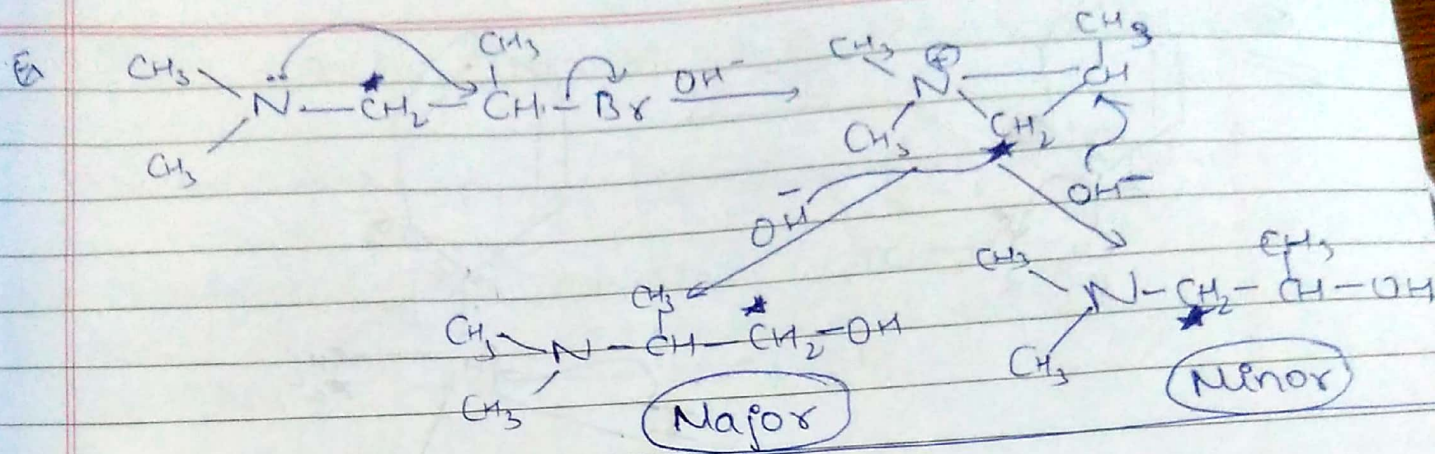
Z \Rightarrow Hetro Atom

- \hookrightarrow $-S, -O, -NH_2, Ph, -X, -OH, -OR, -SR, -SH, -N$
 $-NR_2, -O-C(=O)-R$

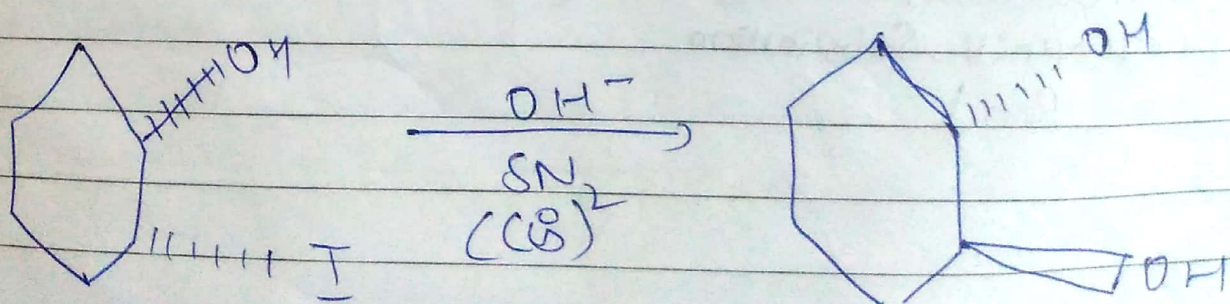
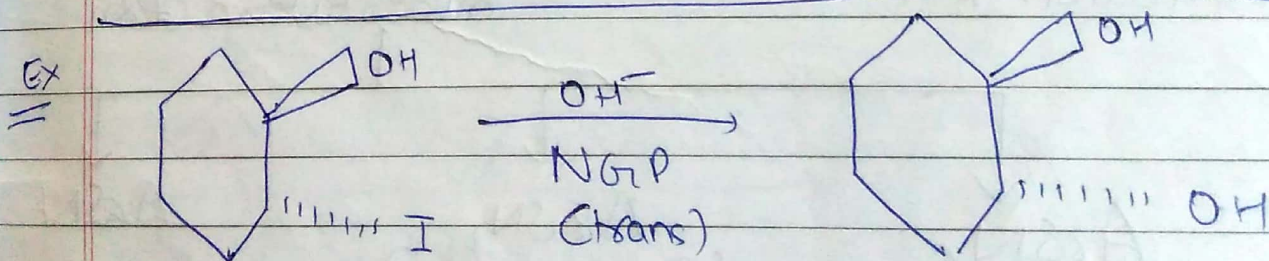
Ex

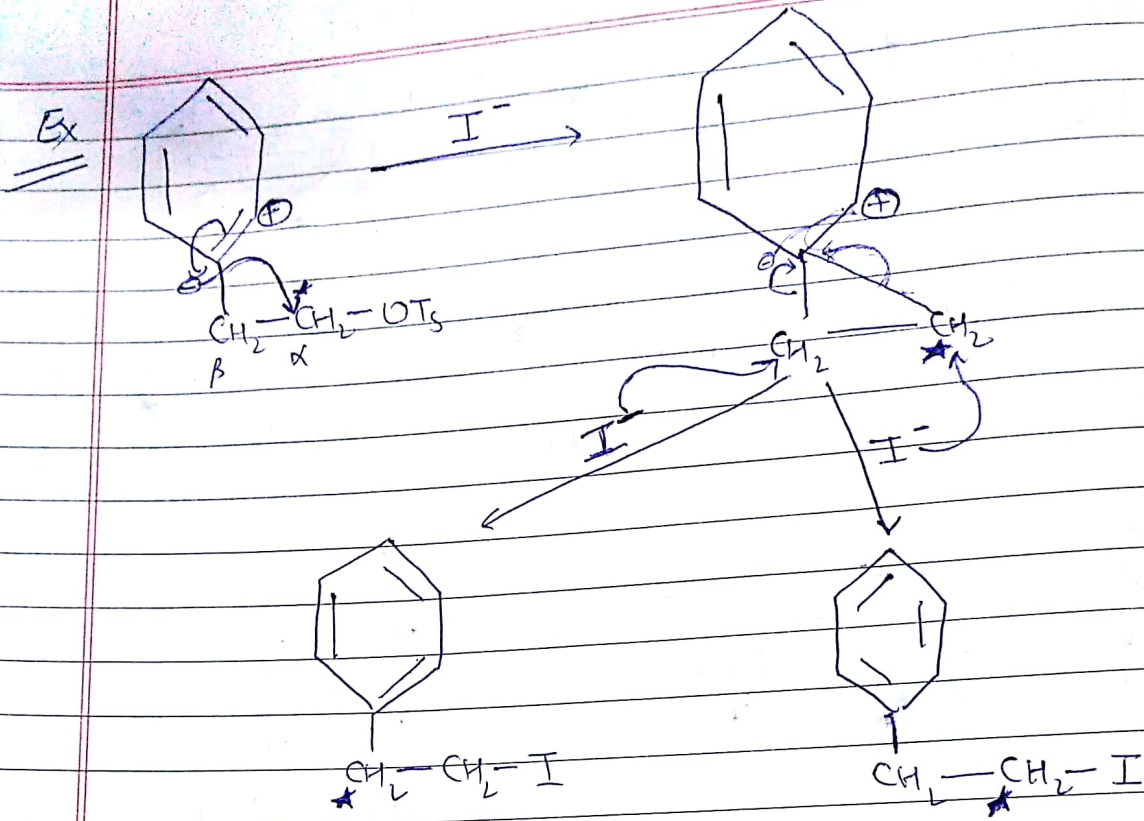


NGP \Rightarrow trans
 $S_N2 \Rightarrow$ cis



* For NGP mechanism, leaving group & nucleophile should be at anti position





Aromatic Substitution \Rightarrow

Electrophilic Aromatic Substitution Rxn

Nucleophilic Aromatic Substitution Rxn

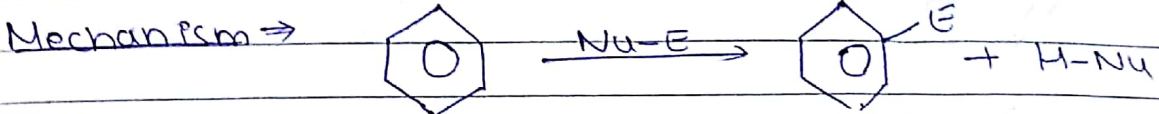
ArSN_1
 (Unimolecular Aromatic Nucleophilic Substitution Rxn)

ArSN_2
 (Bimolecular)

ArSN

Benzene does not show electrophilic addition rxn due to aromaticity loss.

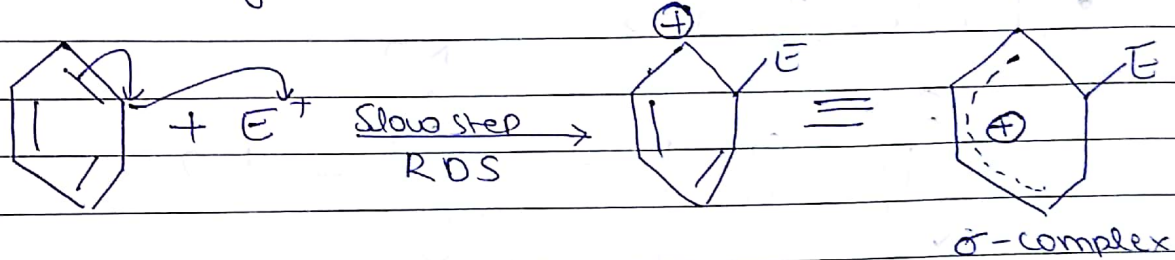
Electrophilic Aromatic Substitution Rxn ⇒



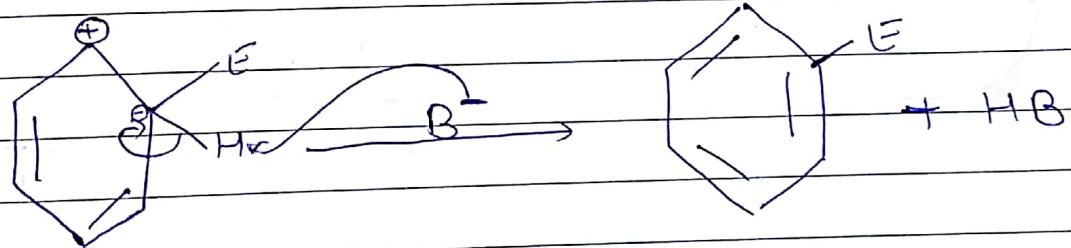
Step 1 ⇒ Formation of Electrophile.



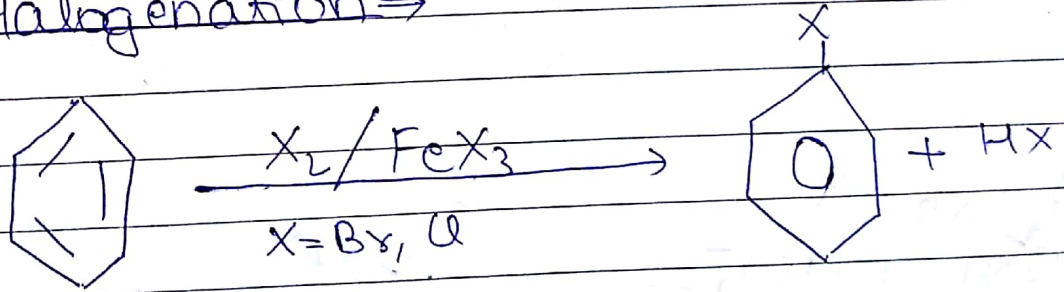
Step 2 ⇒ Formation of σ-Complex



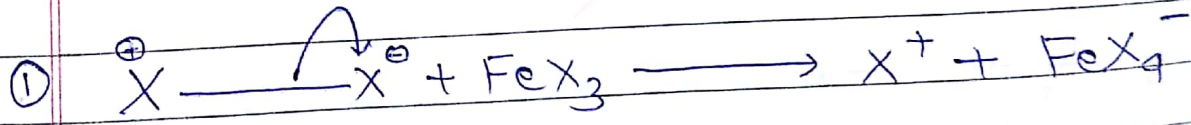
Step 3 ⇒ Removal of Acidic Hydrogen ⇒

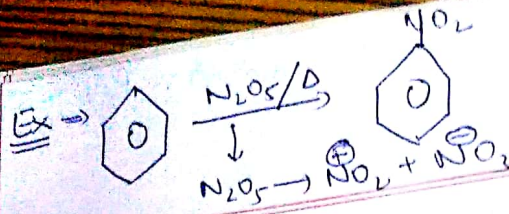


• Halogenation ⇒

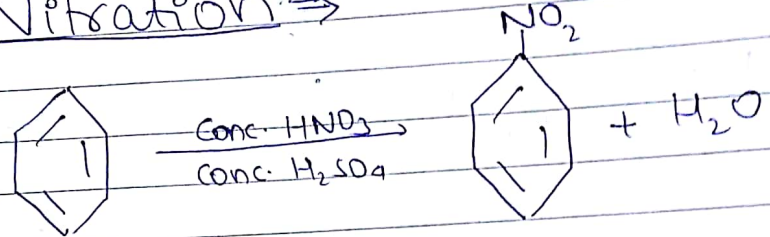


Mechanism ⇒

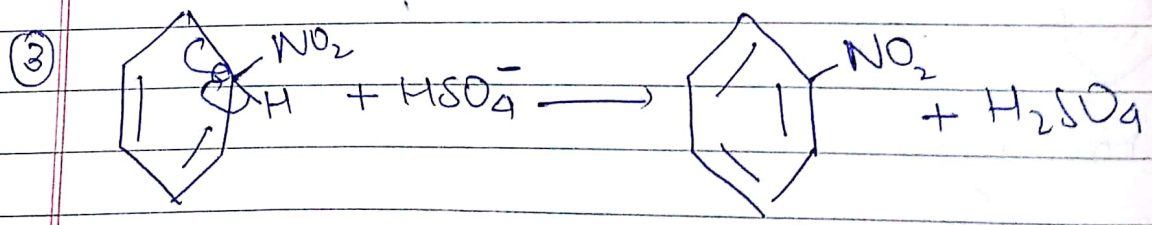
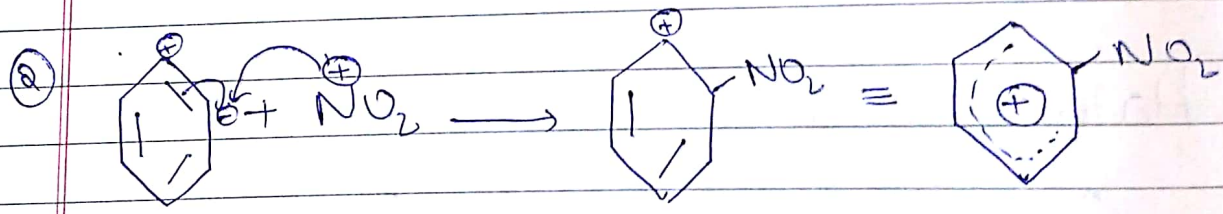
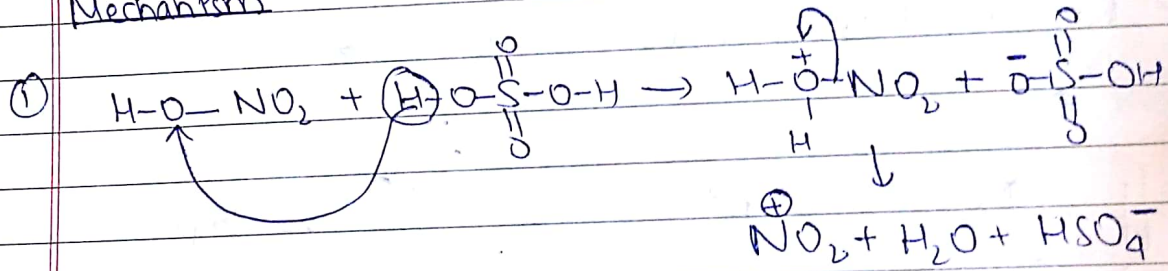




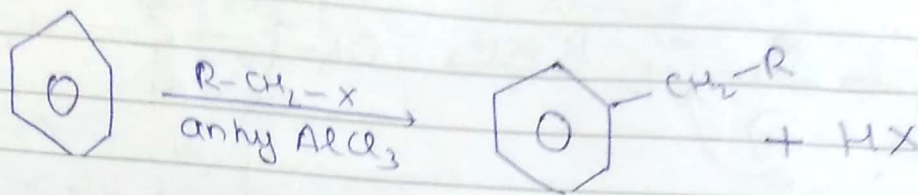
• Nitration \Rightarrow



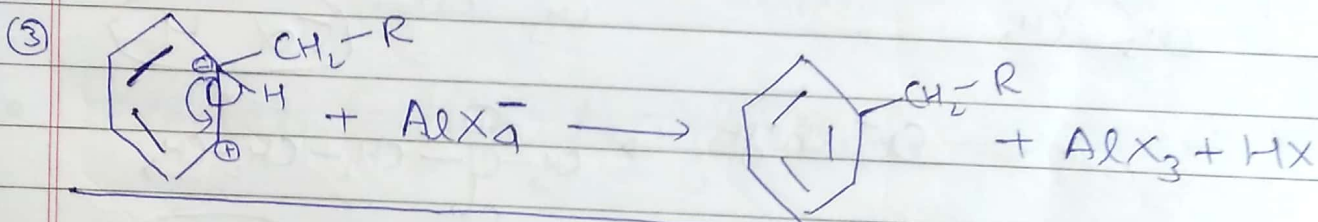
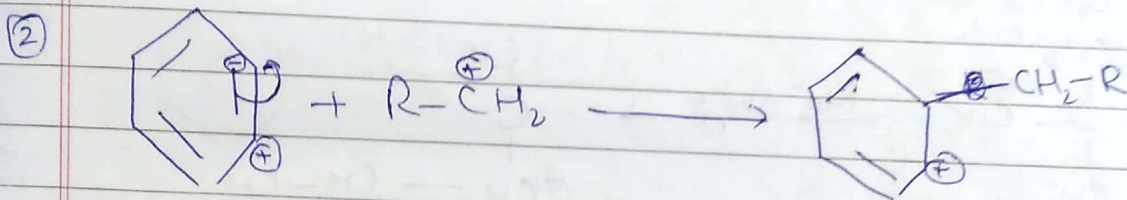
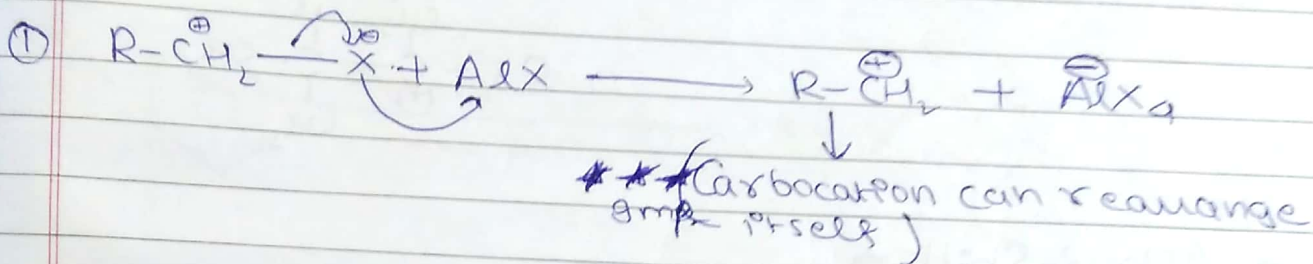
Mechanism



• Friedel Craft Alkylation \Rightarrow



Mechanism \Rightarrow

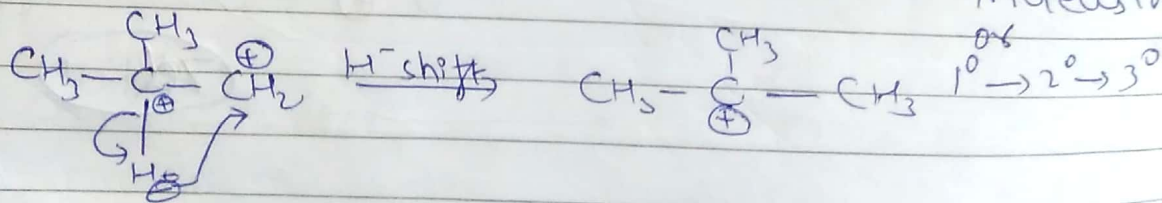


*** Carbocation Rearrangement \Rightarrow

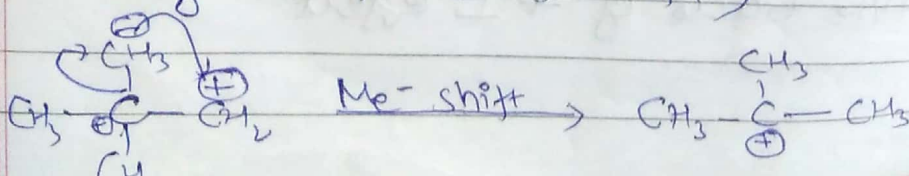
V.V. imp

Hydride Shift (H⁻ shift)

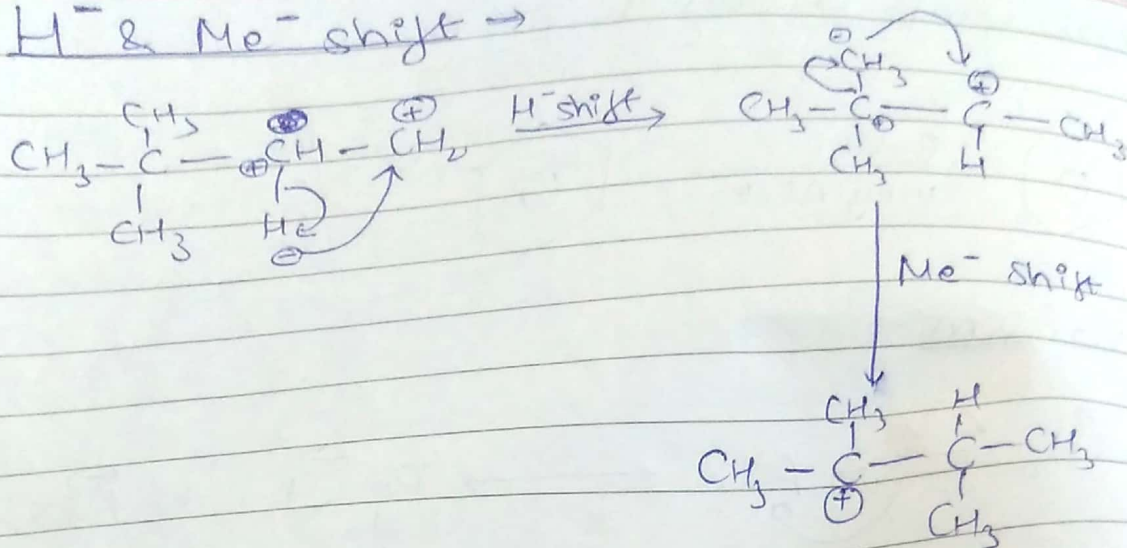
*** (Carbocation will move if α -hydrogen is increasing) ***



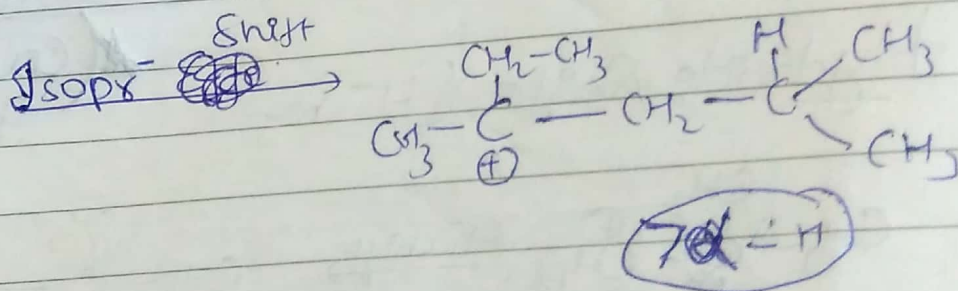
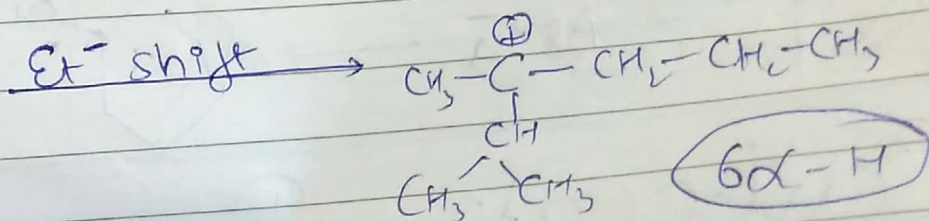
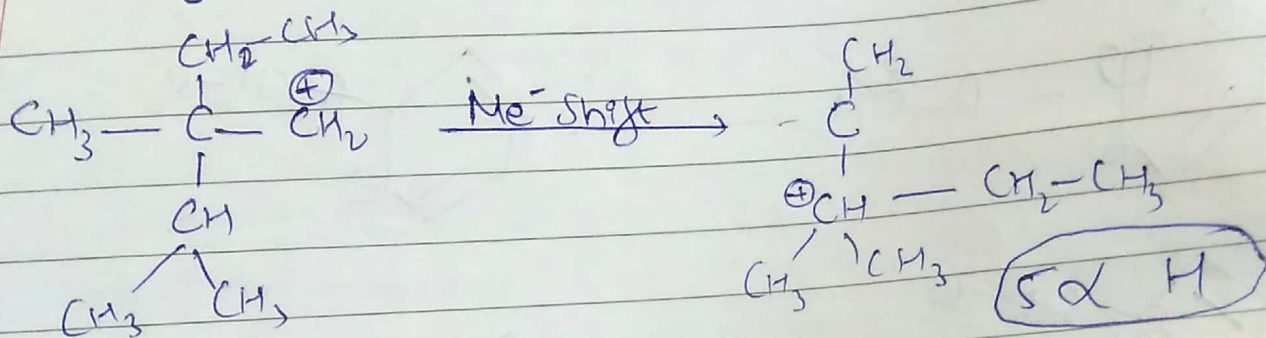
Methyl Shift (CH₃⁻ shift)



→ H⁻ & Me⁻ shift →



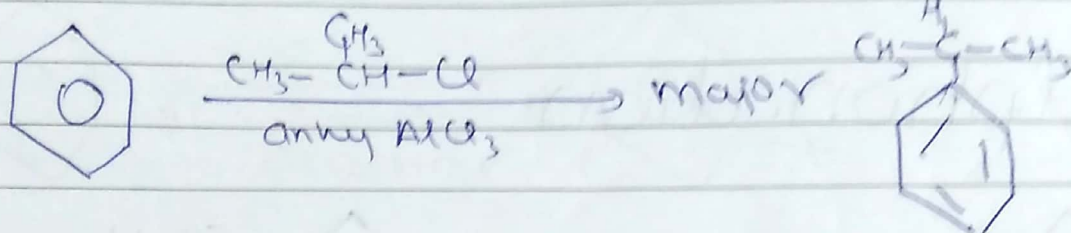
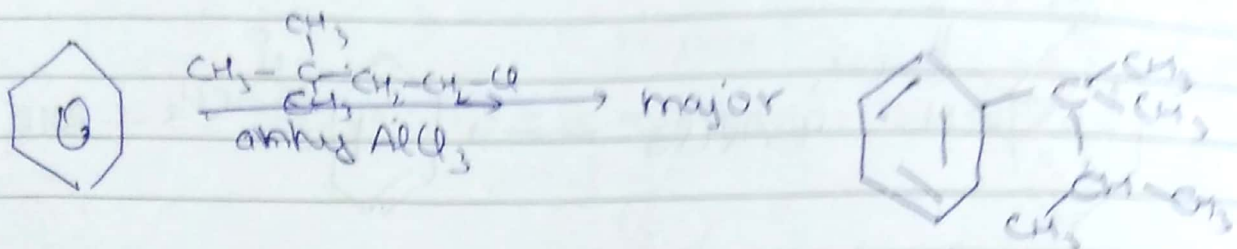
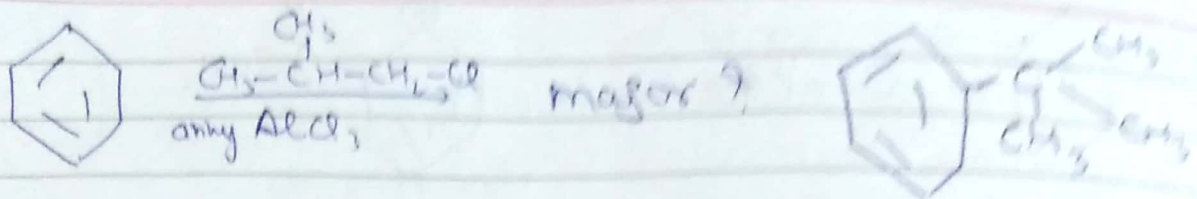
→ Alkyl Shift ⇒



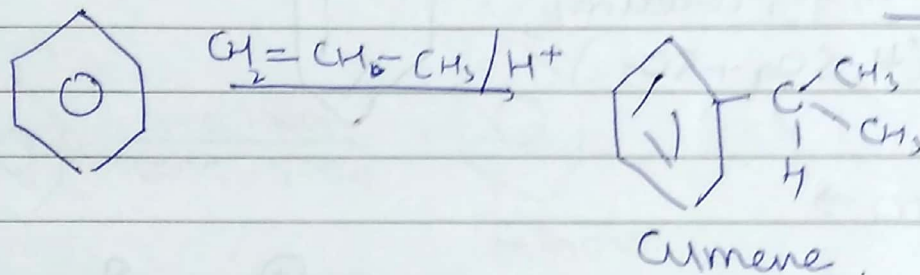
Order ⇒ ~~Me⁻~~ Isopr⁻ > Et⁻ > Me⁻

↳ On the basis of +I effect

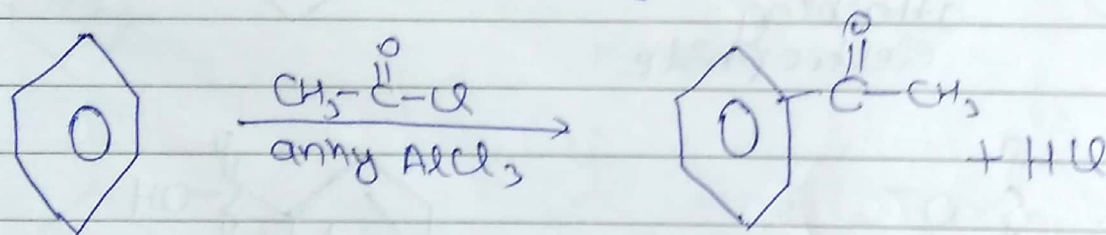
Ex



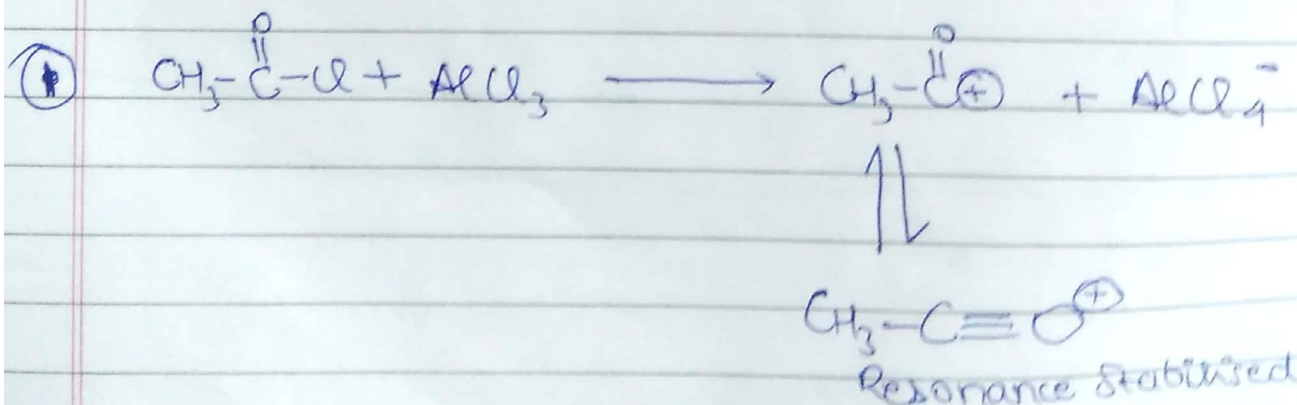
Cumene

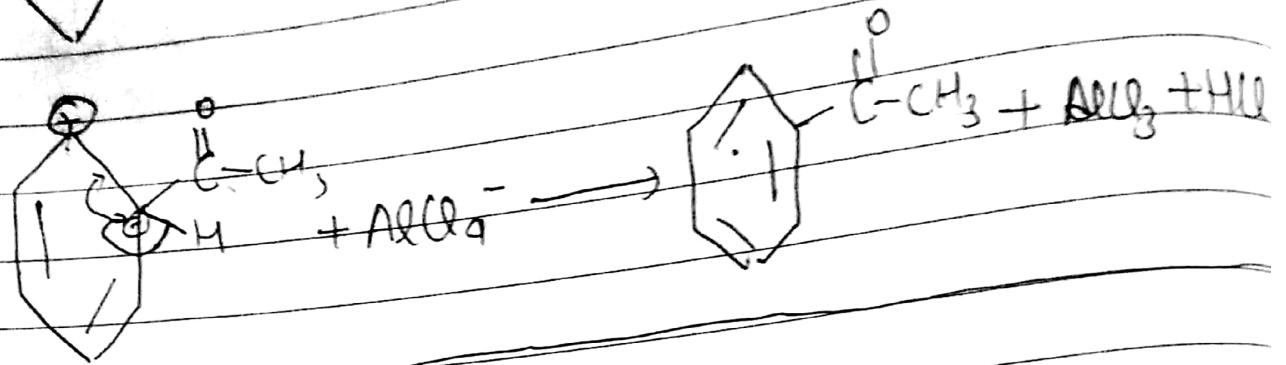
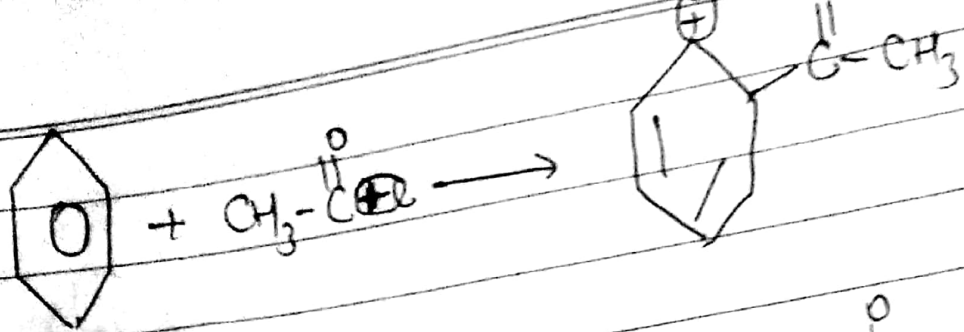


• Friedel Craft Acylation \Rightarrow

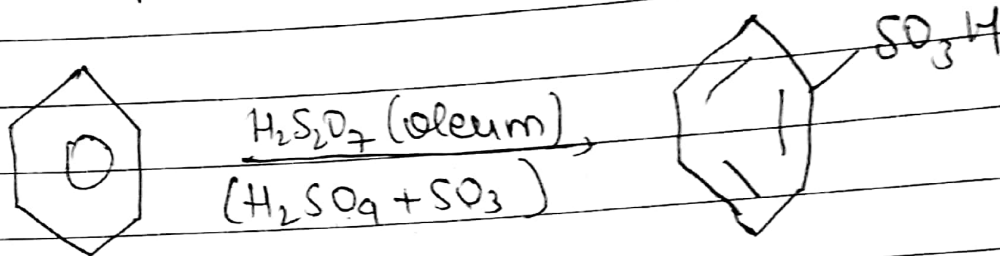


Mechanism \Rightarrow

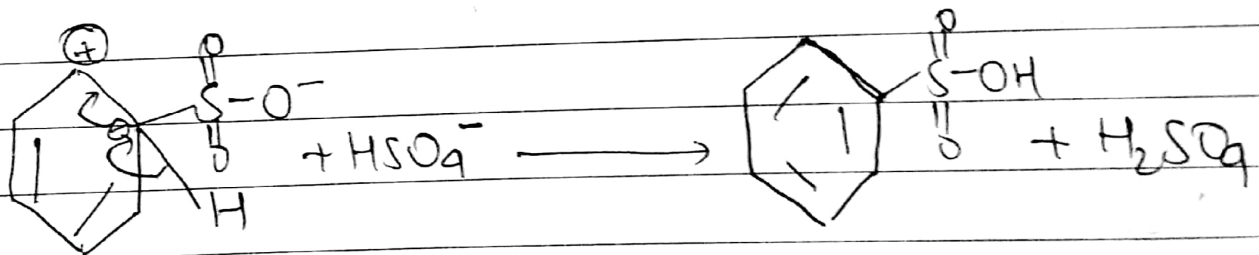
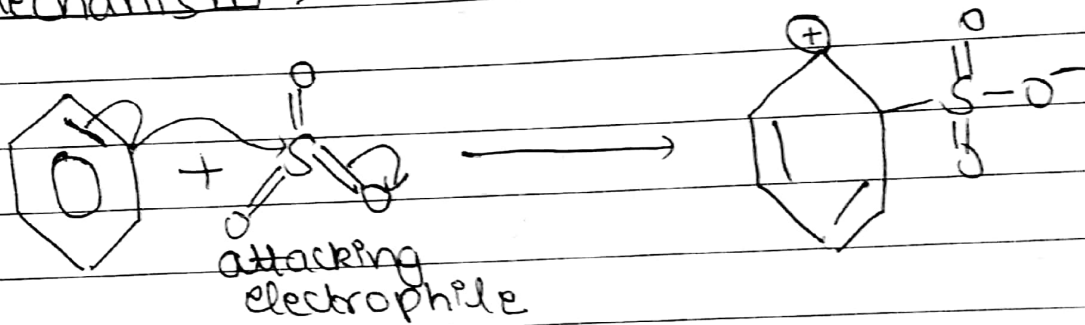


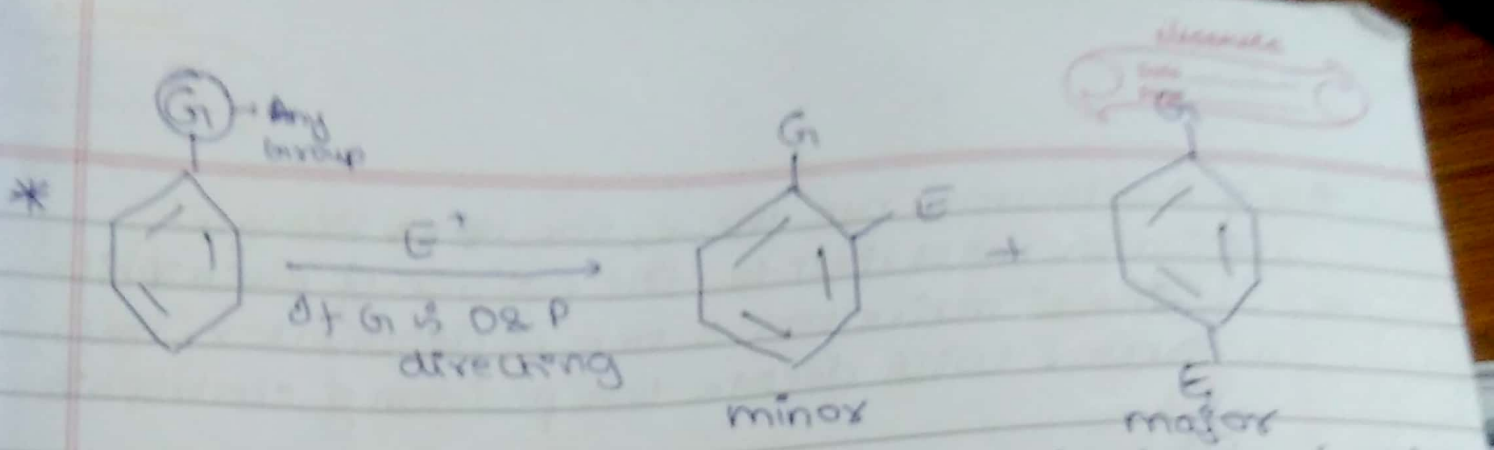


Sulphonation

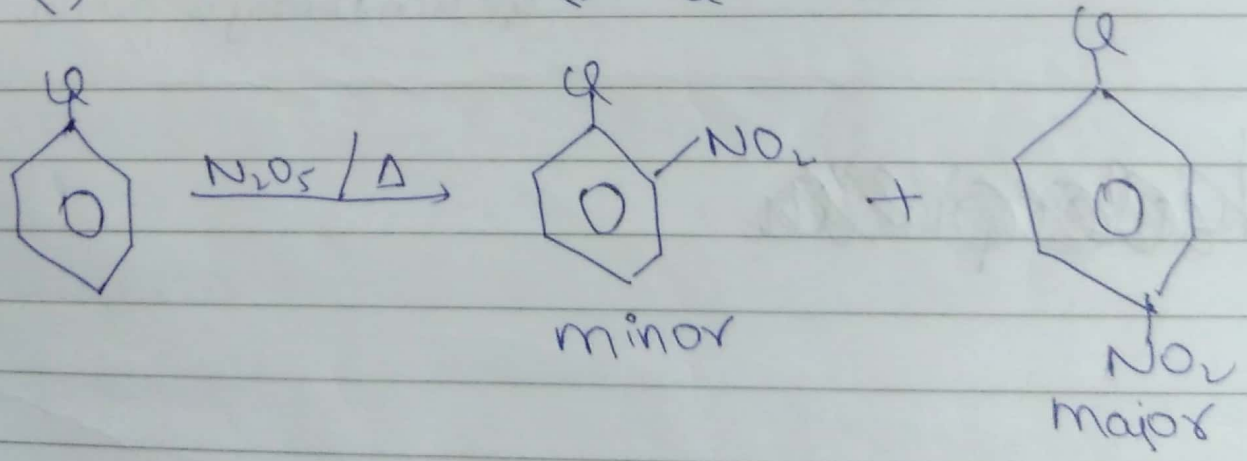
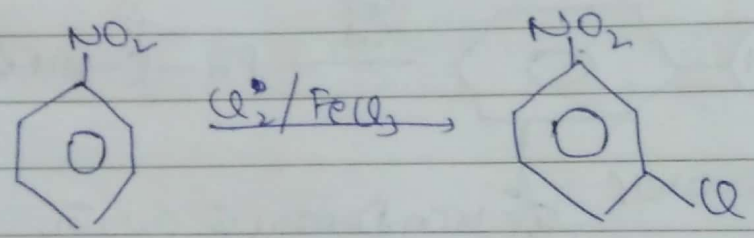
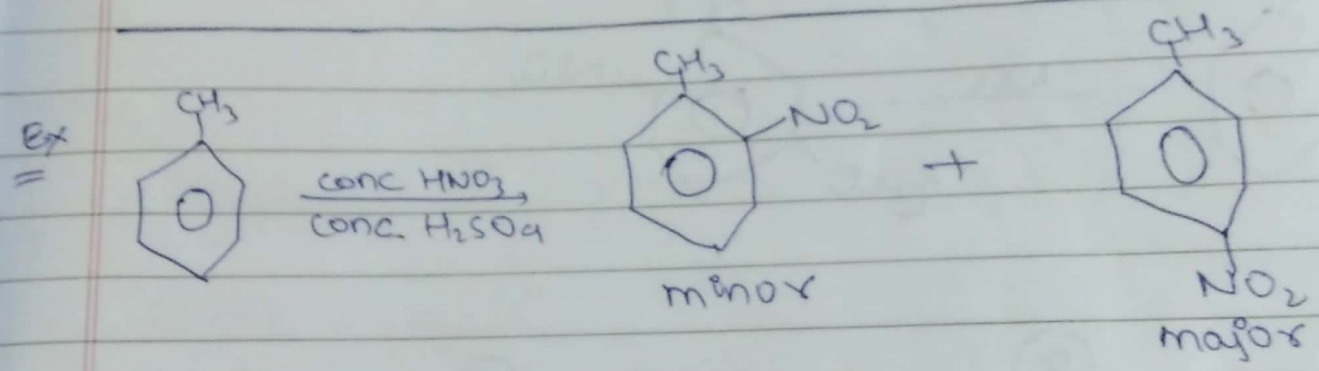
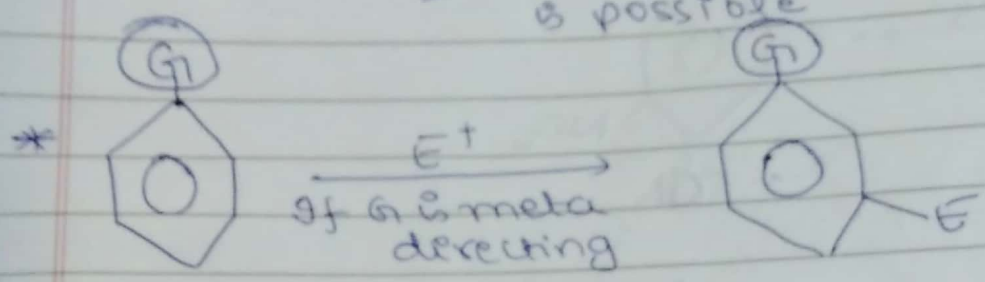


Mechanism \Rightarrow

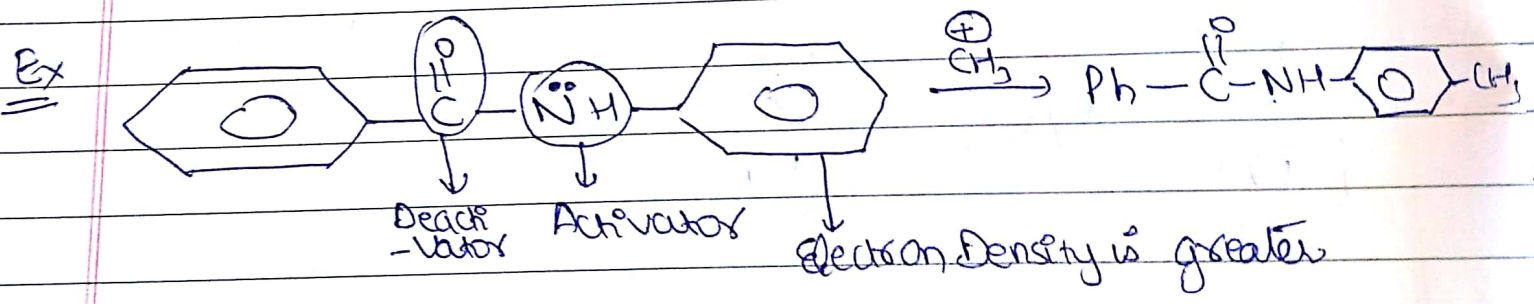
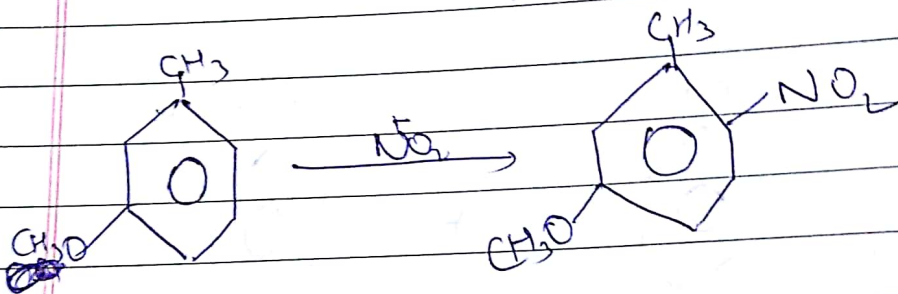
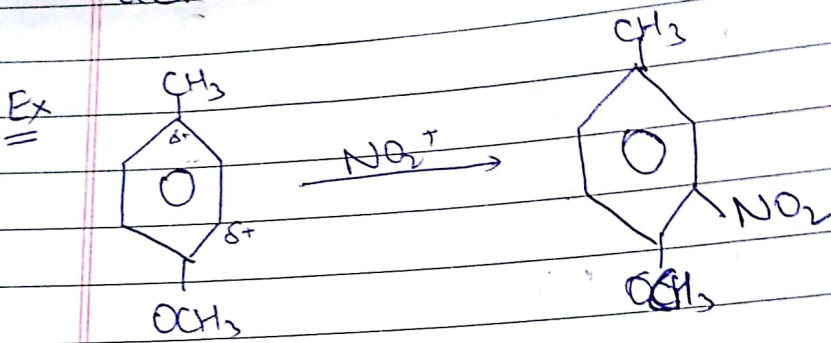




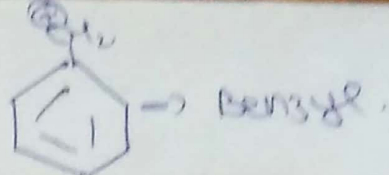
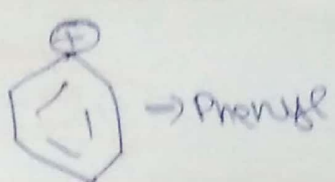
Imp • 1st will be major if hydrogen bonding is possible



- * If 2 activators are there, the more stronger activator will decide the position of electrophile
- * If one is activator & one is deactivator, then activator will decide the position of electrophile



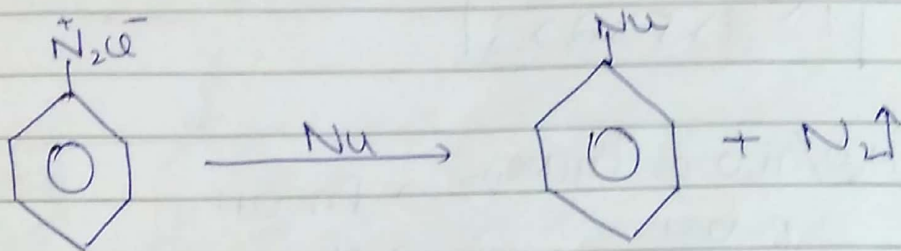
~~Nucleophile~~



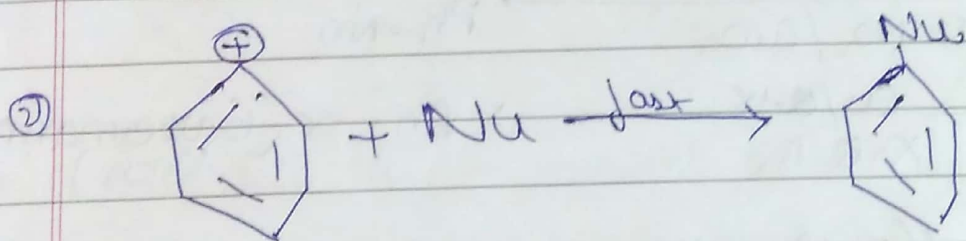
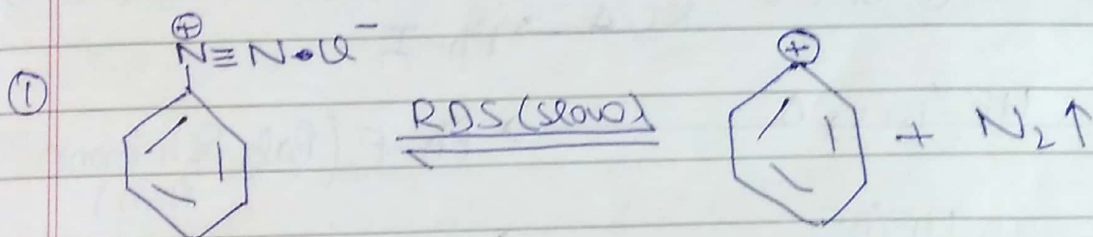
ArSN₂ (Unimolecular Nucleophilic Substitution)

↳ only by Diazonium salt

- * It is a very rare reaction given mainly by aryl diazonium cation
- * Although aryl cation is highly unstable ~~by N₂(gas)~~ ^{by N₂(gas)} it is highly stable so this rxn can occur.

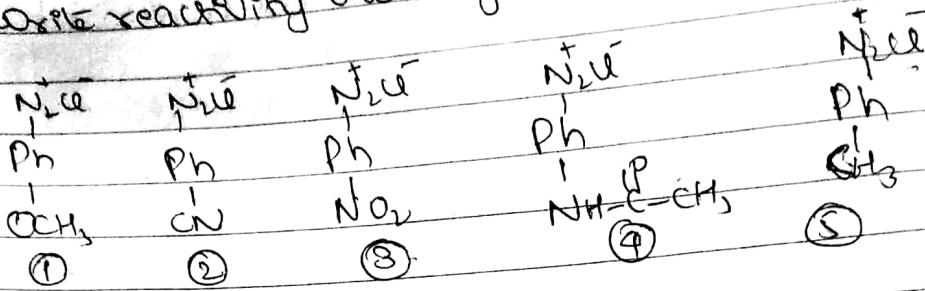


Mechanism →

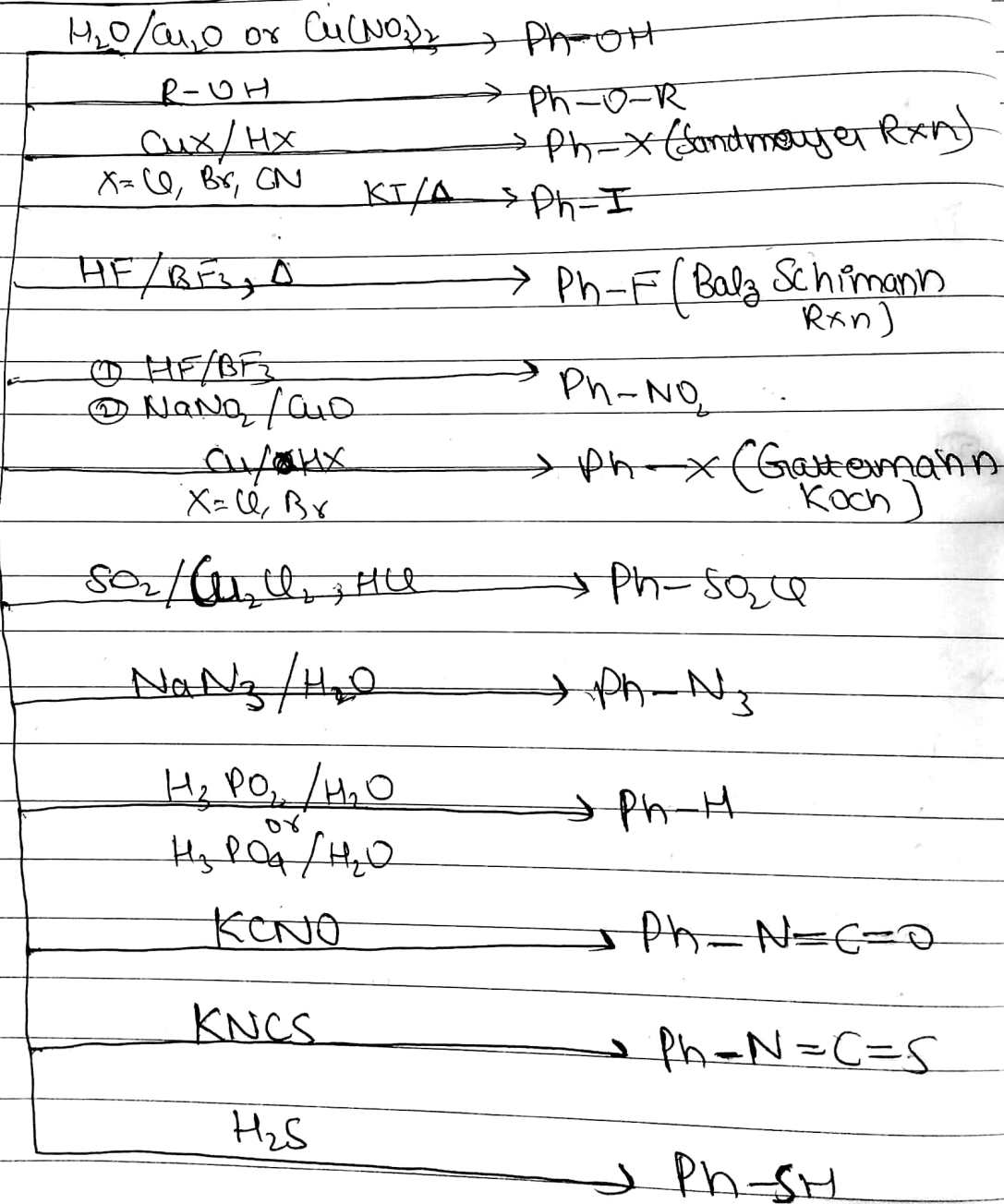


- * Electron Donating Group attached in ortho or para position of diazonium salt increase the reactivity of ArSN₂ rxn.
- * Electron Withdrawing Group (EWG) attached in diazonium salt will decrease the electron density of diazonium salt & hence it will decrease the reactivity of ArSN₂ rxn.

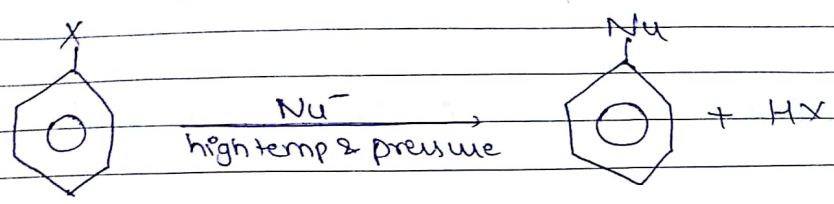
Q Write reactivity order of the following-



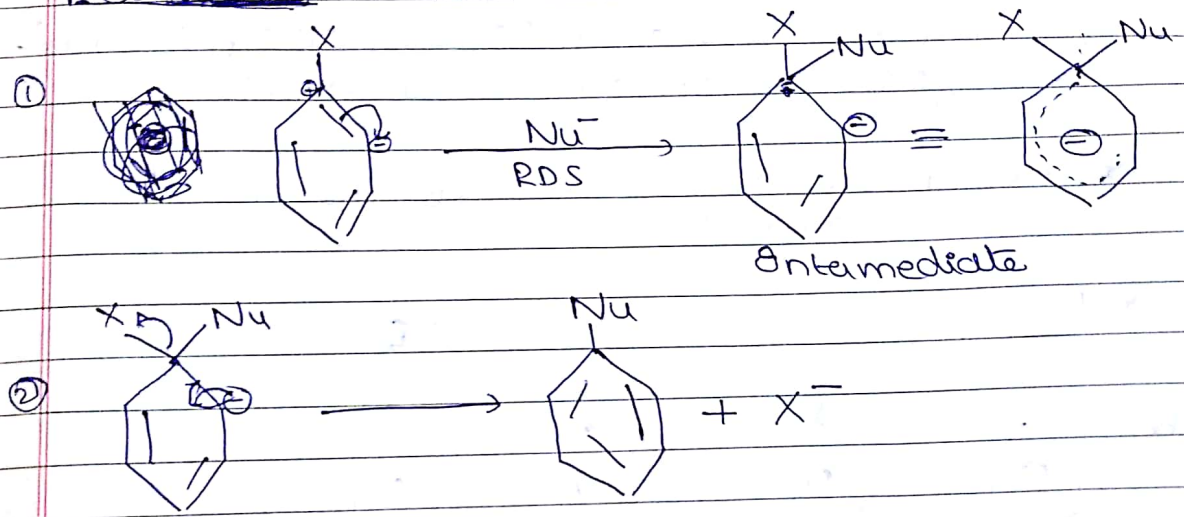
1 > 4 > 5 > 2 > 3



$ArSN_2$ (Bimolecular Aromatic Nucleophilic Substitution)



Mechanism \Rightarrow

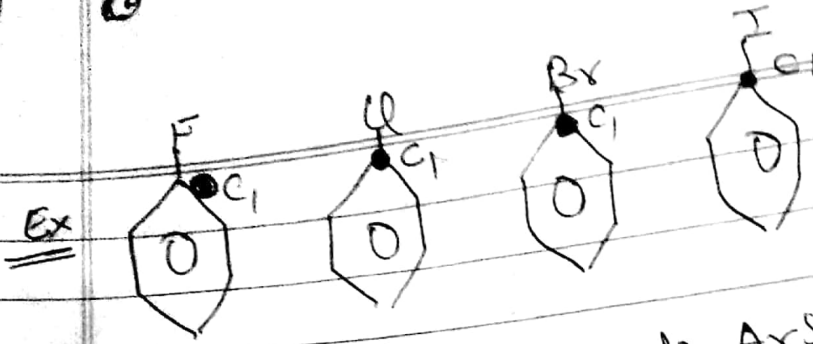


* Generally aryl halide do not give nucleophilic substitution rxn bcoz lone pair on halogen atom is on conjugation with π -bond in benzene so it has partial double bond character. But under drastic condition, this rxn can occur.

* ELOG favour this rxn reactivity bcoz it stabilise the intermediate. \ominus

* EDG destabilise the intermediate, hence it decrease the reactivity of $ArSN_2$.

b

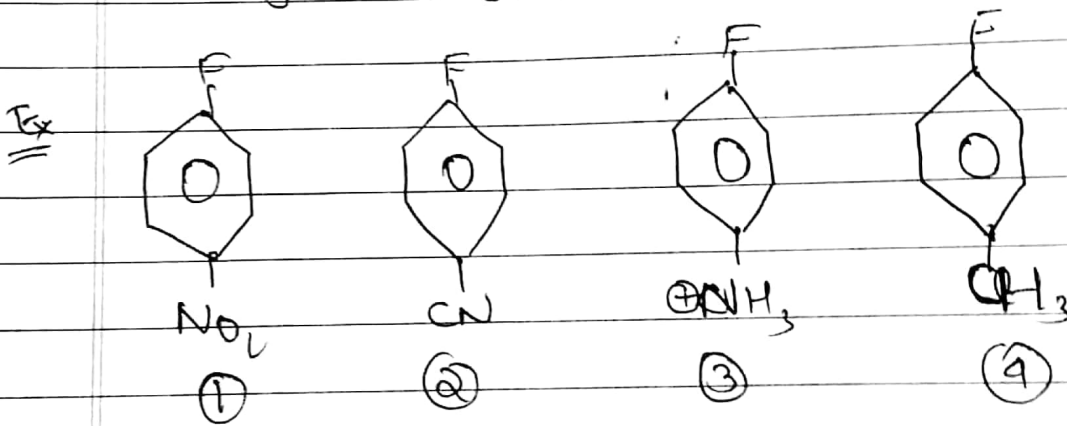


Order of Reactivity towards $ArSN_2 \Rightarrow 1 > 2 > 3 > 4$

* Greater the electronegativity of halogen atom attached to C-1 atom greater is the (+ve) charge developed on C-1 atom (Electrophilicity increases) So it facilitates the attack of Nucleophile.

* Leaving Ability in case of aliphatic SN_1 & $SN_2 \Rightarrow I > Br > Cl > F$

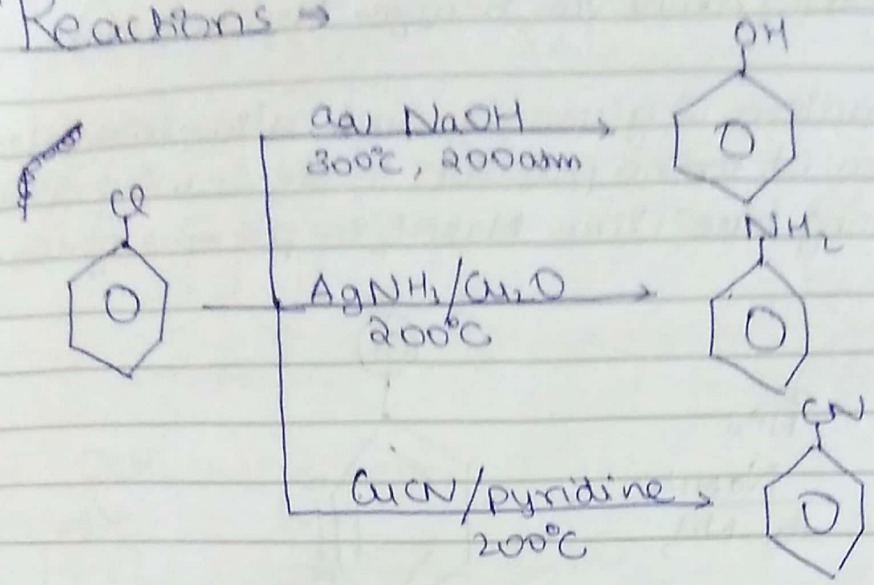
* Leaving Ability in $ArSN_2 \Rightarrow F > Cl > Br > I$



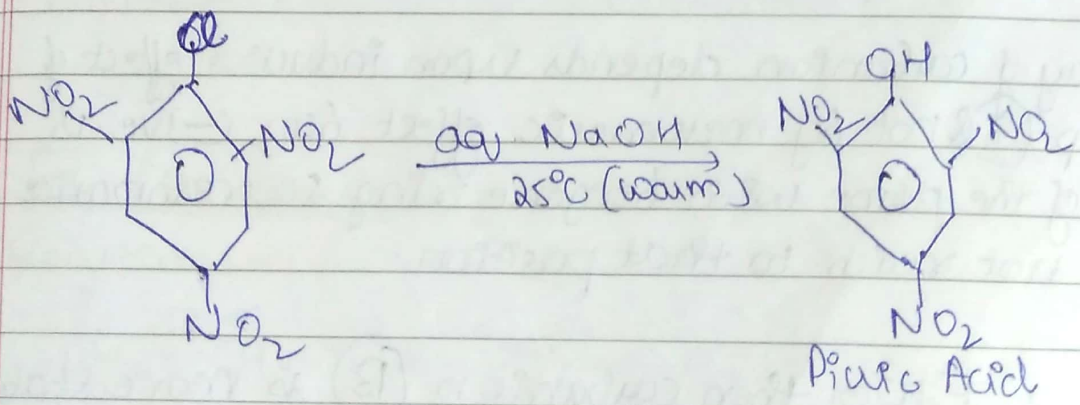
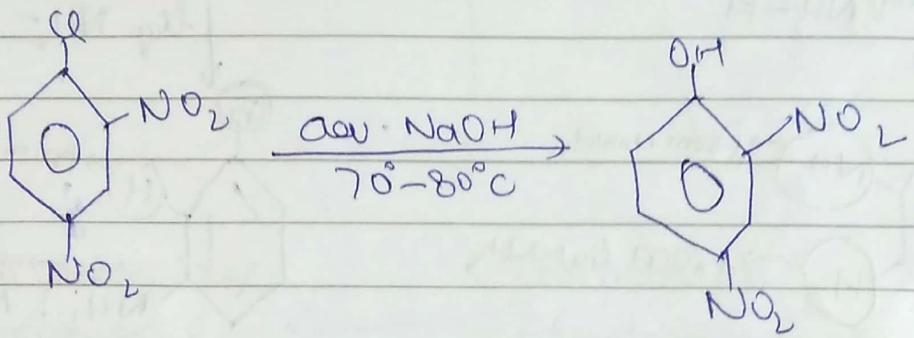
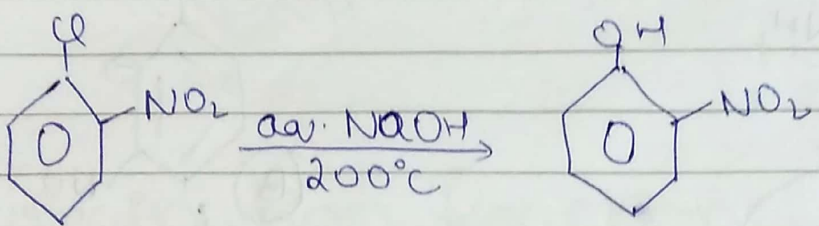
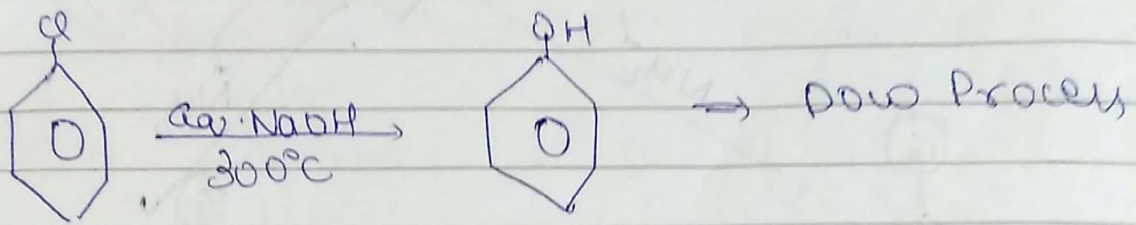
$3 > 1 > 2 > 4$

Reactions →

*

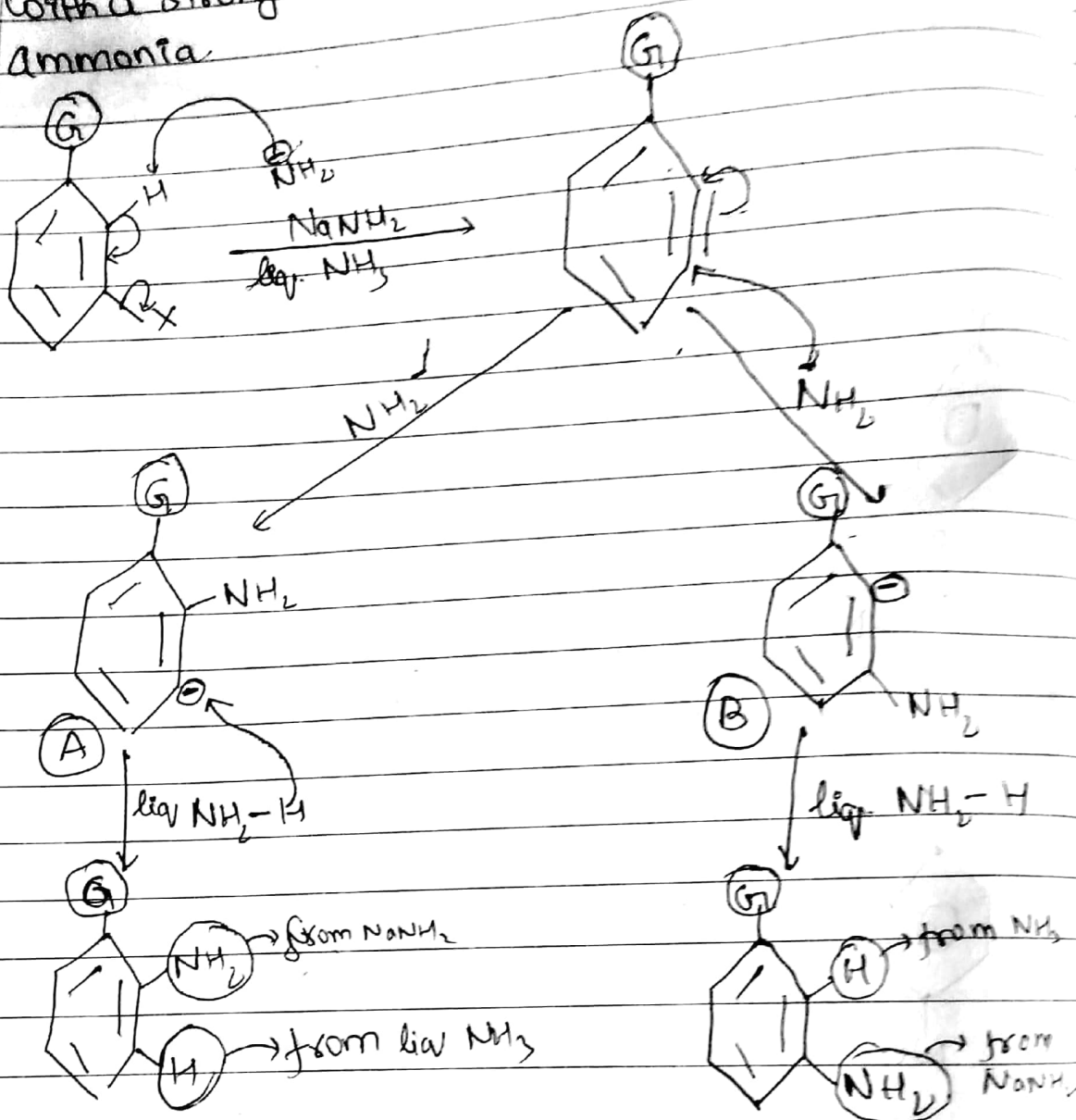


*



Benzynes (ArSN via Benzene Mechanism)

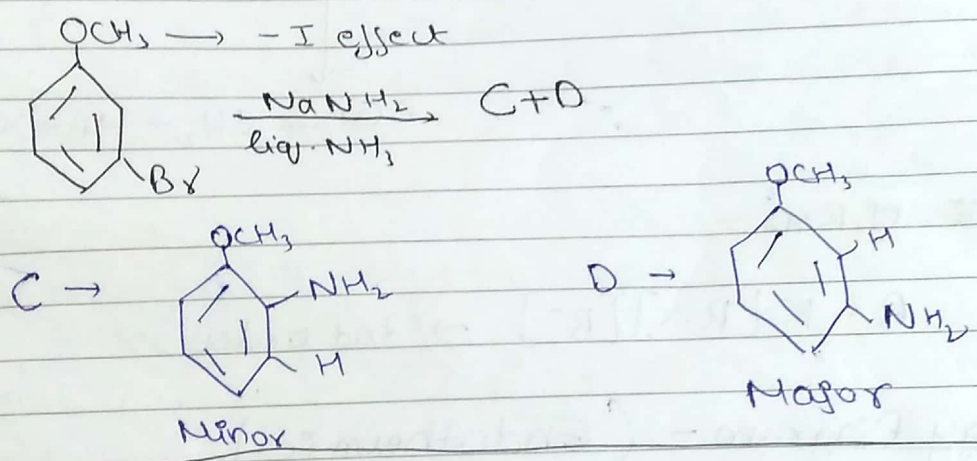
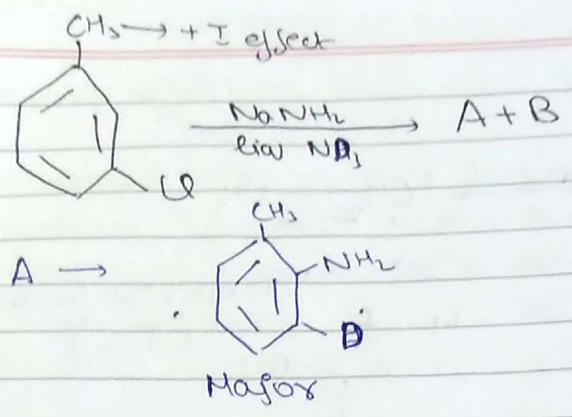
This mechanism is given by aryl halide with atleast 1 hydrogen at ortho position to the leaving group with a strong base like NaNH_2 in presence of liquid ammonia.



* Stability of carbanion depends upon inductive effect of group (G) & not by mesomeric effect bcoz (-Ive is out of the plane with benzene ring so resonance does not reach to that position.

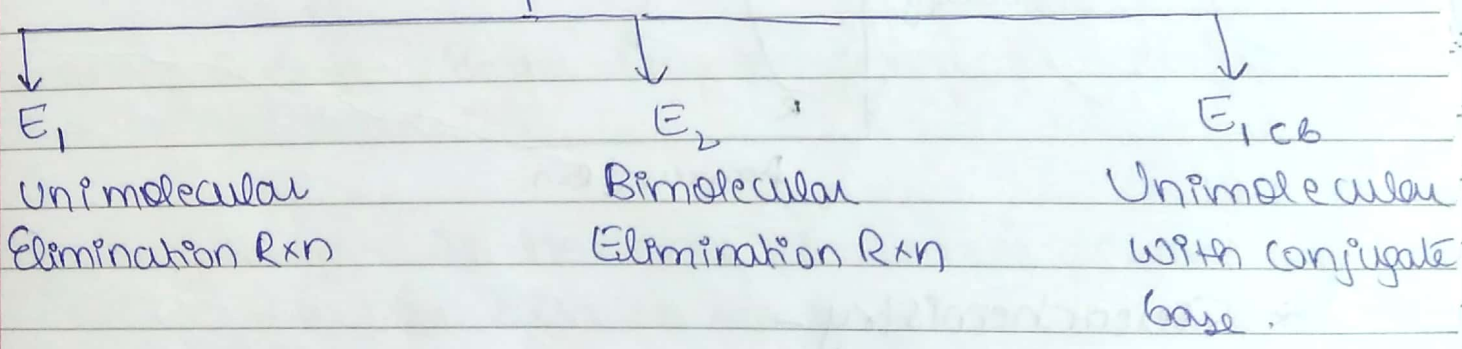
* If (G) is E.W.G then carbanion (B) is more stable
 If (G) is E.D.G " " (A) " " "

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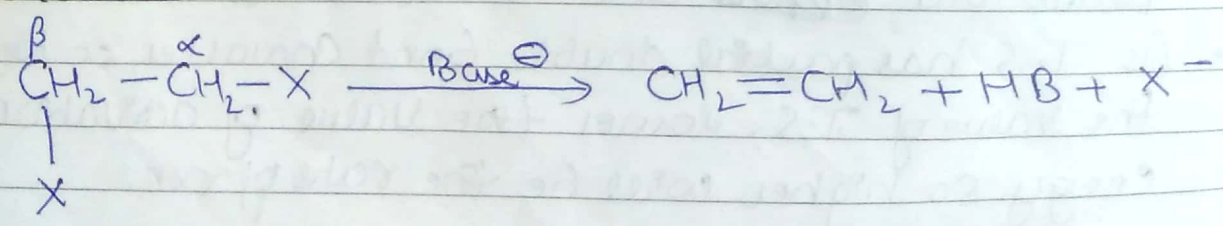
Elimination Reactions - (β -elimination)

(* ~~Exothermic~~ Endothermic)



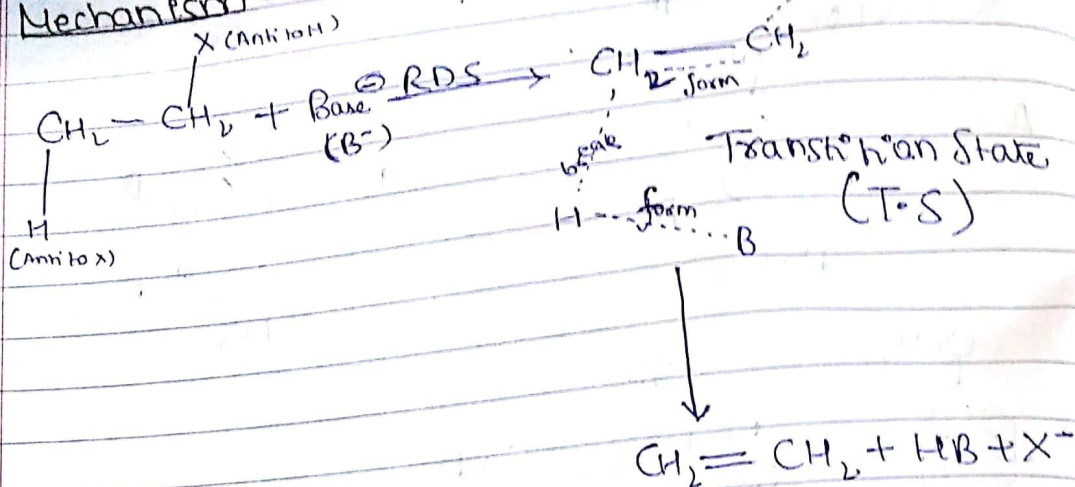
E₂ (Bimolecular) -

* Reactions -



β -elimination \Rightarrow Anti & Coplanar
(Groups)

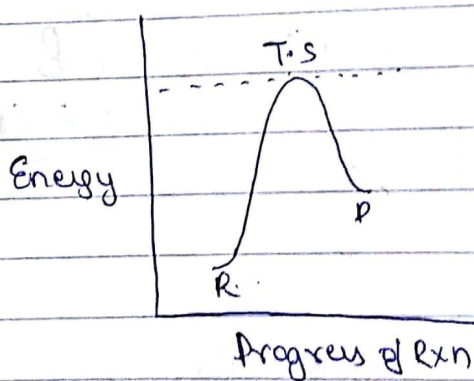
* Mechanism -



* Kinetic of Rxn -

$$R = k [R-X] [B^-] \Rightarrow \text{2nd order}$$

* Energy Diagram - (Endothermic)



* Stereochemistry -

It is 100% anti-elimination and anti coplanar. It means C-H bond & C-X bond should be in same plane but ~~coplanar~~ anti to each other.

- As T.S has partial double bond character, so higher the value of T.S, lower the value of activation energy so higher will be the rate of rxn.

* Isotopic Effect \rightarrow Only where H removal of H is in RDS

classmate

Date

Page

* C-H bond is easier to break than C-D bond.

* Factors affecting E_2 -

- Structure of substrate - As the branching at α, β carbon increases, rate of E_2 rxn increases b/c as the no. of substituents increases, double bond character b/w carbon atom increases. Hence Stability of T.S increases.
Order of reactivity $\Rightarrow 3^\circ > 2^\circ > 1^\circ$

If E_{WG} are present on β -carbon so it increases E_2 rxn. b/c $-I$ effect on β -carbon increases the acidity of β -hydrogen.

- Strength of Base - As strength of base increases, rate of reactivity of E_2 rxn increases

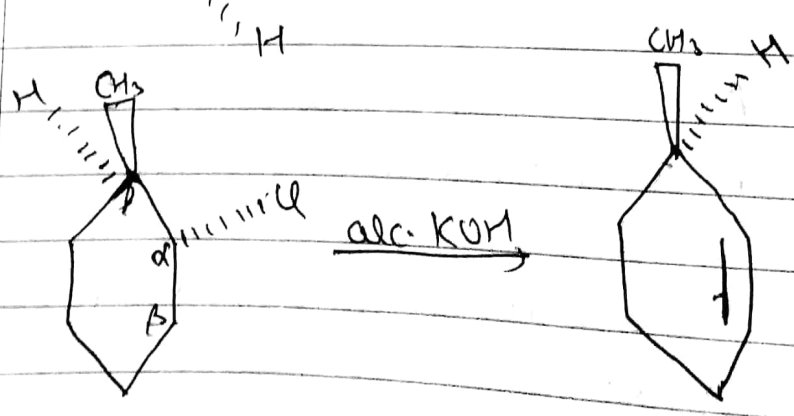
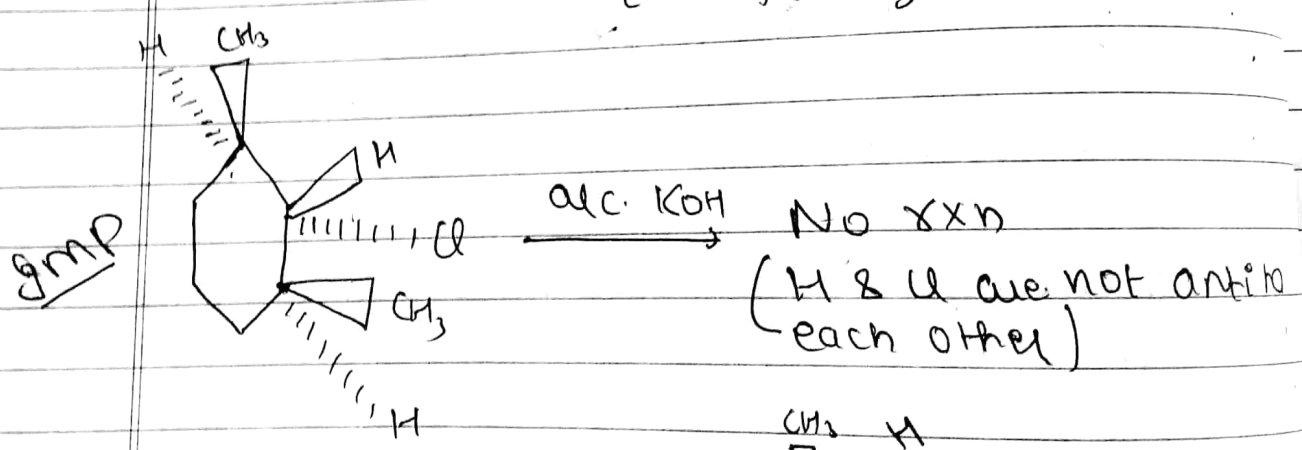
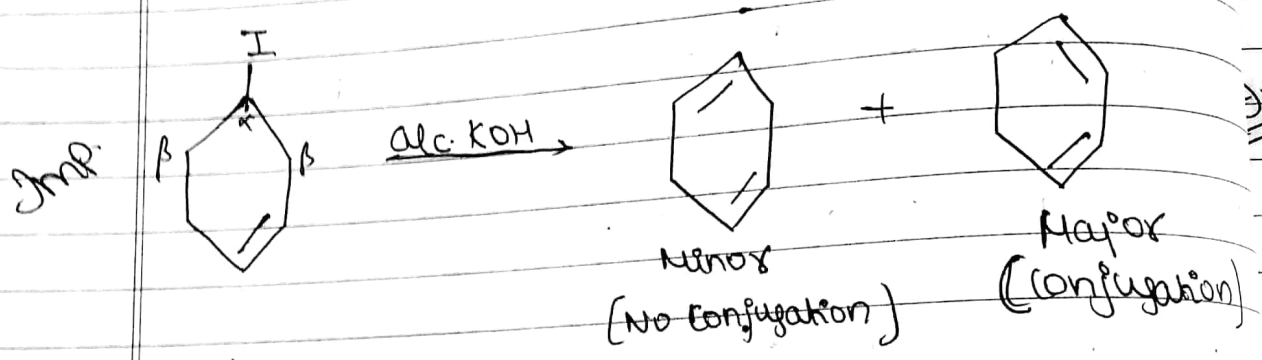
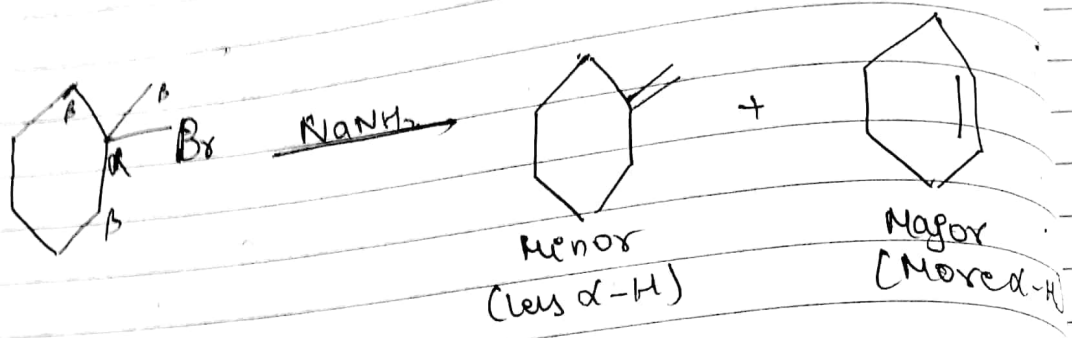
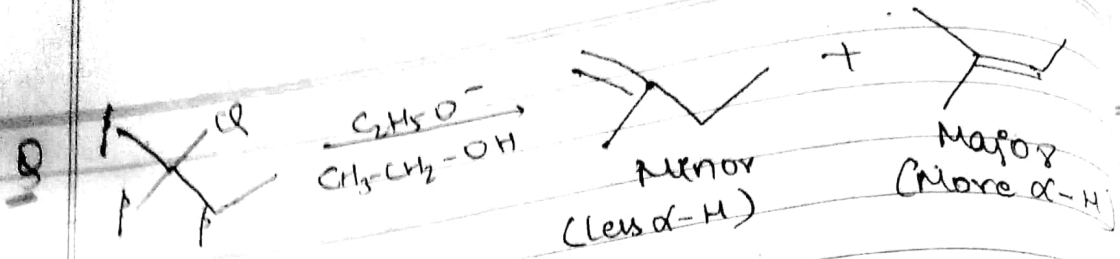
Order $\Rightarrow \text{NH}_2^- > \text{CH}_3\text{O}^- > \text{OH}^-$

- Nature of Solvent - Polar aprotic solvent is required. b/c it increases reactivity as polar aprotic solvent do not solvate anion.

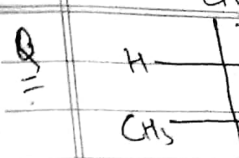
- Leaving Group - Better leaving group are required for higher reactivity.

Imp Effect of Temp - As the temp. increases, chances of elimination rxn also increases.

- Isotopic Effect - Since removal of H is in RDS, so there is isotopic effect.



Saytzeff



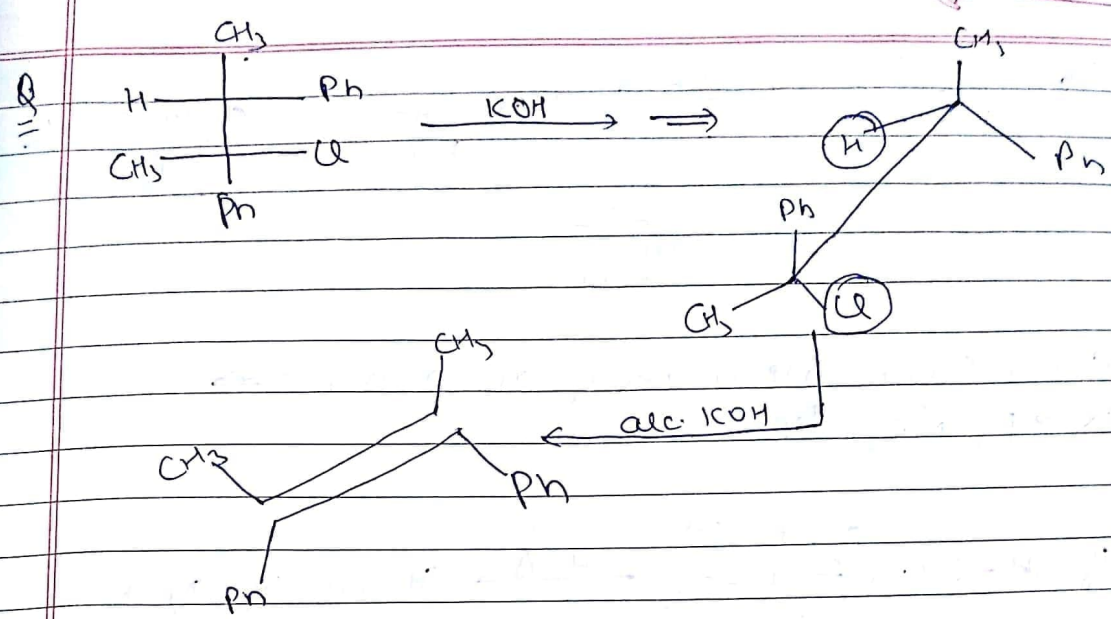
gmp
 * Try
 &
 * Gen
 thi

~~gmp~~
 Case I

Saytzeff
 Rule

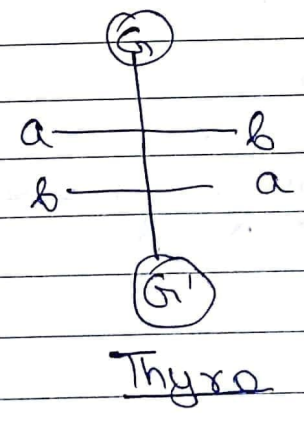
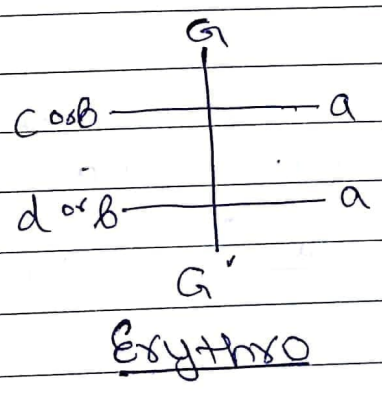
Saytzeff Rule - Remove β -hydrogen & where less no. of hydrogen are present

Date _____
Page _____



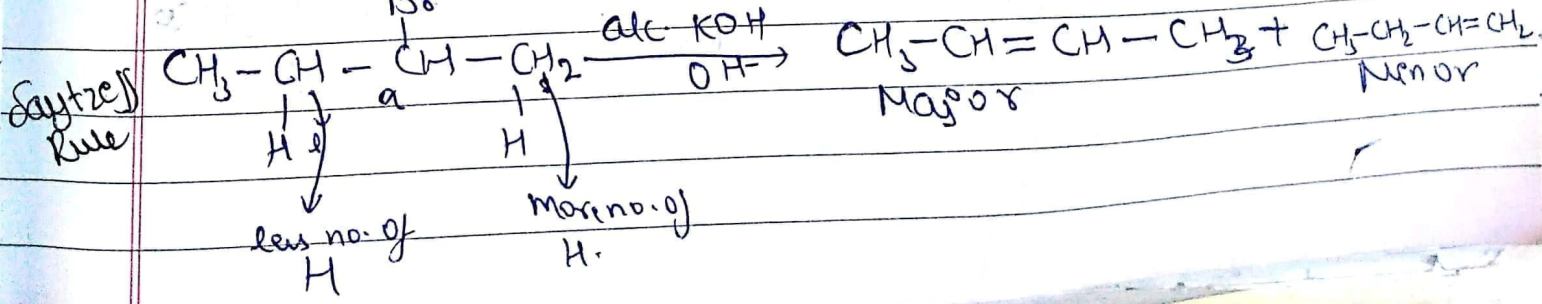
Imp Points \Rightarrow

- * Try to make staggered form in such a way that β -hydrogen & Leaving Group should be anti to each other.
- * Generally erythro form gives 'E' or trans & thyrro form gives 'Z' or cis

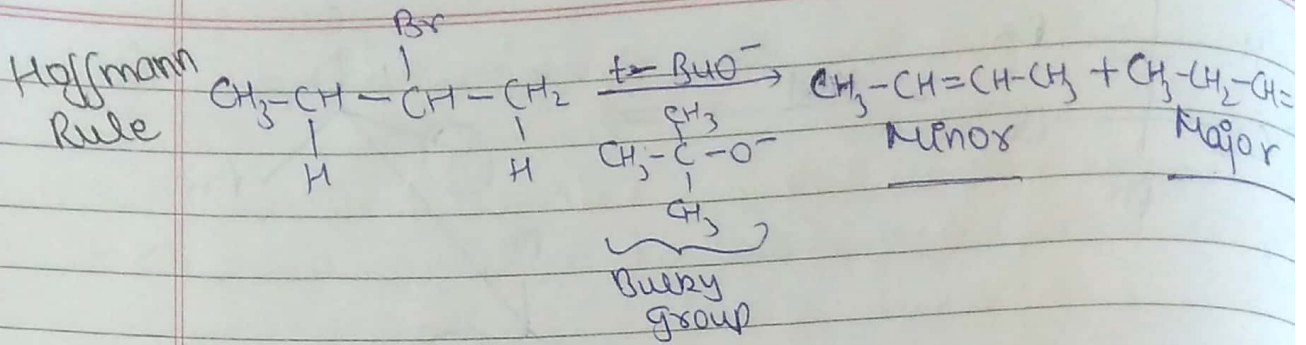


Imp Hoffmann Elimination product will be major. When \Rightarrow

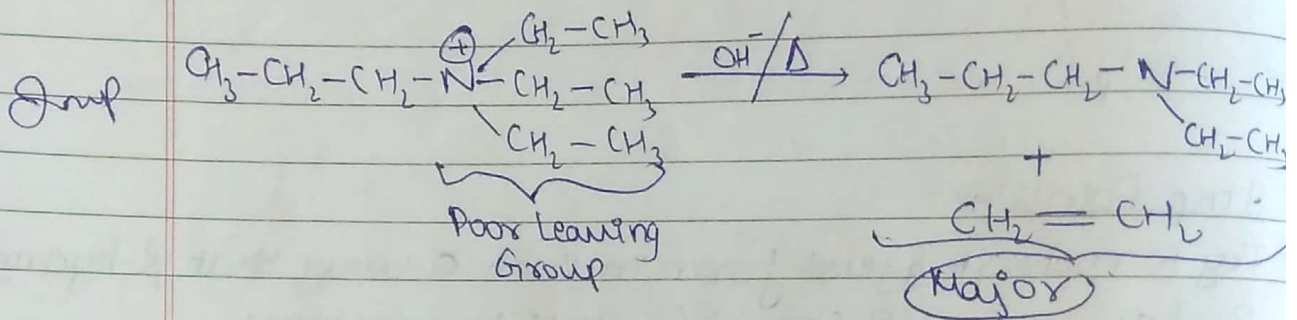
Case I When base is bulky or hindered \Rightarrow



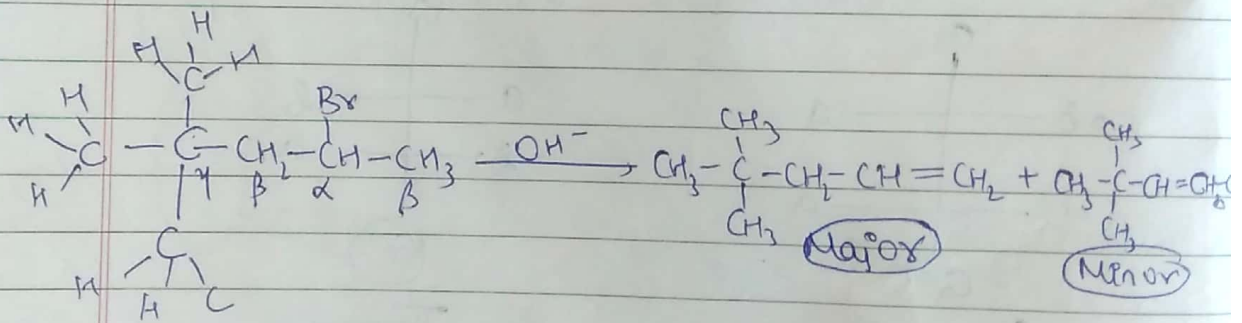
Hoffmann - Remove H⁺ from the position where there is less hindrance



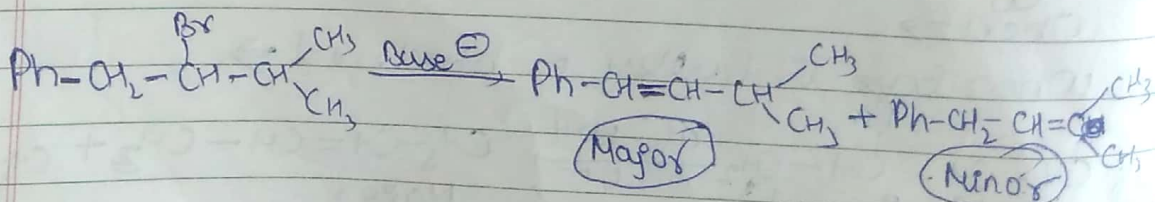
Case II → When bad leaving group are present ⇒
 Ex ⇒ F, NR₃⁺, SR₂⁺



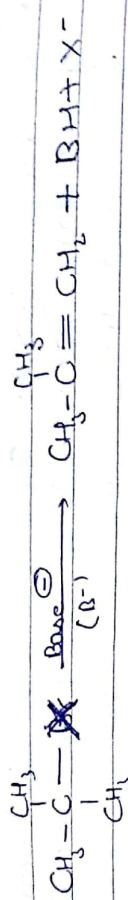
Case III When γ carbon is sterically hindered -



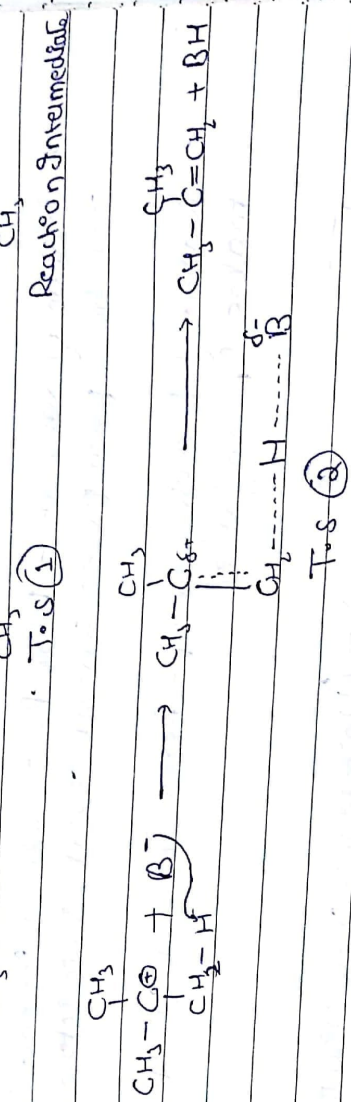
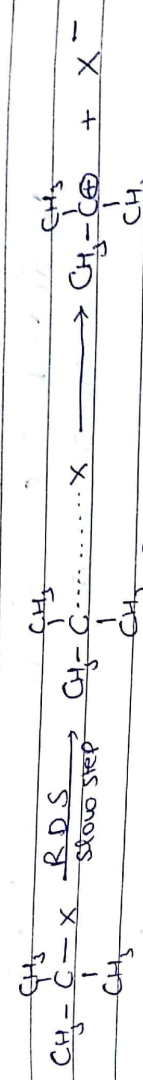
Case IV when phenyl or double bond is in conjugation



E1 Mechanism (Unimolecular Elimination Rxn)



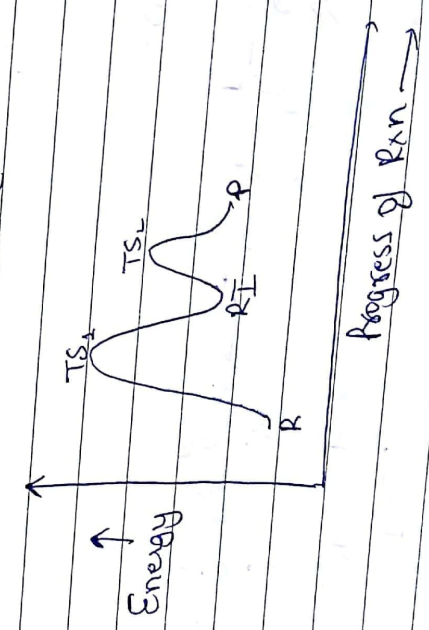
* Mechanism -



* Kinetics of Rxn -

$$R = k [R-X] \Rightarrow \text{1st order Rxn}$$

* Energy Diagram - (Endothermic)

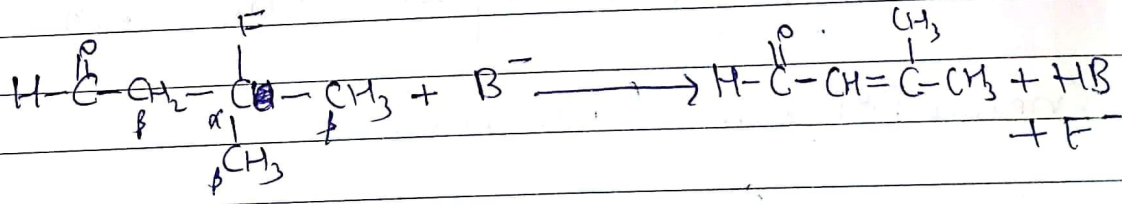


* Factors affecting E_1

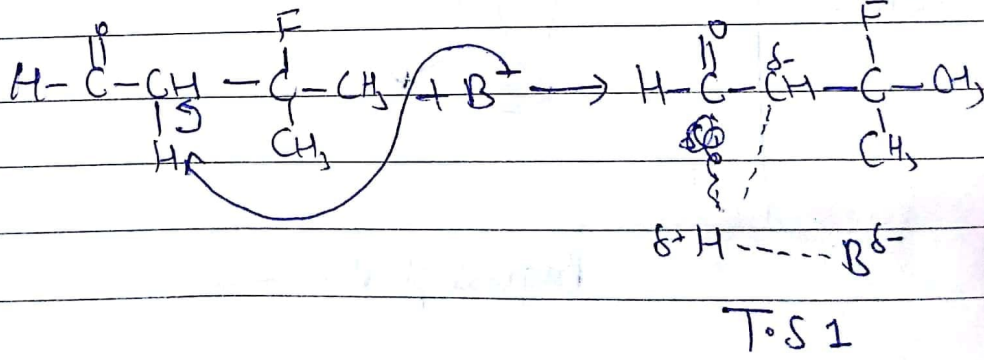
- Structure of Substrate - Since E_1 takes place by formation of carbocation as rxn intermediate, so rate of E_1 rxn depends on stability of carbocation.
- Strength & Concentration of Base - Since base does not appear in RDS, so weak base favour E_1 . Sometimes solvent can act as base.
- Nature of Solvent - Polar protic solvent increase E_1 rxn bcoz polar protic solvent solvate ionic intermediate.
- Nature of Leaving Group - Better leaving group makes E_1 rxn faster.

E_{1CB} (conjugate base) - (Unimolecular with conjugate base)

* General Rxn -

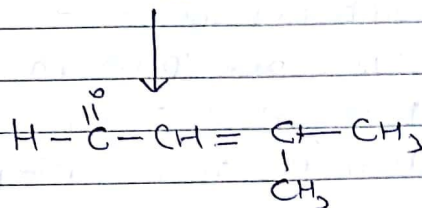
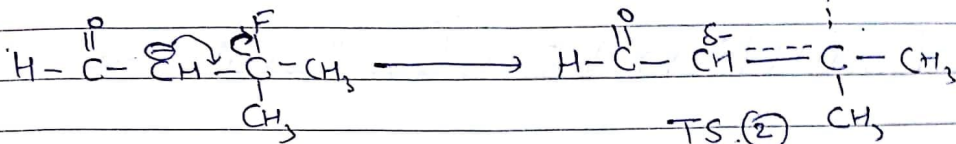
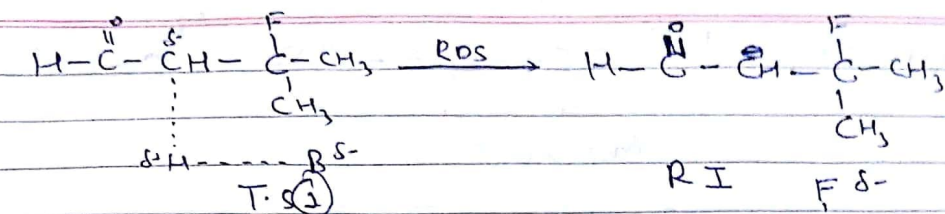


* Mechanism -



Hoffmann Rule \Rightarrow Weak leaving group.

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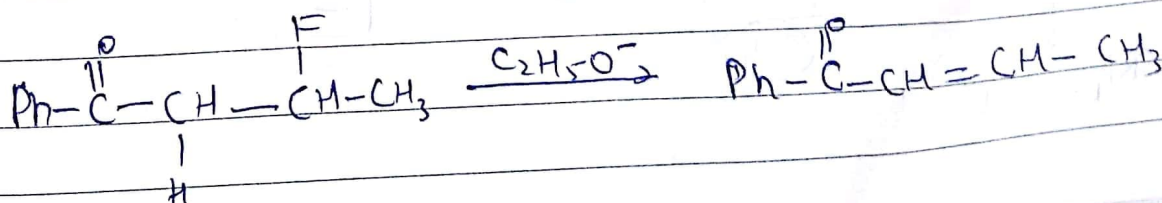
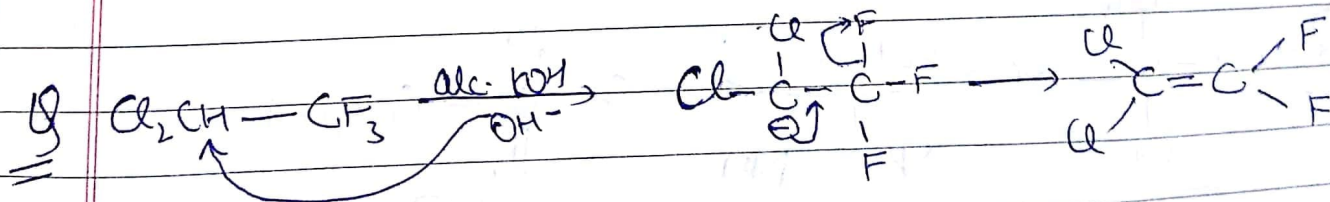


* Kinetics

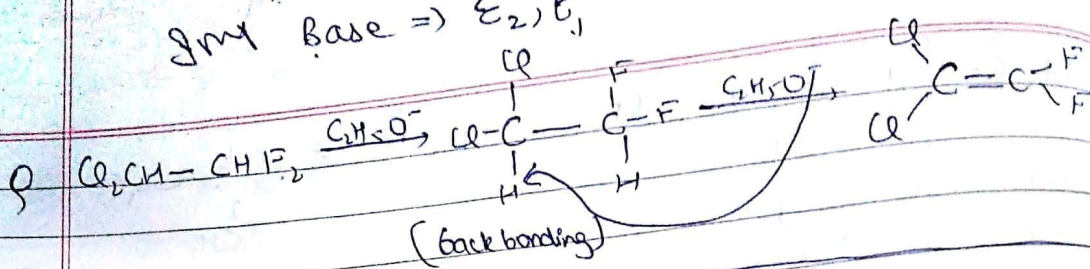
$$R = k [R-F] \Rightarrow \text{1st Order}$$

* Points to Remember

- E_{1cb} is limited to substrate which can stabilise carbanion intermediate. It means β carbon should contain some ~~EWG~~ strong EWG, like carbonyl, nitro, cyano, sulphonyl etc.
- Product formation takes place by Hoffmann rule.
- Leaving group should be poor
- Rxn takes place in presence of strong base.



Nucleophile \Rightarrow S_N1, S_N2
 Base \Rightarrow E_2, E_1



SN2 Substitution vs Elimination \Rightarrow

*** * *** Points to Remember -

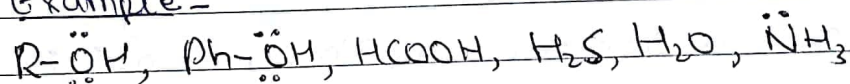
- (-ve) charge species has more basic character than nucleophilic character. but (-ve) charge with big size atom has more nucleophilic character than basic character.

Example -

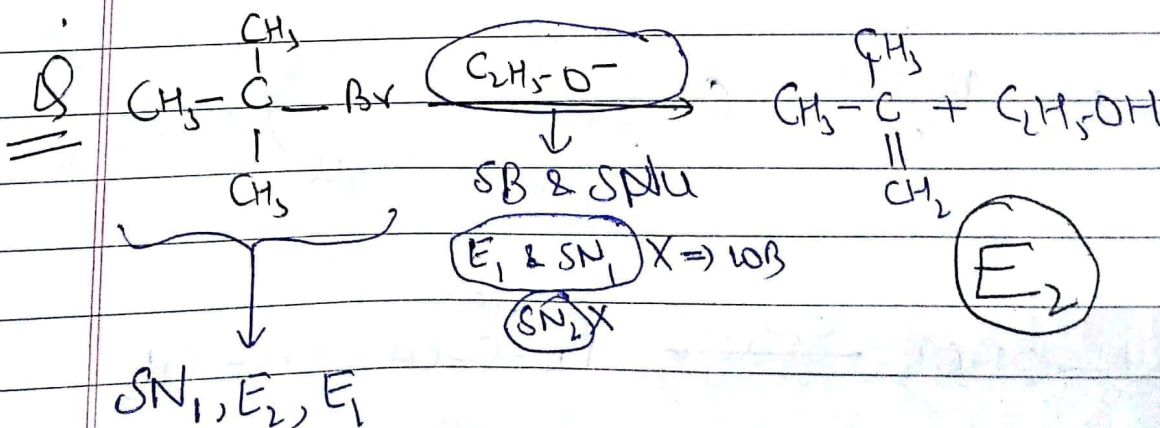
$\{$ More Basic Character \Rightarrow $C_2H_5O^-$, NH_2^- , $t-BuO^-$, $alc. KOH$
 More Nucleophilic Character \Rightarrow I^- , Br^- , CN^- , SH^- , CH_3COO^- , $aq. KOH$

- Donor atom with lone pair has more nucleophilic character than basic character.

Example -

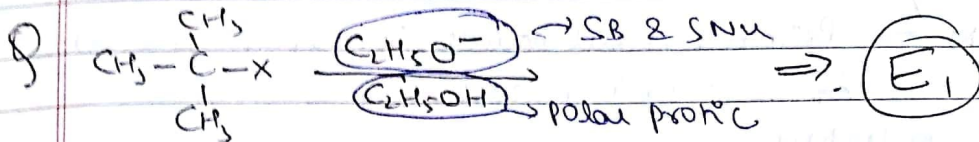


- Generally heating favours elimination.
- Generally primary alkyl halides favour S_N2 rxn & tertiary alkyl halide favours S_N1 & E_1

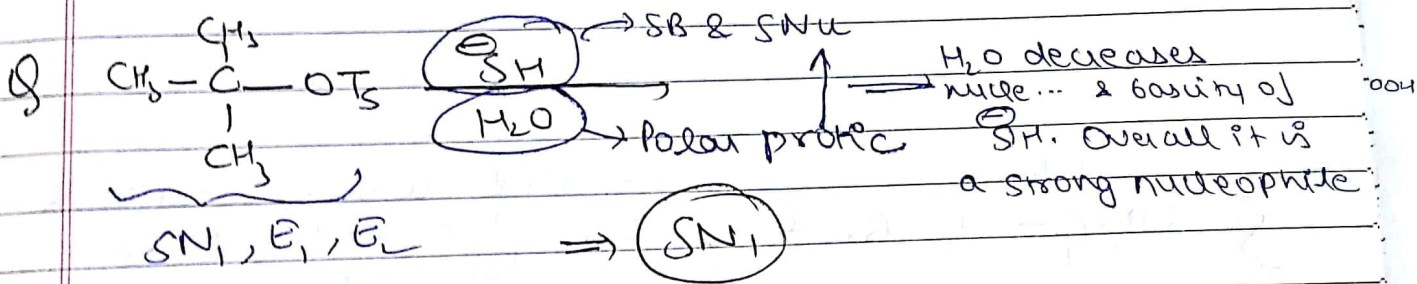


+ S_N1 & $E1$ \rightarrow gives with weak base or weak nucleophile
 gmp. S_N2 & $E2$ \rightarrow " " strong base or strong nucleophile
 ($E2$)

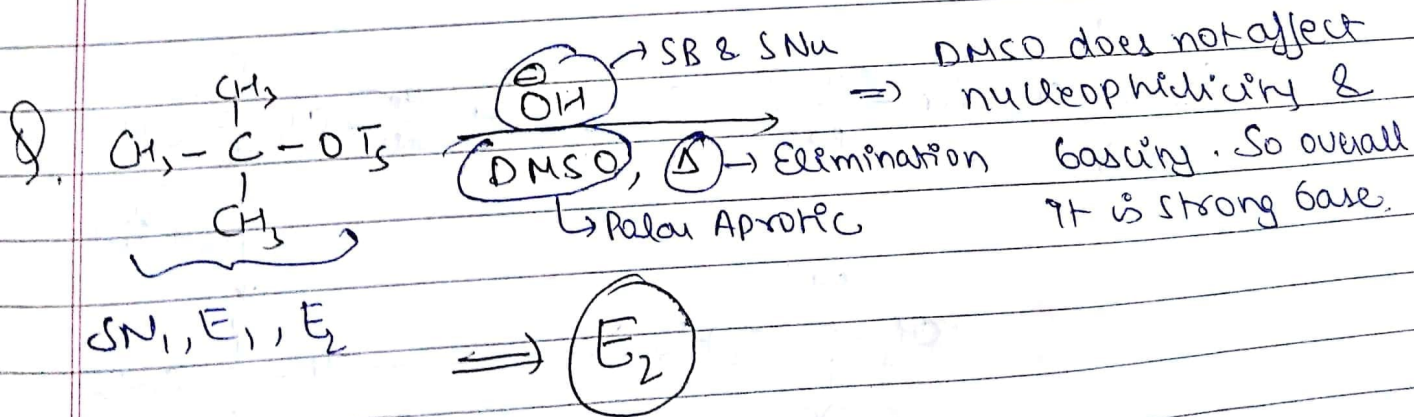
- Ethoxide ion is strong base & strong nucleophile so it favours S_N2 or $E2$ but (-ve) charge species have more basic character than nucleophilic character so it favours $E2$ rxn



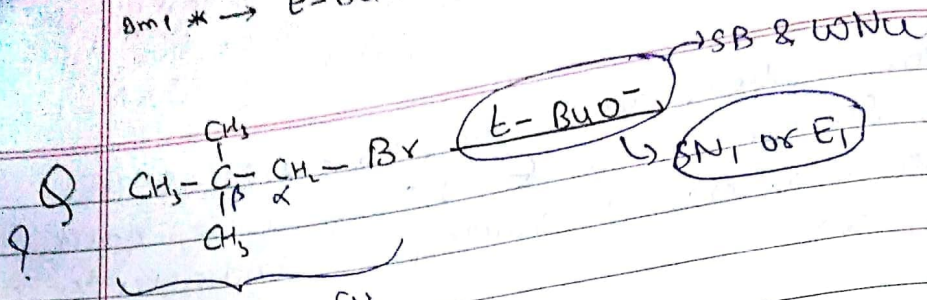
- Since RO^- is strong base & strong nucleophile but due to solvation, its basic & nucleophilic character decreases so it favours either S_N1 or $E1$ but (-ve) charge species have more basic character. so overall it favours $E1$



- SH^- is a strong base & strong nucleophile but SH^- has more nucleophilic character than basic character but due to solvation nucleophilic & basic character decreases. so overall it will give S_N1 rxn

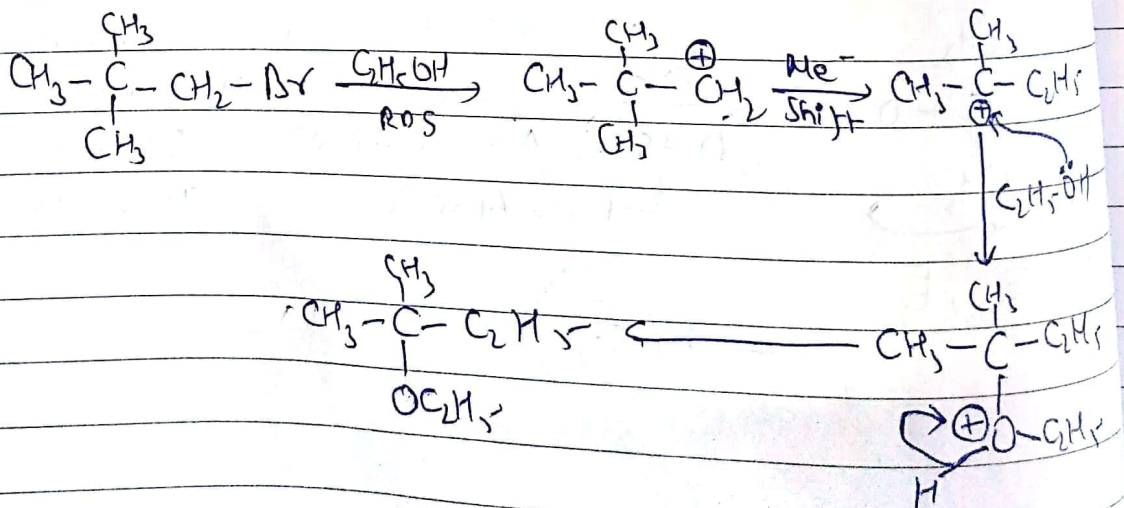
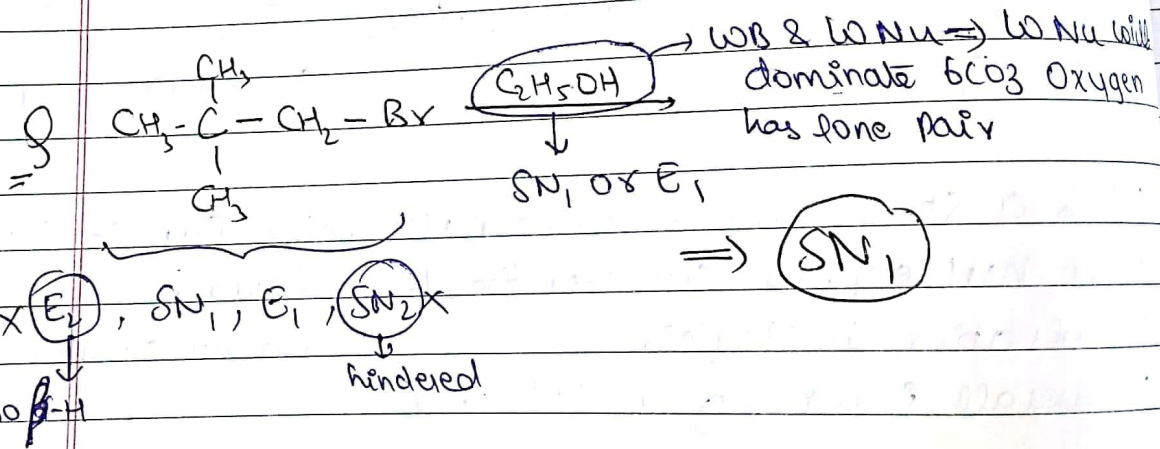


Sm1 * \rightarrow $t\text{-BuO}^- \Rightarrow$ SB & WNU



$\times \text{E}_2 \Rightarrow$ no β -Hydrogen
 $\times \text{E}_2 \text{ or } \text{SN}_2 \Rightarrow$ Primary Alkyl halide but from back side so it is hindered

$\text{SN}_1 \Rightarrow$ WNU
 $\text{E}_1 \Rightarrow$ WB



Imp \Rightarrow Ring Expansion \Rightarrow Hydride Shift \Rightarrow Methyl Shift

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Imp *** Ring Expansion \Rightarrow

Stability order of Rings \Rightarrow

