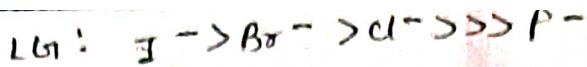
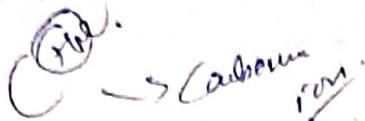
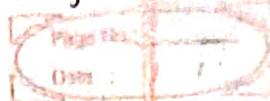


08/11/23.



W. Boys → strong L.B.

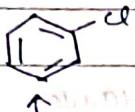
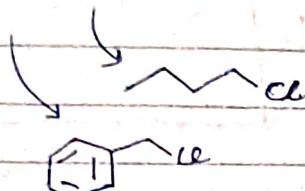


GOC

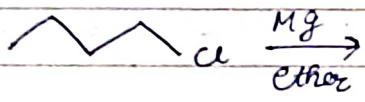
Gilliland reagent

Nucleophilic Substitution Rxn.

→ Alkyl halide (in presence of Mg & ether)



Aryl halide.



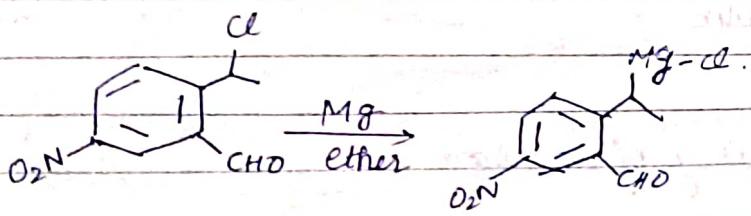
$\begin{matrix} CH_3-CH- \\ | \\ CH_3 \end{matrix}$ (isopropyl).

$\begin{matrix} CH_3 \\ | \\ CH_3-C- \\ | \\ CH_3 \end{matrix}$ (t-butyl)

$\begin{matrix} CH_3 \\ | \\ CH_3-C-CH_2- \\ | \\ CH_3 \end{matrix}$ (neopentyl).

$CH_2=CH-$ (Vinyl).

$CH_2=CH-CH_2-$ (Allyl)



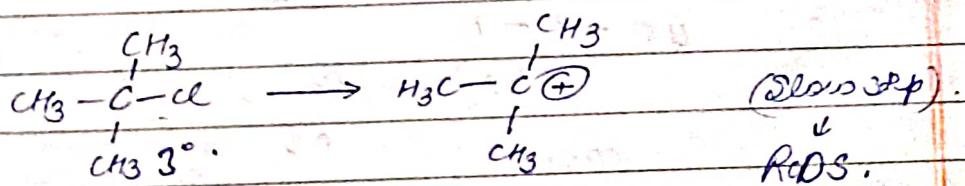
Insertion rxn.

* Ag in presence of Ag NaOH & Ag KOH. $\rightarrow S^N1 \& S^N2$ Rxn.

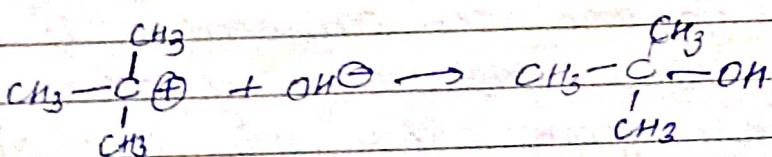
• S^N1

→ Two step process.

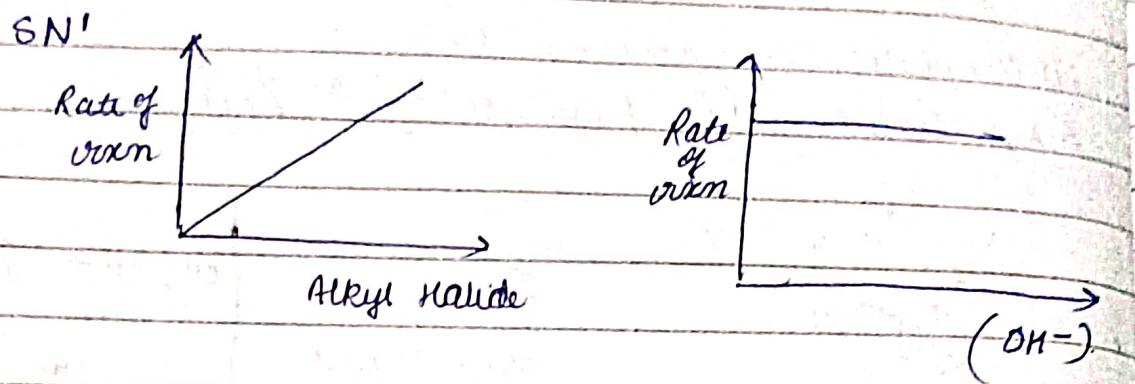
→ Step - I



$R-O-S$.



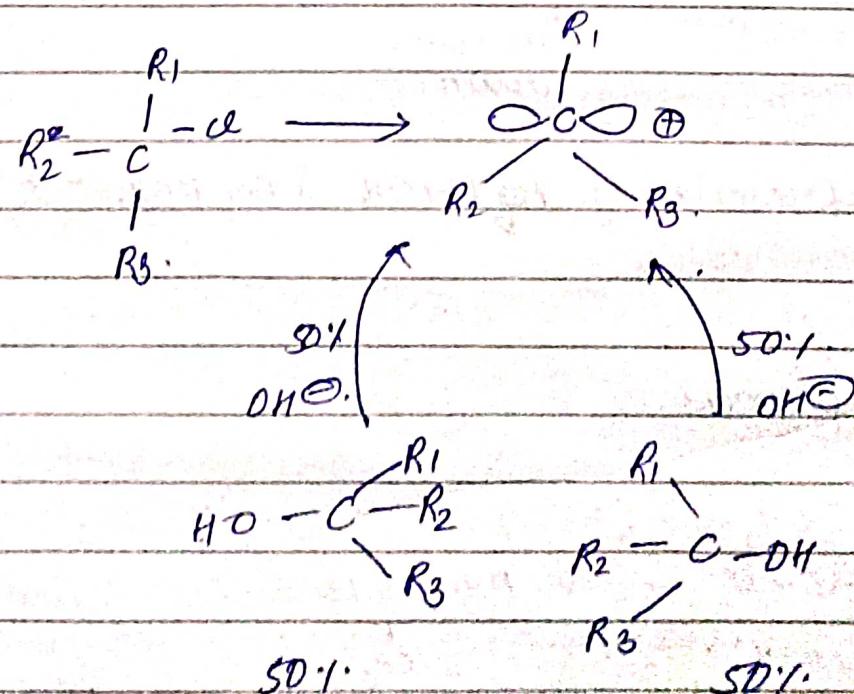
Q2 How to verify SN^1 rxn. experimentally.



→ For SN^1 rxn., rate of rxn \propto conc. of Alkyl Halide

$\leftarrow S N^1 \rightarrow 1^{st}$ Order.
Substitution. ↓
Nucleophilic

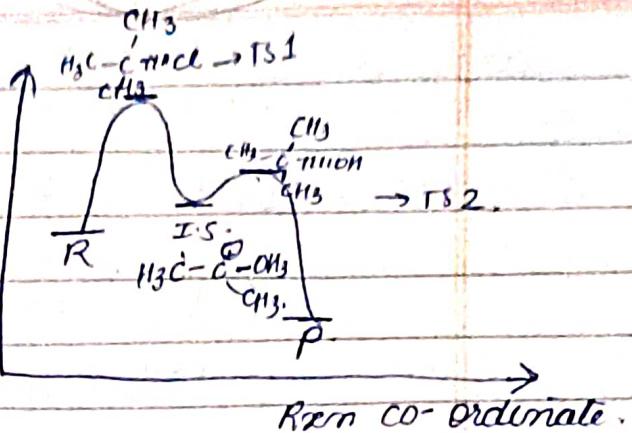
* Stereochemistry of SN^1 rxn.



In SN^1 Rxn once the carbocation is developed there is equal probability of attacking a nucleophile from either side. This leads to formation of racemic mixture.

Graphical Analysis:

- bond formed \rightarrow energy released.
exothermic rxn
- bond break \rightarrow energy absorbed.
endothermic rxn

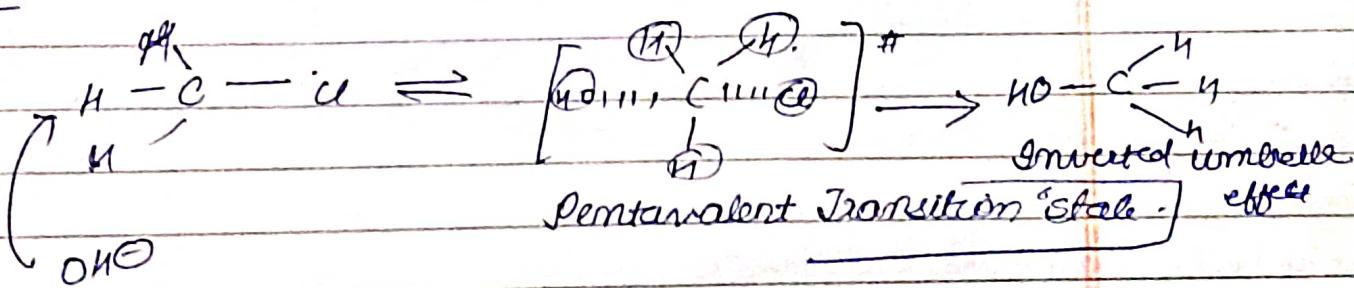


\rightarrow How can you distinguish b/w Intermediate & transition state?

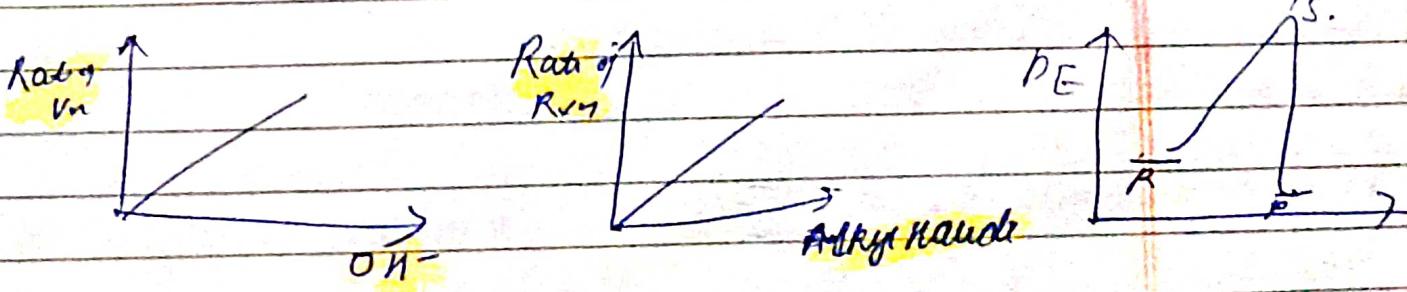
- Sol^b
- $\text{I}_1 \rightarrow$ always b/w two basic state
 - $\text{I}_2 \rightarrow$ more energy
 - $\text{I}_3 \rightarrow$ less energy.

The first step has high activation energy. It is because of this it is a slow step.

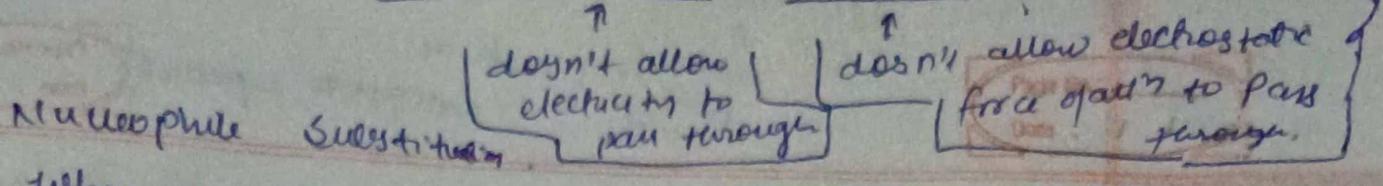
* S_{N}^2 One step process.



Backside:



diff bet' insulator & dielectric.



Whenever the ques' is asked to determine the S_N^2 rxn. remove halogen from Alkyl Halide and generate carbocation. If the carbocation is Highly stable then it will give best S_N^2 rxn.

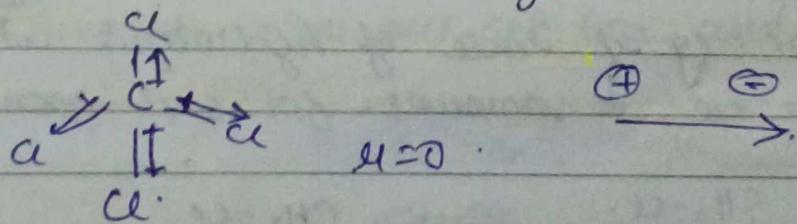
In order to determine the rate of S_N^2 rxn. Always see the stability of pentavalent transition state; the transition state should be less sterically hindered.

* Solvent effect.
Polar
Non-polar.

Polar \rightarrow dielectric const more than 15

Non-polar \rightarrow dielectric const less than 15.

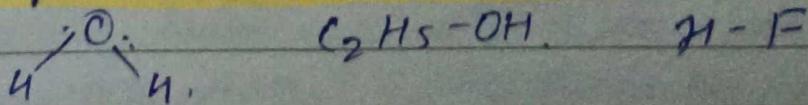
In case of a non-polar solvent the dipole moment of a molecule must be zero.



Polar solvent

Polar
Protic Polar
Aprotic

* Polar protic solvent \rightarrow FON \rightarrow directly attached w/ H.

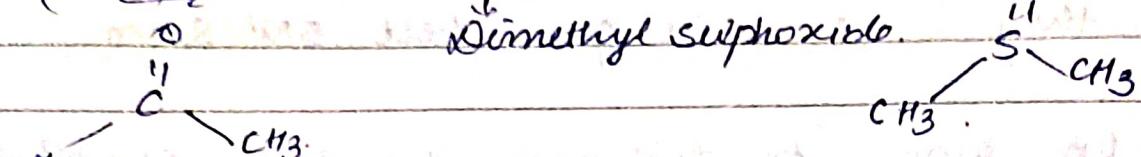


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F- O - N H salt H directly
attack not strong.

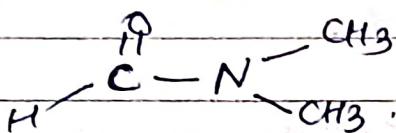
* Polar Aprotic :- F - O - N H salt H directly
attack not strong.

~~Acetone~~ DMSO.



Acetone.

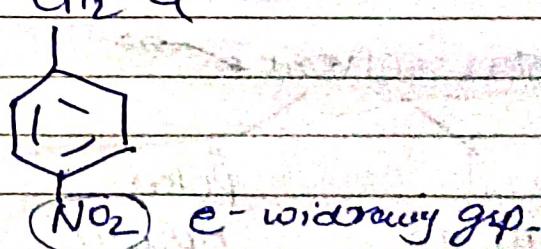
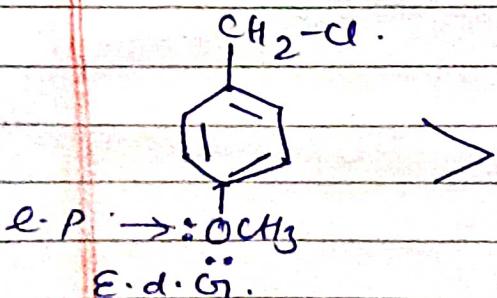
DMF \rightarrow Dimethyl formamide.



* In S_N' rxn since there is formation of carbocation, solvent which can stabilise carbocation will preferably give S_N' rxn.

Q:- Arrange the molecules - Rate of Hydrolysis.

For eg if rate of hydrolysis is asked we've to answer for S_N' rxn.

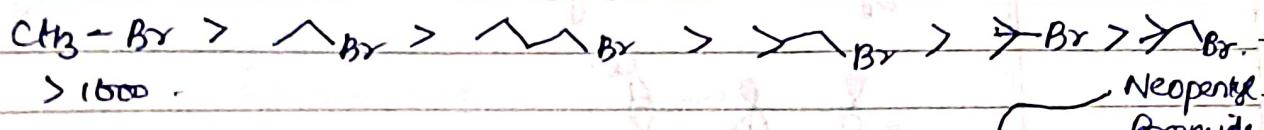


Most stable

carbocation.

SN^2 rxn. is preferable in polar aprotic solvent because pentavalent transition state is a polar transition state. If we take polar protic solvent the rate of SN^2 rxn will decrease because the solvent will solvolyse the nucleophile.

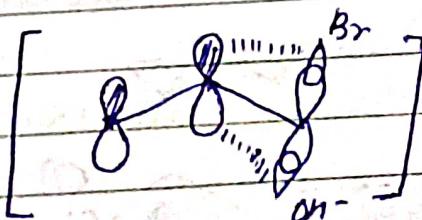
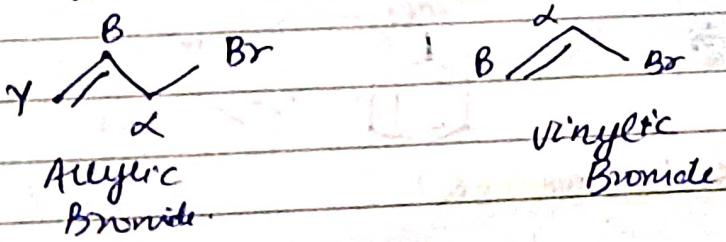
* Rate of SN^2



This molecule is highly sterically hindered and hence prevents the backside attack of nucleophile. So least SN^2 rxn.

rg.
ck

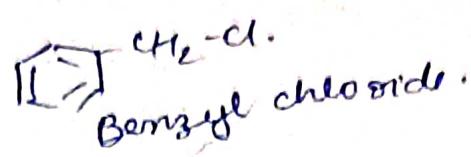
* Allylic Bromide gives best SN^2 Rxn. and good SN^1 rxn.



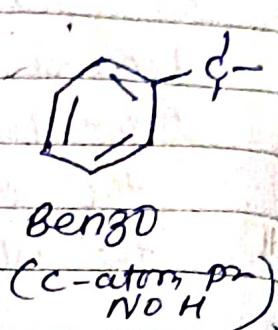
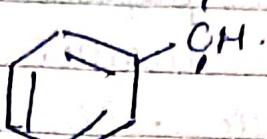
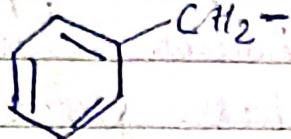
In allylic bromide we can see that the pentavalent transition state is stabilised by a pi bond so because of this it gives best SN^2 Rxn.

Rate of S_N^2

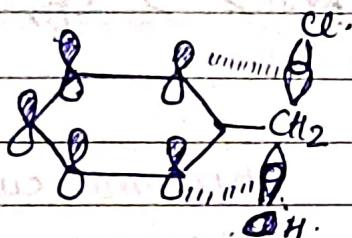
(Q3)



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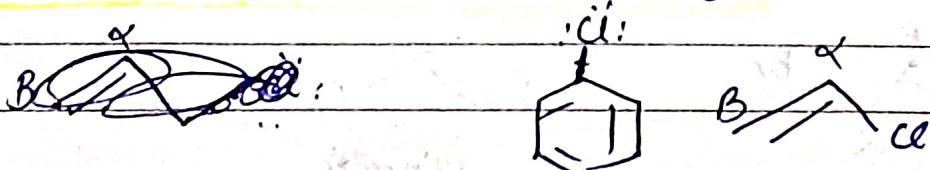


Benzyl chloride gives excellent S_N^2 & good S_N^1 .

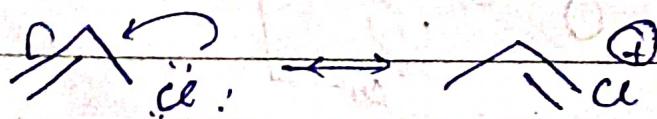
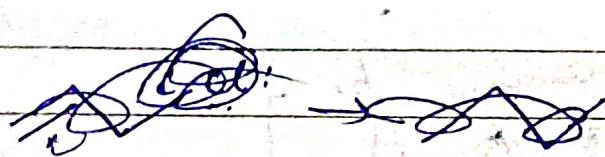


→ In benzyl chloride, the π bond of a benzene ring stabilizes the pentavalent transition state.

(Q4) Vinylic chloride; chlorobenzene

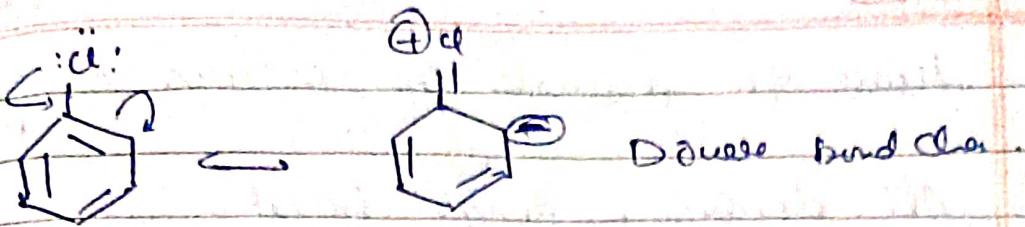


Neither S_N^1 nor S_N^2 .



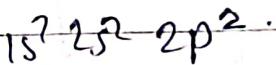
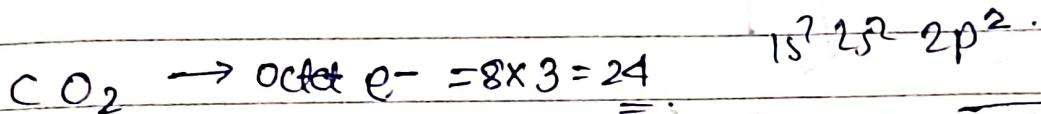
double bond character

Teach Resonance.



These molecules neither give S_N^1 nor S_N^2 bcs of resonance. There is development of double bond character b/w carbon & halogen. That's why it won't give S_N^1 & S_N^2 .

Resonance

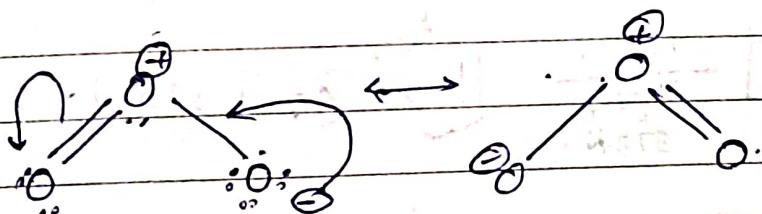


$$\text{Valence } e^- = 2 + (6 \times 2) = 16$$

nearest noble gas.

$$\frac{8}{2} = 4$$

Mathematical concept :-

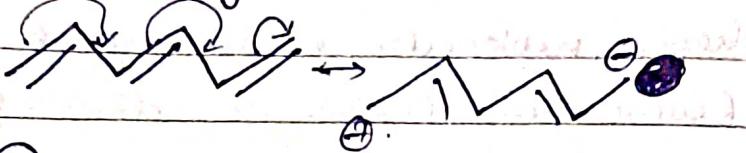


Resonance is a hypothetical concept. It actually do not take place. When a property of a molecule can't be determined by a single Lewis dot structure, we make use of resonance.

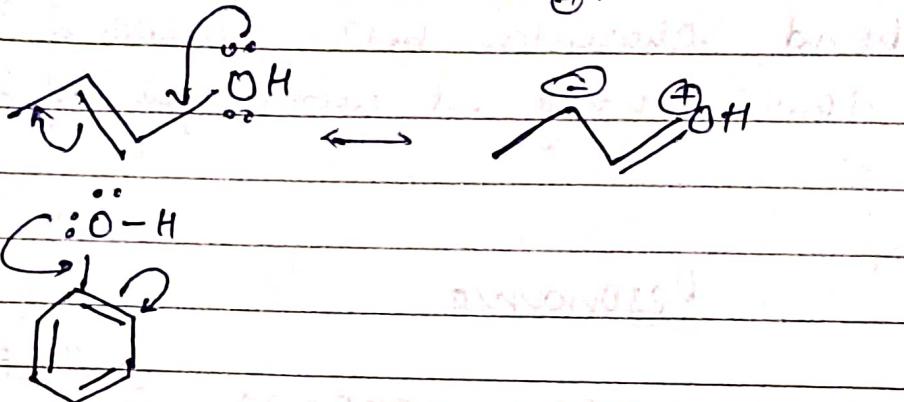
In resonance we draw the similar Lewis dot of a molecule which is indistinguishable.

* Have to observe the occurrence of ortho effect.

1) Alt. double & single bond.

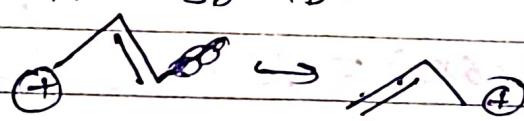


2)

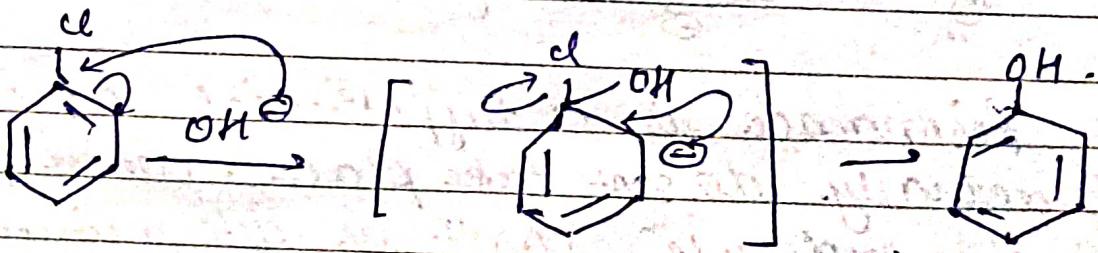
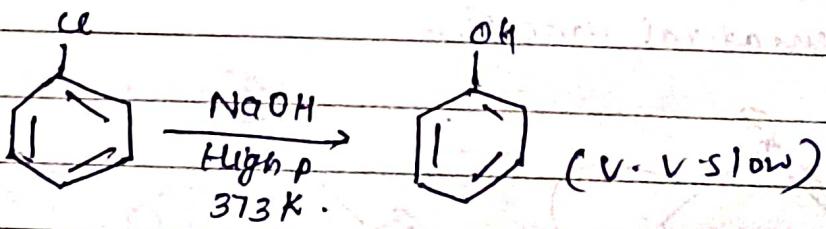


3)

+ve -SB-dB.



Aryl Halide :-



This rxn is known as Addⁿ Elimination Rxn.

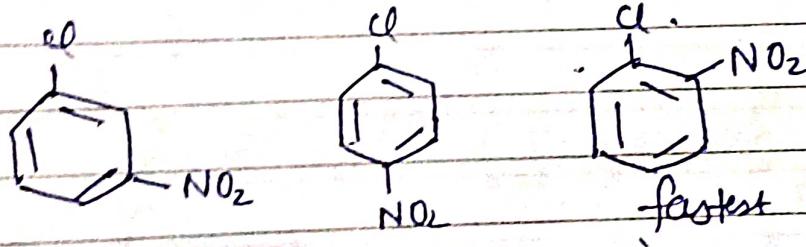
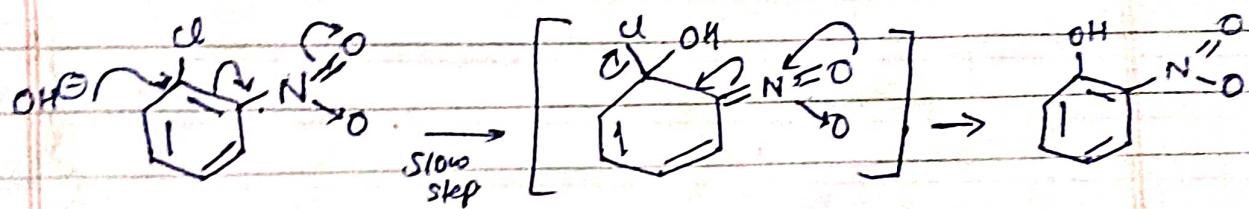
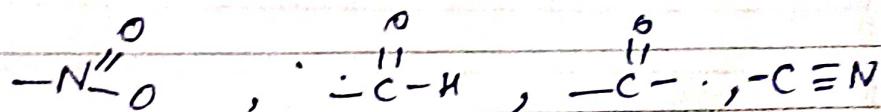
$\text{SnAr} \rightarrow \text{Aromatic Nucleophile}$
Substitution - rxn,

where nucleophile is substituting halogen or aromatic ring.

→ This can be enhanced by attaching e-withdrawing grp to stabilize the carbocation.

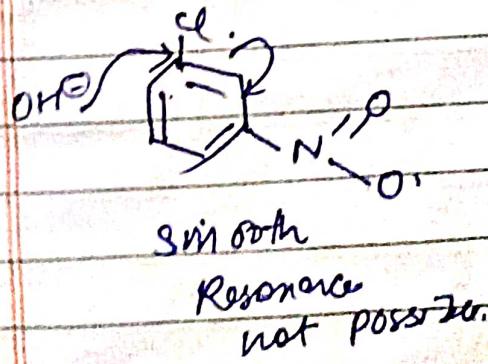
↑ Note :-

Any molecules having double bond or triple bond is considered as e-withdrawing molecule.

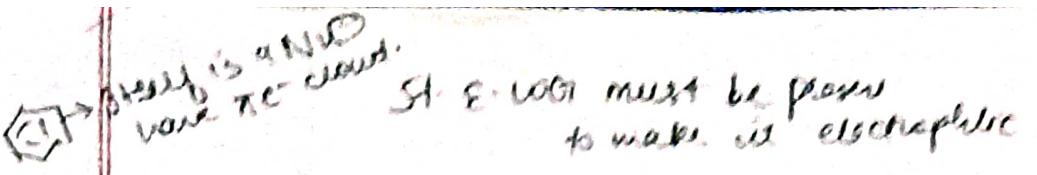


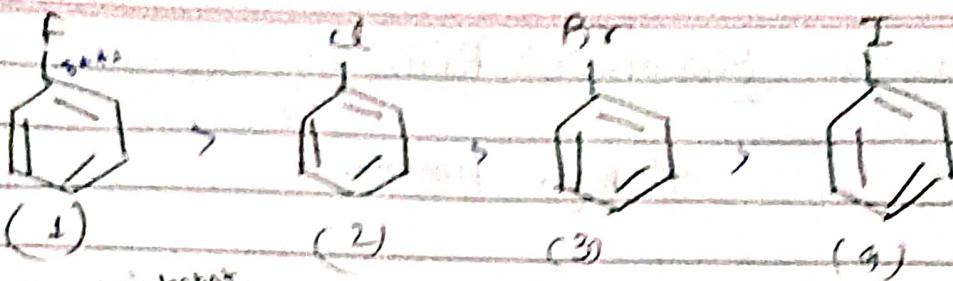
↓
2nd fast

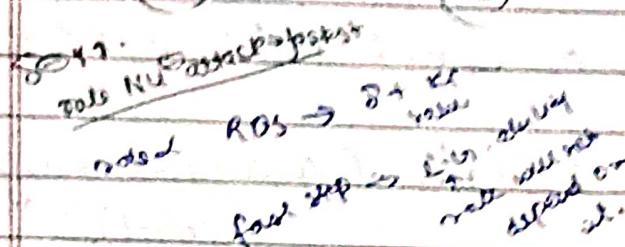
③ > ② > ①



→ Since the attack of nucleophile is a slow step and a rate determining step. Therefore more closer the NO_2 from electrophile carbon faster will be SNAr .


Step 1 is a Nucleophile, hence it's electrophilic.




Note $R-O-S \rightarrow S^+ O-R$ is always slowest or second step.

- Note :-

Cond'n for S_NAr Reacn :-

- (1) EWGI enhances S_NAr rxn, O-Substituent have stronger effect than para. followed by meta.
- (2) If EN atom attached directly to a benzene ring, charge will be the rate of rxn because attack of nucleophile ion on a benzene ring is a slow step & a rate determining step.

Elimination Rxn.

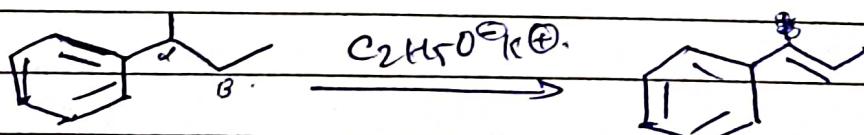
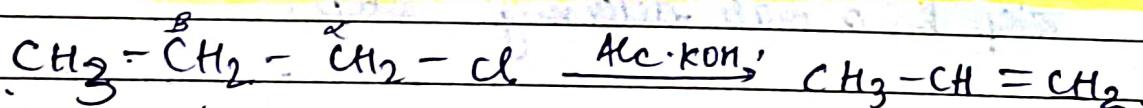
Alkyl Fluoride.

- (a) Alcoholic KOH / NaOH. or $\text{C}_2\text{H}_5\text{O}^- \text{Na}^+ / \text{C}_2\text{H}_5\text{O}^- \text{K}^+$
 (b) $t\text{-BuO}^- \text{K}^+$.
 (c) $\text{C}_2\text{H}_5\text{O}^- \text{Na}^+$. H_3PO_4 or $\text{H}_2\text{SO}_4 / \text{A}$. (Applicable only in alcohol).

In this rxn we convert alkyl halide into alkene or alcohol into alkene by a rule called ~~Saytzeff~~ & Saytzeff rule.

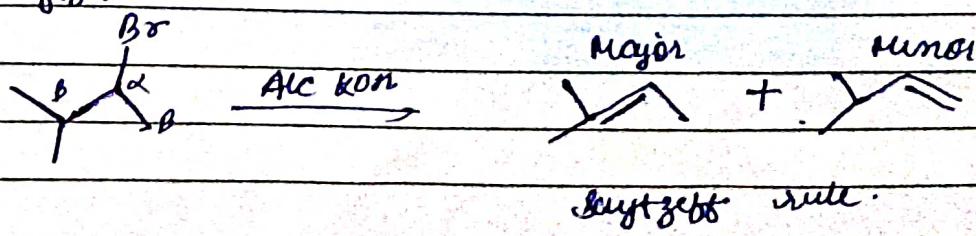
* Steps to perform elimination rxn.

- (1) Identify α -carbon & β -carbon
- (2) Remove one β -Hydrogen & halogen
- (3) Generate double bond ~~with the~~ ~~as~~ on both α & β carb.



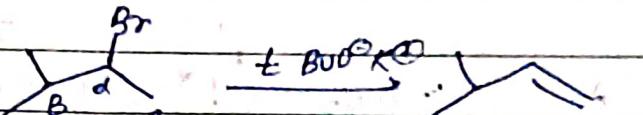
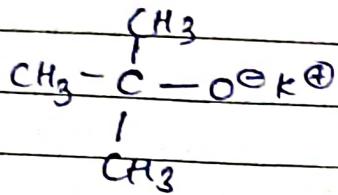
Note:-

- If there are more than one type of β -Hydrogen always generate double bond on that α - β carbon which gives highly substituted alkene. This is called ~~Saytzeff rule~~.



* Condⁿ under which least substituted alkene will be formed.

* $t\text{-BuO}^{\ominus}\text{K}^{\oplus}$:

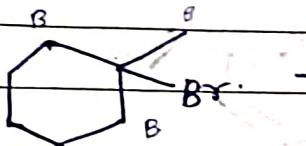


\downarrow Alc ROH

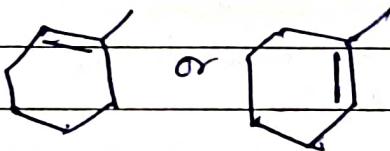
Major

Major -

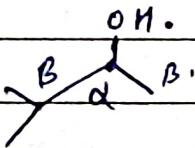
$t\text{-BuO}^{\ominus}\text{K}^{\oplus}$.



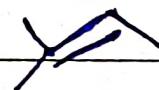
\downarrow Alc. 100°



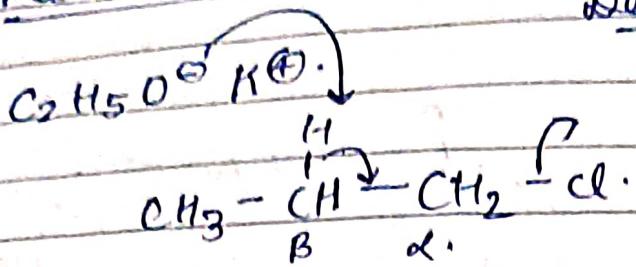
* $\text{H}_3\text{PO}_4 / \text{H}_2\text{SO}_4 + \Delta$



$\xrightarrow{\text{H}_3\text{PO}_4}$



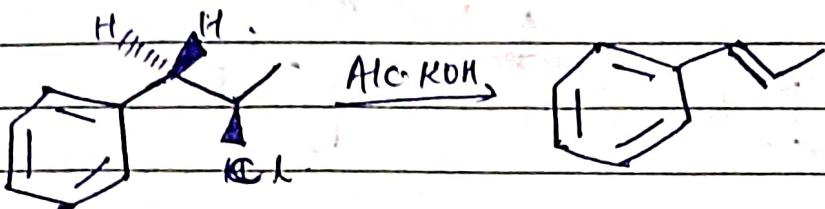
Mechanism :-



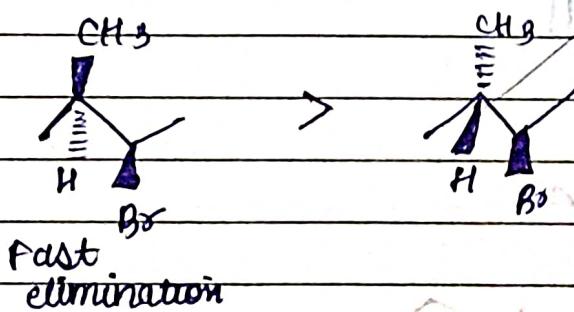
Dehydrohalogenation

E₂ rxn.

Name of Transition state i.e. E₂.
 → Anti-periplanar T.S.

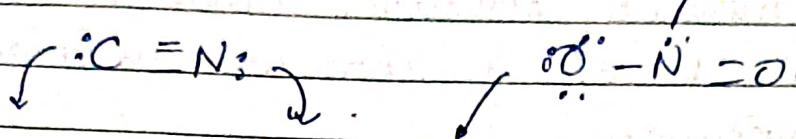


In anti-periplanar T.S. Halogen and B-hydrogen must lie in opposite dir.

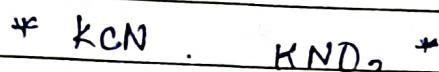


Amidicent Nucleophile

(2)



Amidicent nucleophiles can donate e^- from either side.



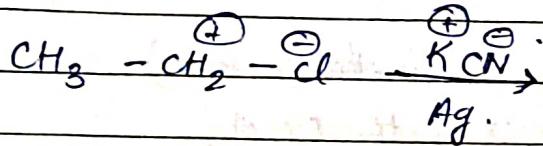
$\text{KCN} \rightarrow$ ionic bond

+

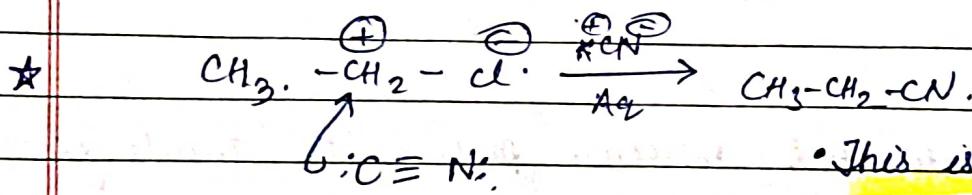
covalent bond

+

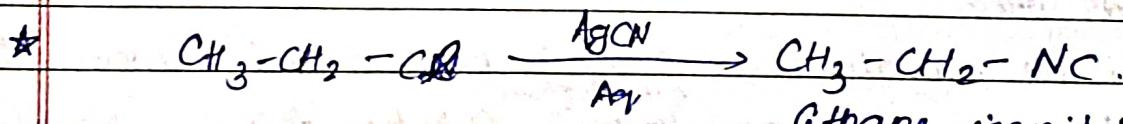
positive bond.



Less EN \rightarrow more E·D·Capacity

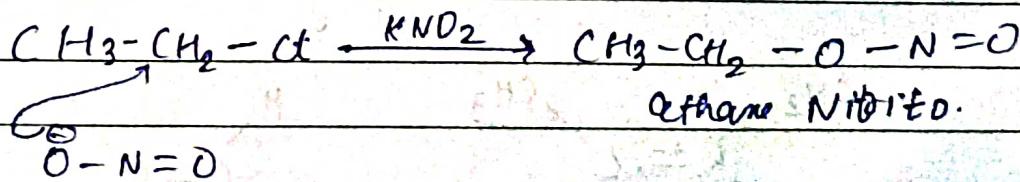


This is an ionic compound.

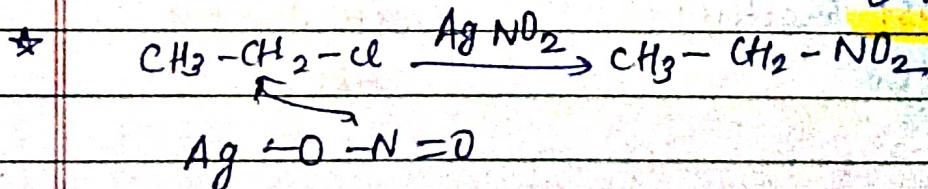


Ethane isonitrile.

- AgCN is covalent comp.
- $\text{AgCN} \rightarrow$ only way to deplete e^- is from N.



Although NO is more EN but O have more e^- so EDC +.



Am of un. is to convert all the
non-polar substance
into polar compd.

Alkene (olefin).

↓.

Any molecule possessing a double bond or triple bond is considered as unsaturated compound.



→ highly carcinogenic



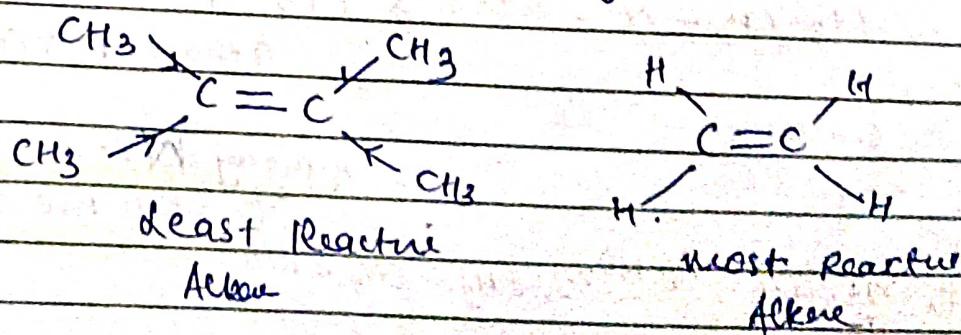
epoxide (doesn't dissolve in H₂O)
(React with DNA)

* NOTE :-

Every unsaturated molecule prefer to undergo addn rxn.

Q. What is unsaturated comp.? Benzene is unsaturated?
Benzene undergoes electrophilic substitution rxn whereas unsaturated molecule undergo addn rxn.

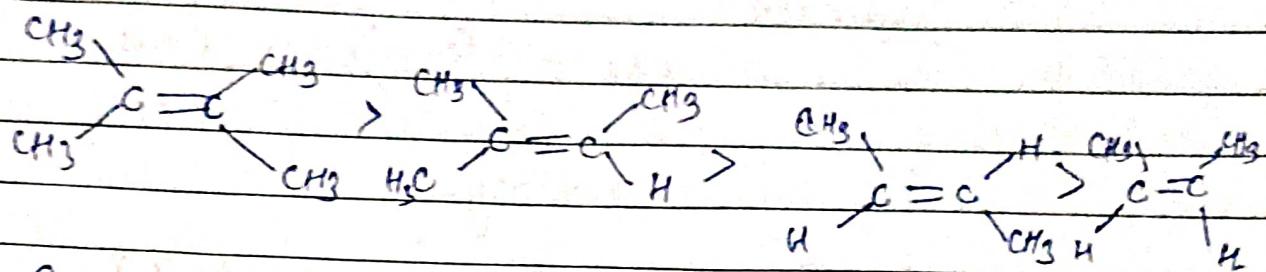
* At the double bond of alkene breaks easily such alkenes are highly reactive.



How Alkene React.



- * More the no. of alkyl group attached to a double bond more stable will be the alkene molecule.



Cis-alkene is more reactive than a trans alkene because the bulky methyl group are very close to each other and they repel each other.

- * Stability of Alkene.

Heat of combustion $\propto 1$.

Stability
of
Alkene.

- * Heat of Hydrogenation

$\propto 1$

Stability of
Alkene

- * Note:-

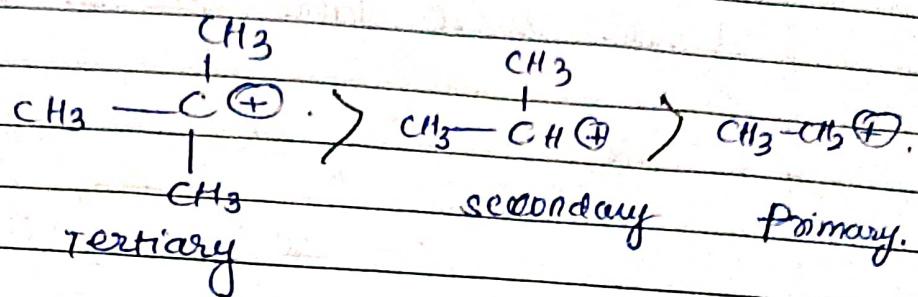
Heat of Hydrogenation is not a preferable method to predict the stability of Alkene because it has tendency to undergo rearrangement.

11/12/23

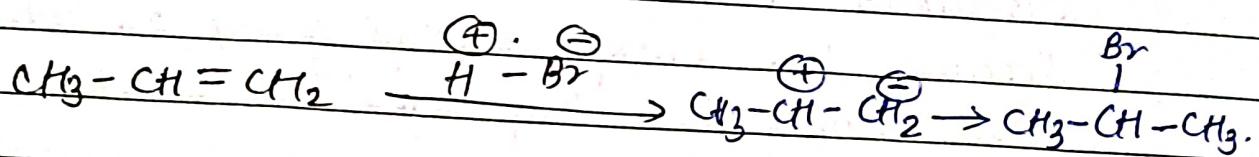
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* HOW ALKENE REACTS

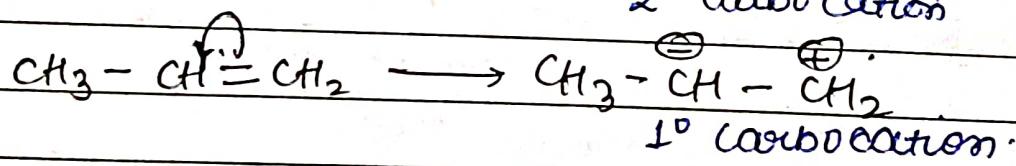
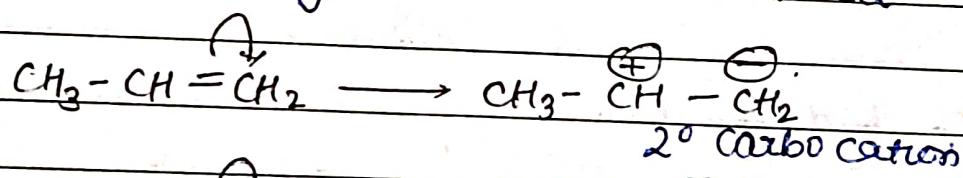
Carbocation



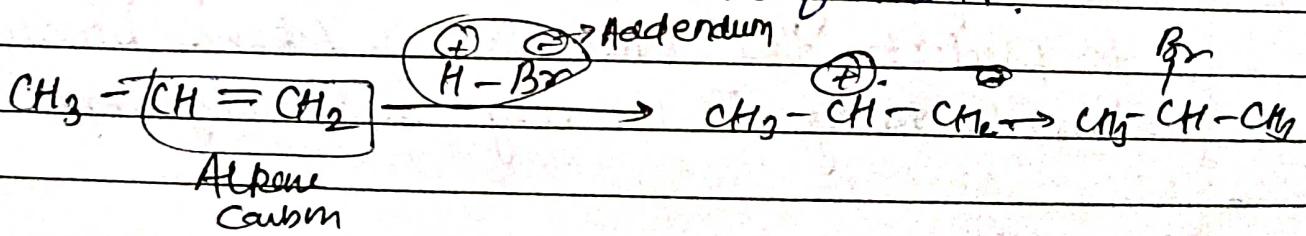
EDG ↑↑ stability ↑↑



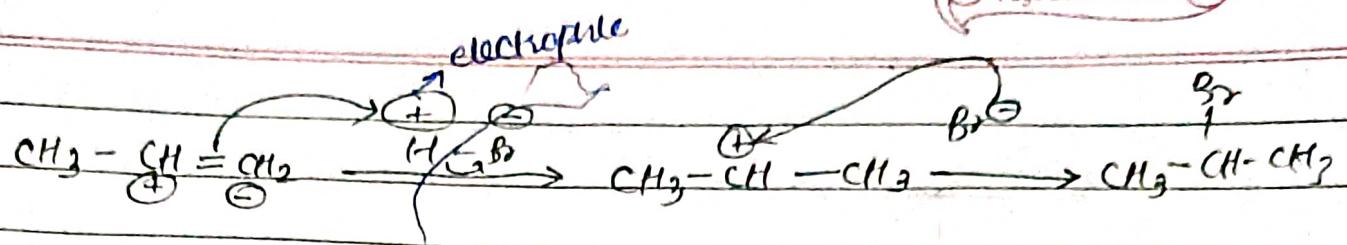
→ Alkene has a property to show electromeric effect i.e. it will develop charge only when reagent is added in it.



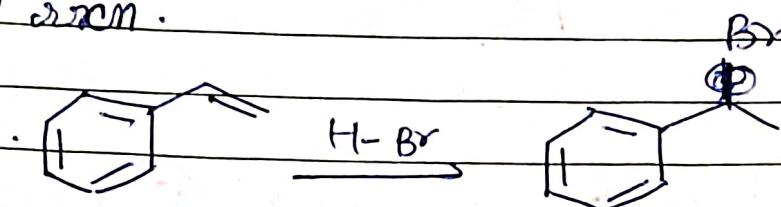
→ Break π -bond of alkene in such a way that most stable carbocation is formed.



Acc. to Markonikoff rule -ve part of addendum attaches to that part of carbon atom of alkene which has less no. of hydrogen atom.



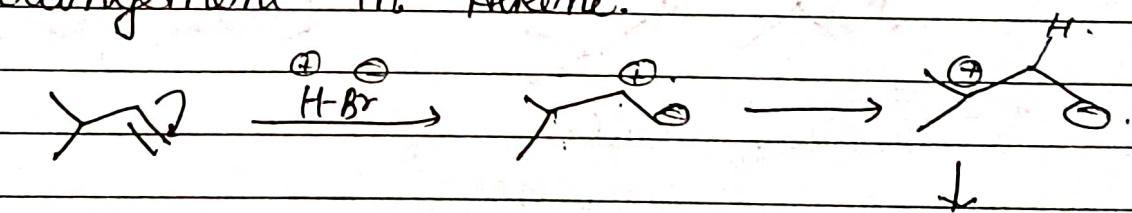
- * From above mechanism we observe, that reaction of Alkene is initiated by electrophile, both part of carbonium gets attached to it. Hence, Alkene gives electrophilic addition reaction.



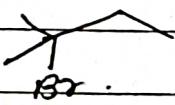
NOTE:-

- Always make carbocation beside benzene using on double bond.
- Tertiary carbocation is more stable than benzyllic carbocation.

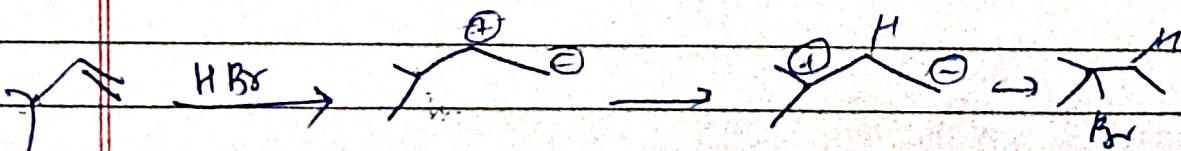
* Rearrangement in Alkene.

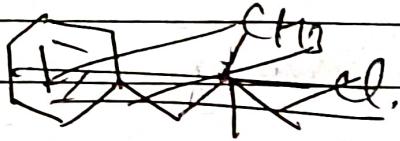
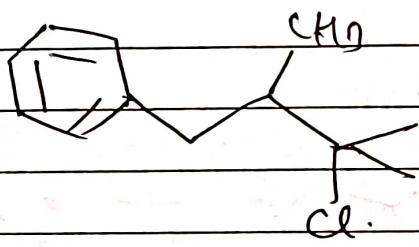
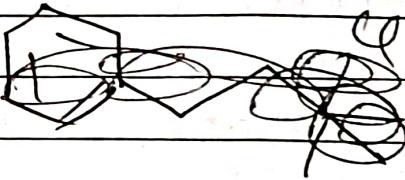
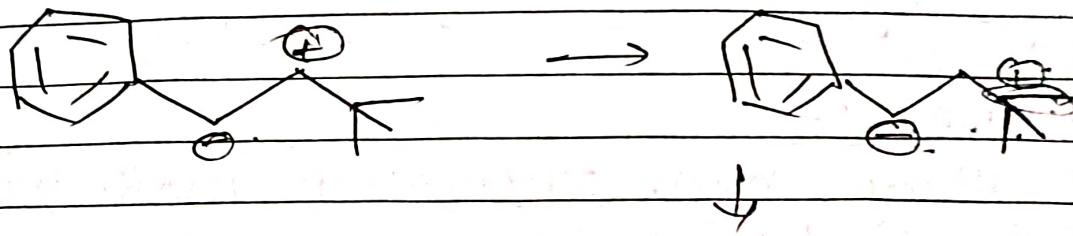
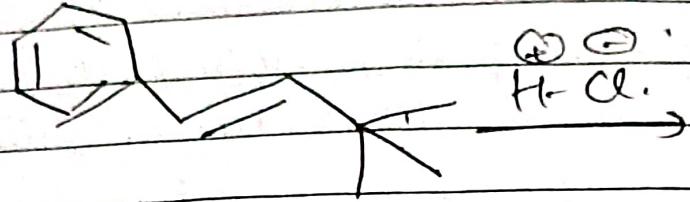


Wagner Meerwin Rearrangement.

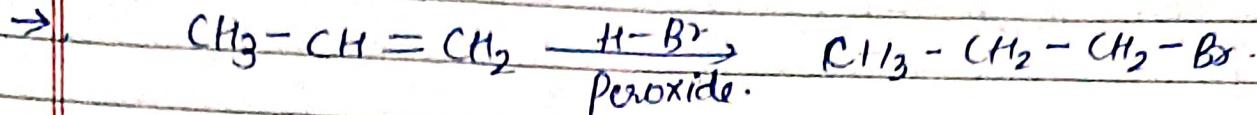


- whenever I break a π -bond of Alkene and generate a unstable carbocation, I should also check whether arrangement of Hydrogen or methyl group next to the carbon having $\delta+$ ve charge can generate more stable carbocation or not.





★ Ane - Markonikoff's Rule / Kharash. effect / Peroxide effect :-

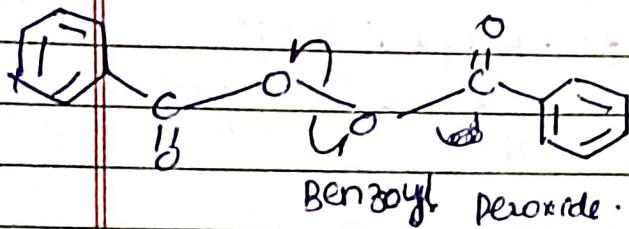
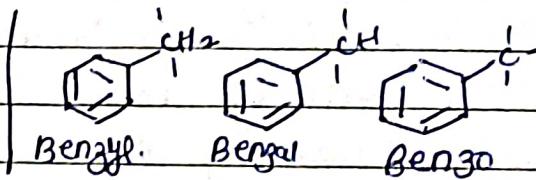


→ Peroxide effect is observed only with HBr & not with HF, HCl or HI.

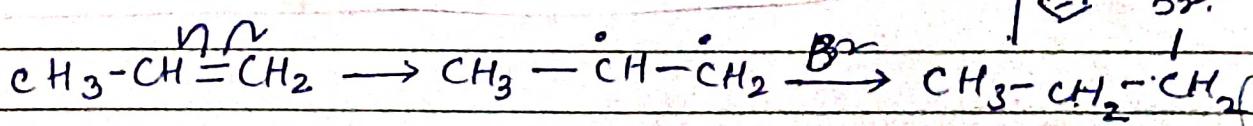
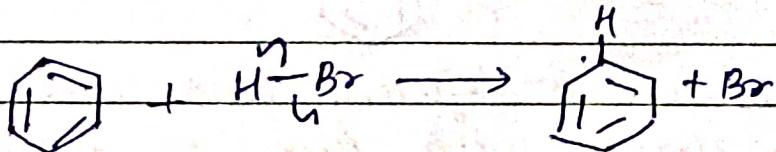
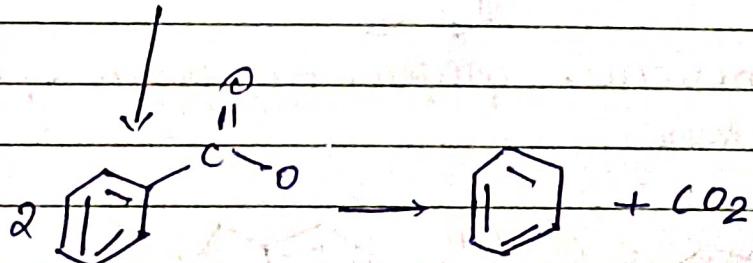
→ It do not take place in presence of Hydrogen peroxide. (H_2O_2)

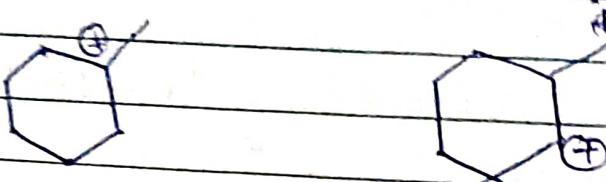
→ In this rule negative part of addendum attaches to that part carbon-atom of alkeno having more number of hydrogen-atom.

Benzoyl peroxide :-



↗ → fish hook arrow.

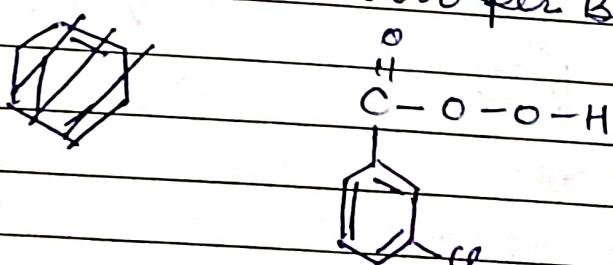




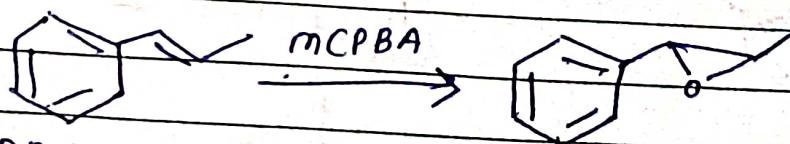
* m CPBA NOTE:-

Peroxide effect is only observed in HBr and not in HCl & HI because HCl bond is very strong & it can't homolyse easily. In case of HI the molecule gets homolyzed easily but Iodine radical prefers to combine among themselves forming Iodine molecule.

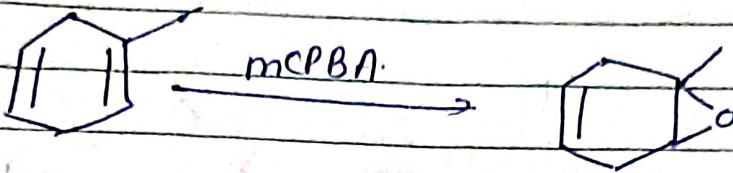
* m CPBA \rightarrow meta - chloro per Benzene acid.



This molecule prefers to form epoxide with alkene.

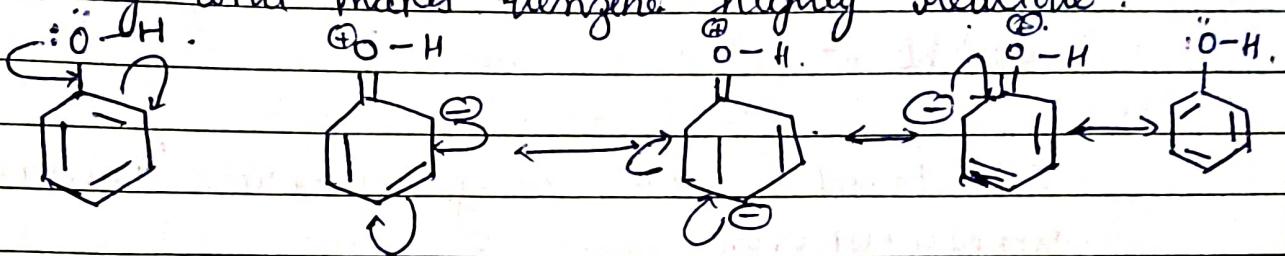


m CPBA is an e- deficient molecule. It prefers to attack alkene with high e- density.



Electron density on Benzene ring.

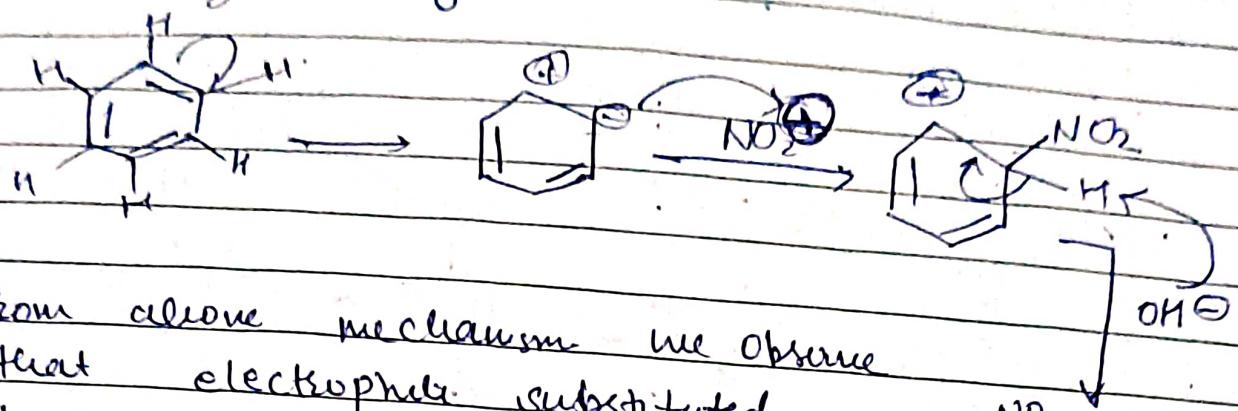
- Any substituent having lone pair of e^- when attached directly to a benzene ring increases e^- density on a ring and makes benzene highly reactive.



In the above structure, there is development of -ve charge on a ring which increases e^- density on a ring and such substituent are called ring activator.

Eg $\rightarrow \ddot{\text{N}}\text{H}_2$; $-\ddot{\text{O}}-\text{CH}_3$; $-\text{CH}_3$

* How benzene Ring React's:-



* From above mechanism we observe that electrophilic substituted hydrogen of a benzene ring. Therefore, the rxn is called electrophilic substitution reaction.



* HCl will not react with benzene.

* Friedel-Crafts rxn :-

→ In Friedel-Crafts rxn we can attach alkyl group (Friedel-Crafts alkylation), or acyl group (Friedel-Crafts acylation):

