Reaction Mechanism

Organic rxn

Substitution

If an atom or gp is replaced by another atom or gp is called substitution rxn.

$CH_3-g + \overset{\ominus}{O}H \rightarrow CH_3OH + g^{\ominus}$

Addition

If atoms or gp's are added without removing any atom or group is called addition.

e.g.: $CH_2=CH_2 \xrightarrow{Br_2} \underset{\underset{Br}{|}}{CH_2}-\underset{\underset{Br}{|}}{CH_2}$

Elimination

If atoms or gp's are removed without adding any atom or gp is called eli.

$CH_2(Br)-CH_2(Br) \xrightarrow{Zn}$

$CH_2=CH_2 + ZnBr_2$

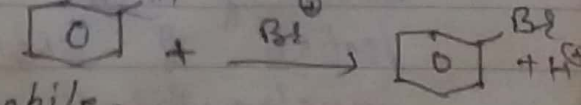
→ In all substitution one σ bond is cleaved and one new σ bond is formed.

→ In addition one π-bond is cleaved and two σ bonds are formed.

→ In all β-eliminations two σ-bonds are cleaved and a π-bond is formed.

Substitutions :→

→ Nucleophilic sub :— eg:- $CH_3-g + \overset{\ominus}{O}H \rightarrow CH_3-OH + g^{\ominus}$
If attacking reagent is Nucleophile.

→ Electrophilic sub :— eg: 
If attacking reagent is Electrophile.

* Nucleophilic substitution: →

All Nucleophilic sub. in general can be expressed as →

$$R-L + Nu^{\ominus} \rightarrow R-Nu + L^{\ominus}$$

leaving gp.

C-L bond is cleaved and C-Nu bond is formed. Hence following pathways can be proposed.

(A) 1st C-L bond is cleaved and then C-Nu bond is formed.

$$R-L \xrightarrow{rds} R^{\oplus} + L^{\ominus} \quad -(1) \quad \text{slow}$$

$$R^{\oplus} + Nu^{\ominus} \rightarrow R-Nu \quad -(2)$$

- It is two step pathway occuring through the generation of carbocation intermediate
- 1st step is rds. (Rate determing step).

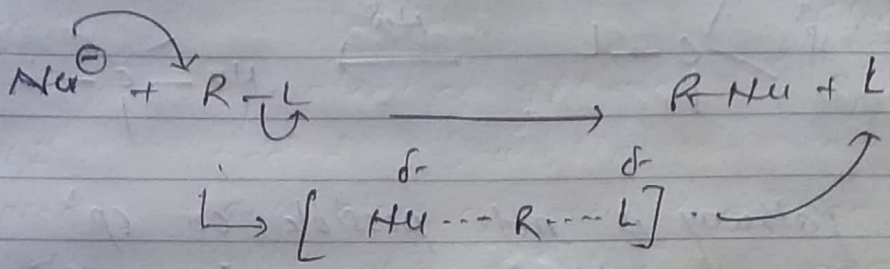
∴ Rate ∝ [substrate]^1

order = 1
Molecularity = 1

- This pathway is called unimolecular nucleophilic substitution (S_N1).

→ Rate of S_N1 rxn depends only on the concentration of substrate but "not on $Nu^{\ominus}$" nucleophile.

(B) Both cleavage of C-L and formation of C-Nu bond takes place simultaneously.



→ It is a single step pathway occuring a (transition state).

∴ Rate ∝ [substrate][Nucleophile].

order = 1+1 = 2

Mol. = 2

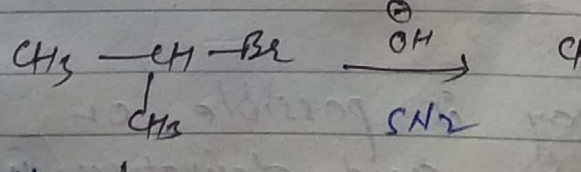
Hence this pathway is called bimolecular nucleophilic substitution (S_N2).

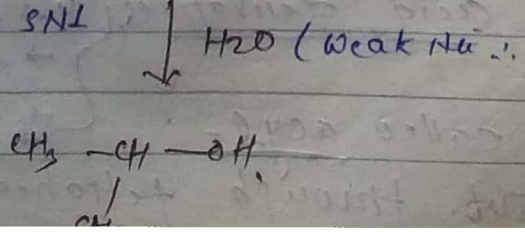
→ The rate law of S_N2 reaction depends upon both the conc. of substrate and nucleophile.

S_N1, Rate ∝ [sub]

S_N2, Rate ∝ [sub][Nu⁻].

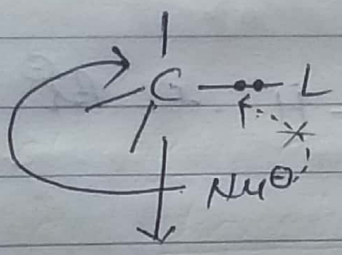
(HB) Weak Nu⁻ favours S_N1 and Strong Nu⁻ favours S_N2.

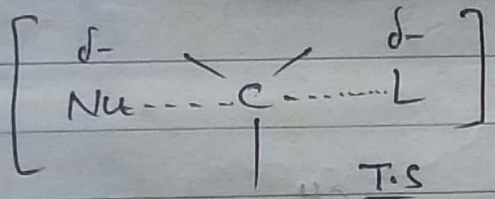




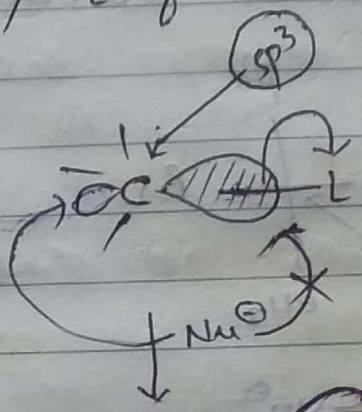
* T.S of S_N2 rkn :-

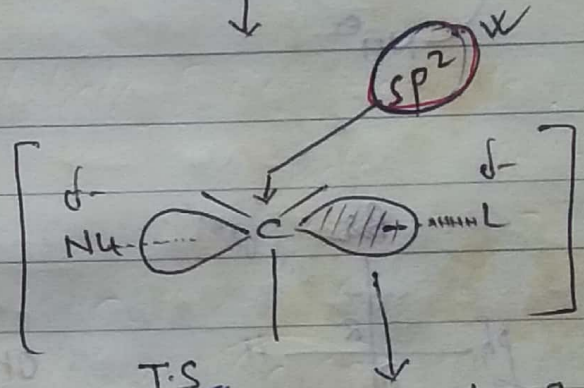
In S_N2 rkn $Nu^\ominus$ attacks from the back side of leaving gp, because in front side attack $Nu^\ominus$ is strongly repelled by bond pair of C-L bond.





T.S





T.S

As size of both lobes in T.S is same (i.e- p orbital)
∴ sp^2

As soon as $Nu^\ominus$ attacks on the smaller lobe of sp^3 orbital, this lobe begins to increase in size and bigger lobe begins to decrease in size.

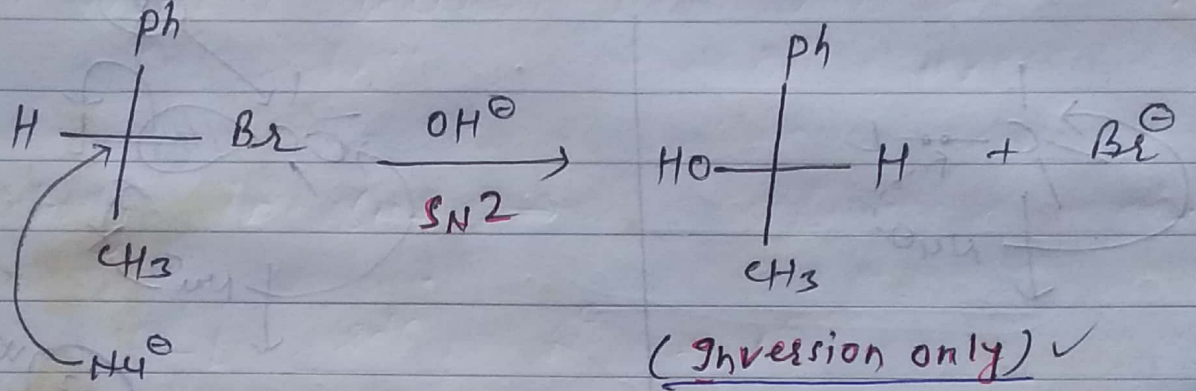
- In this practice, a moment comes when both lobes are of equal size. This is nothing but a p-orbital.

∴ In T.S the site of rkn (C) is sp^2 Hybridized

* stereochemistry of (S_N2) :→

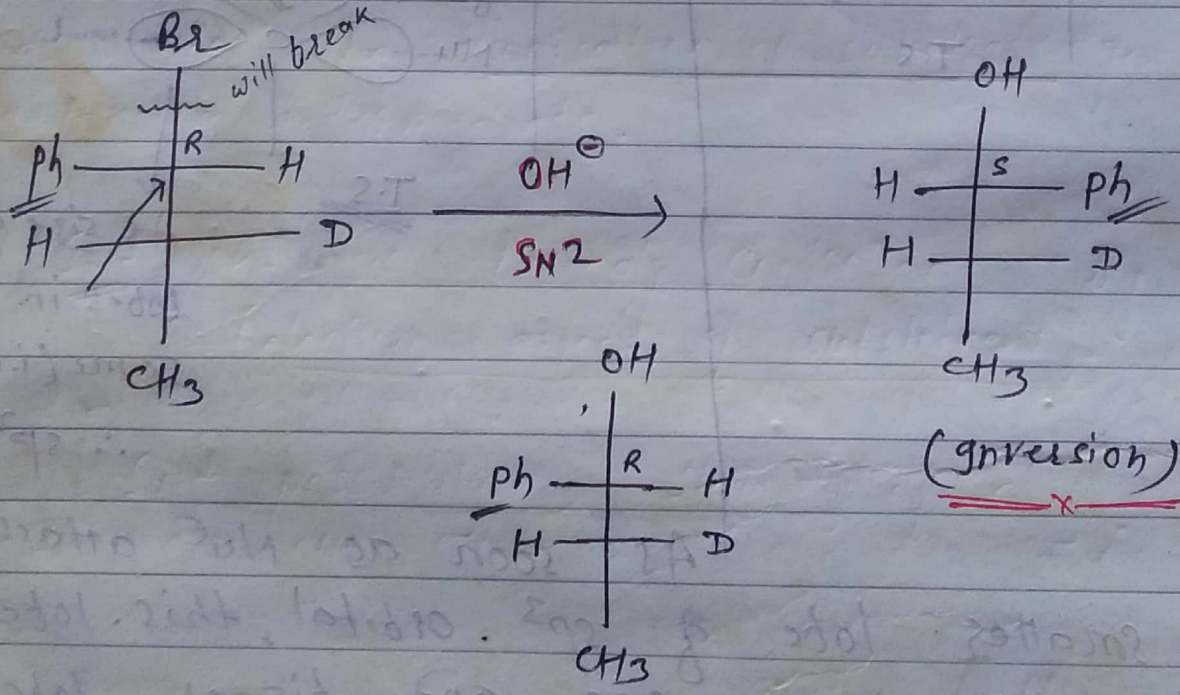
Since in S_N2 rxn, $Nu^{\ominus}$ attacks on the back side of leaving gp, inversion of configuration occurs.

→



(Inversion only) ✓

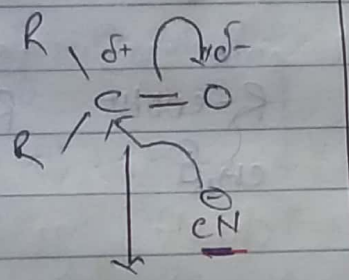
→



** Addition reactions: →

- In all addition rx^n, one electrophile and one nucleophile is added on the substrate.
- If E⁺ is added 1st then it is called electrophilic addition
- If Nu⊖ is added 1st then Nucleophilic addition.

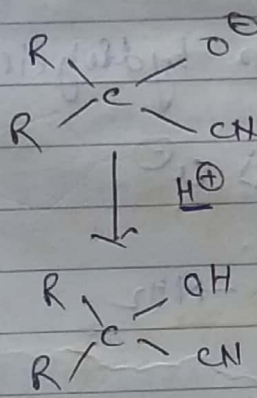
* Nucleophilic addition: ⇒

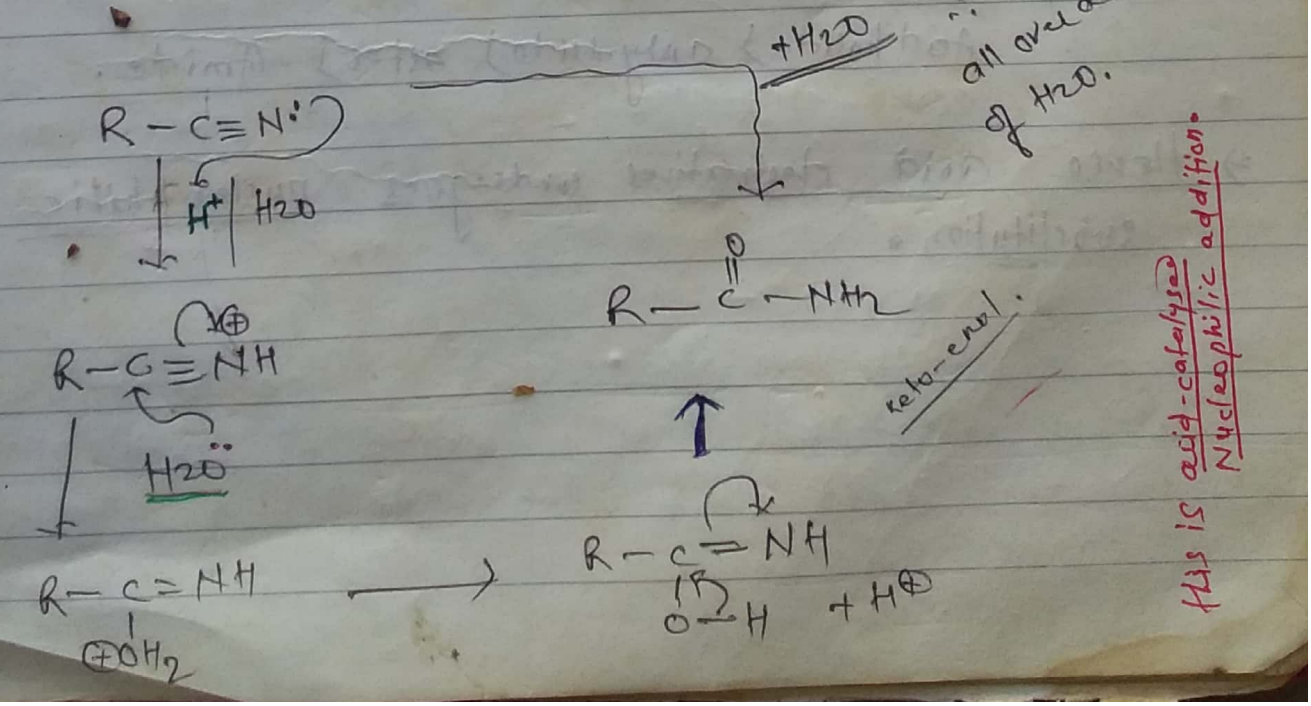


→ A Nucleophilic addition.

→ Aldehydes and ketones generally undergoes nucleophilic addition.

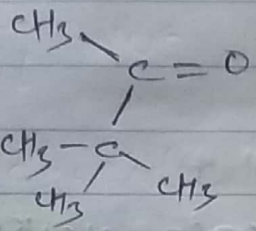
Cyanohydrin.





o/ $CH_2=O$

$CH_3-CH=O$



ease of $Nu^{\ominus}$ addition:

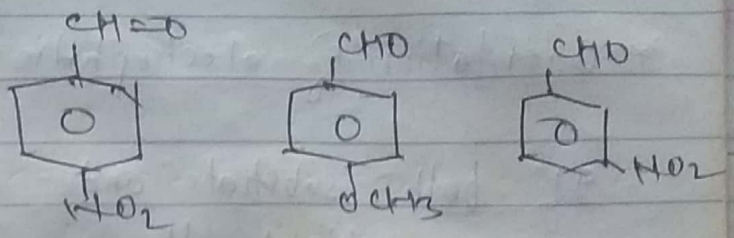
I > II > III > IV

Acceptors ↑

donors ↓

ease of nucleophilic addition

o/



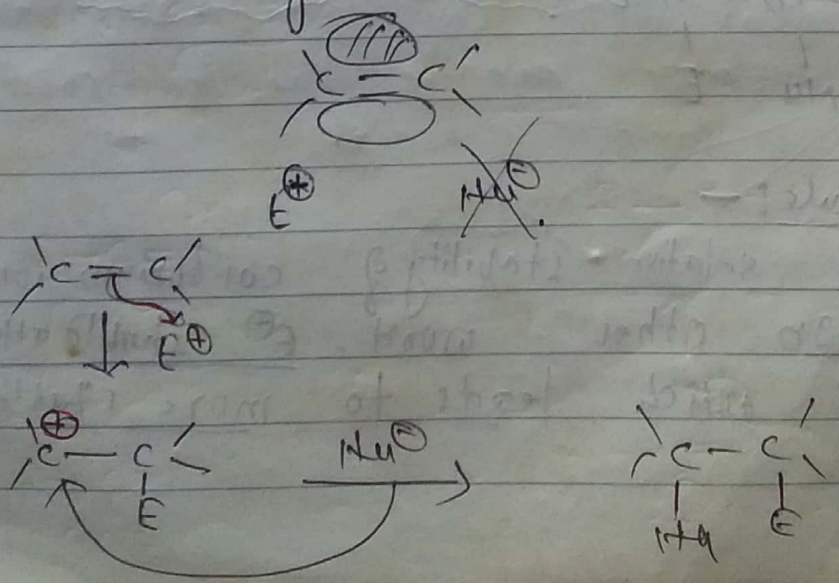
ease of nucleophilic addition

I > III > II.

⊛ Electrophilic addition:—

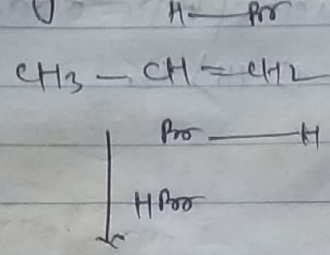
It occurs on homoatomic multiple bond.

e.g. $C=C$, $C\equiv C$.



* Orientation of electrophilic addition:—

If both substrate and addendum (reagent) are unsymmetrical then orientation stands.

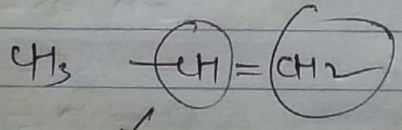


$CH_3-CH_2-CH_2$ (Pro) ✗

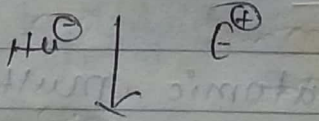
$CH_3-CH(Pro)-CH_3$ ✓

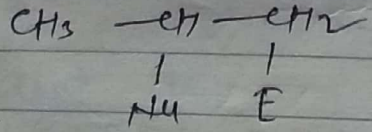
In such case Markowni-koff's rule is ~~add~~ applied.

This rule state that $E^{\oplus}$ should go on less substituted C and nucleophile on more substituted C of the double bond.



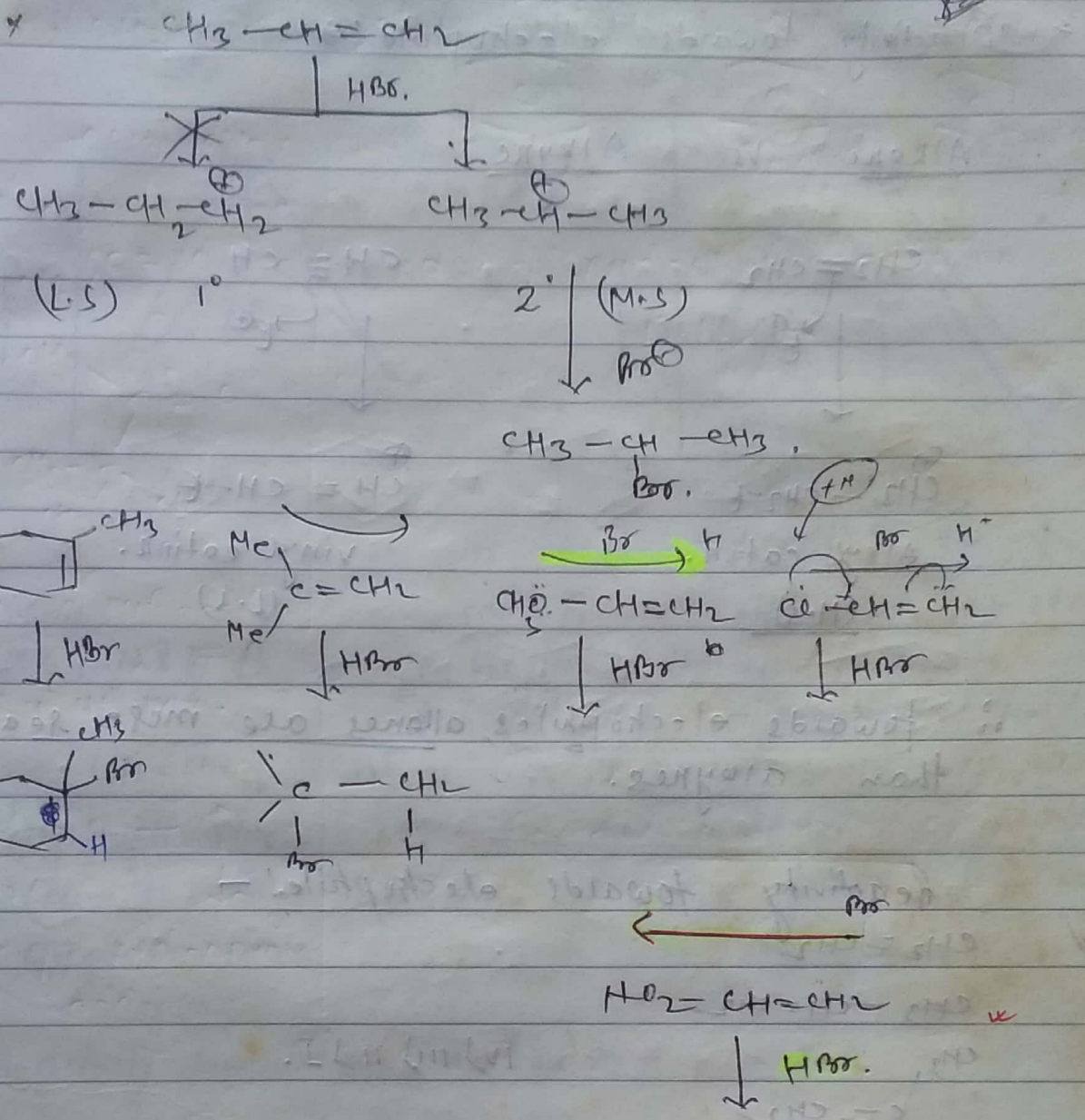
More substituted.





Basis of M' Rule:—

It is the relative stability of carbonium ion intermediate. In other word, $E^{\oplus}$ should attack on that C which leads to more stable carbocation.



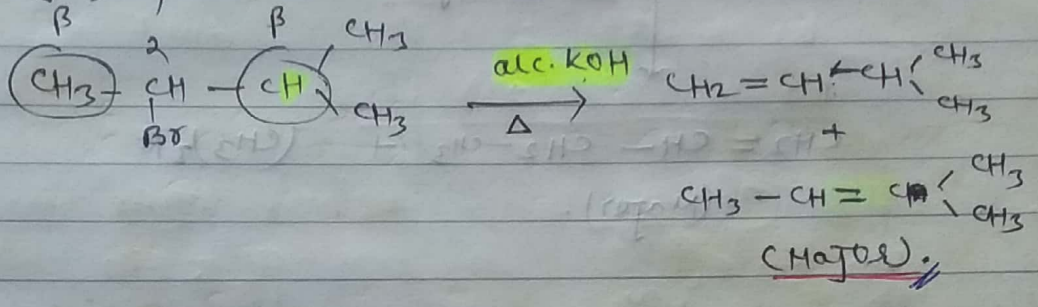
⇒ In case of halogen reactivity is controlled by -I

NB. but orientation is controlled by +M.

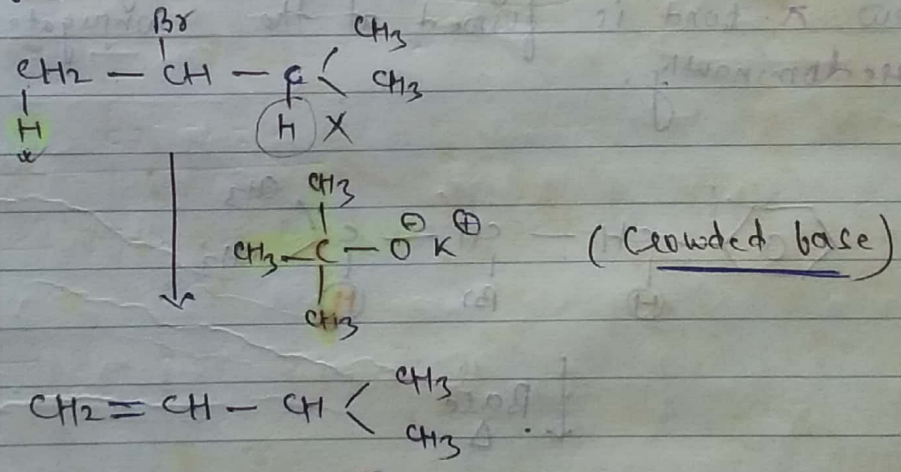
* Orientation of elimination:—

① Zaitsev Rule / Saytzeff rule:—

This rule states that M.S alkene will be major product.

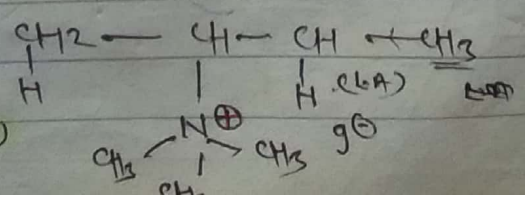


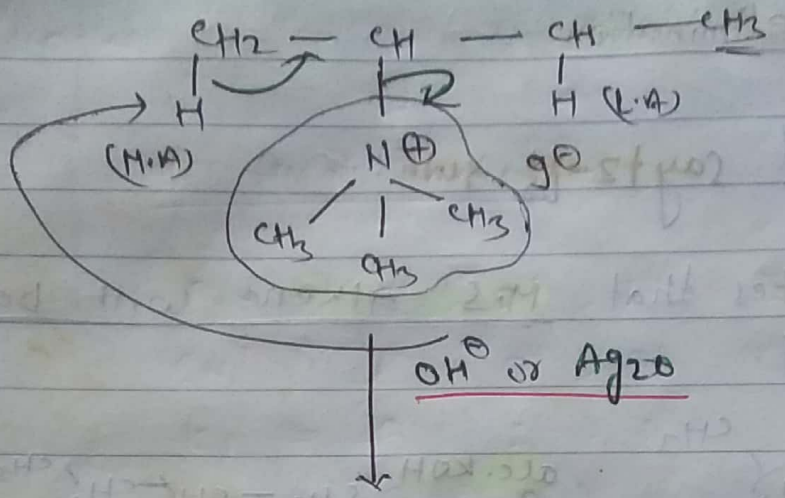
- If base is crowded (means bigger size base) then antizaitsev product is often formed predominantly for steric reason.



② Hofmann's Rule:—

This rule is applied when the leaving gp is cationic, in such cases more acidic β-H is predominantly removed.



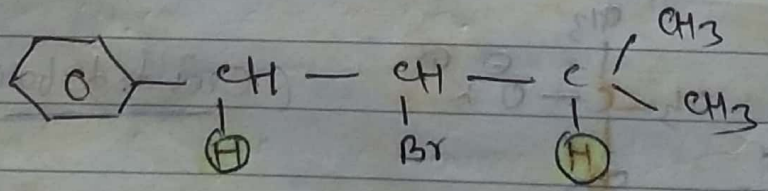


$CH_2 = CH - CH_2 - CH_3 + (CH_3)_3N$

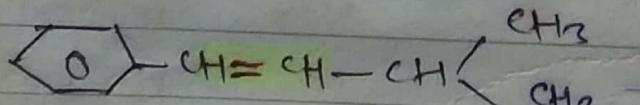
(Major).

⊛ Rule of Conjugation:—

If molecule already has a resonating group then new π-bond is formed at the conjugated position predominantly.

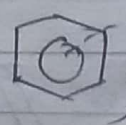


Base
Δ

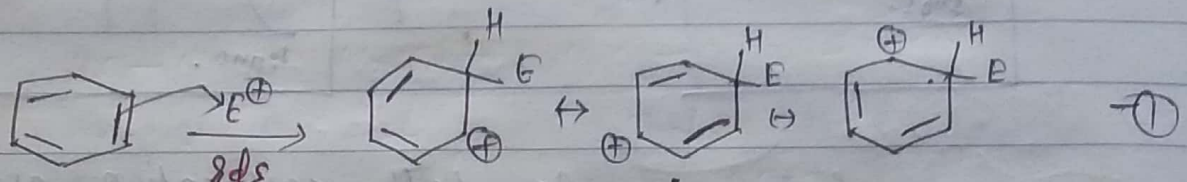


Major.

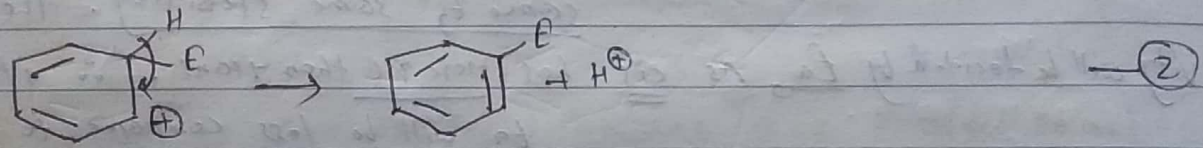
(**) Electrophilic aromatic substitution :⇒



On benzene electrophilic substitution is favoured. this is because π cloud of benzene attacks $E^{\oplus}$ and repell $Nu^{\ominus}$.



— (1)



— (2)

- It is a two step pathway occuring through the generation of a σ-complex.
- First step is rds.

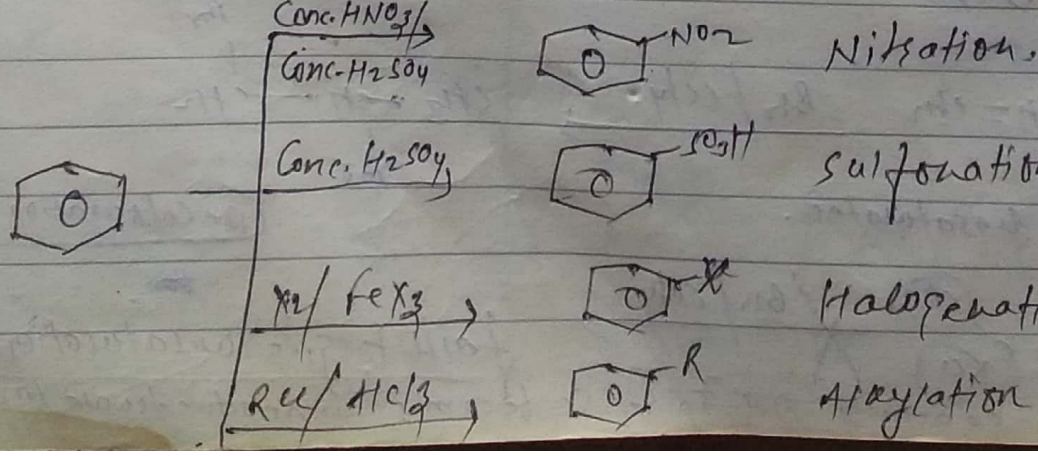
∴ Rate ∝ [Benzene][E^+]

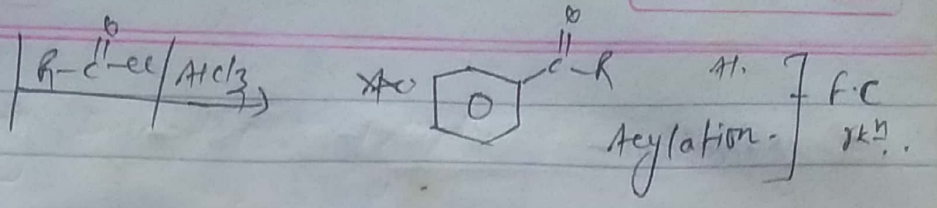
Order = 1+1 = 2

Mol = 2

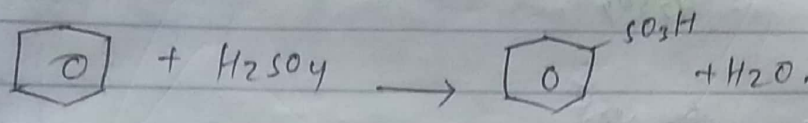
This pathway is called bimolecular electrophilic substitution (S_E2)

** Common electrophilic aromatic substitutions:—

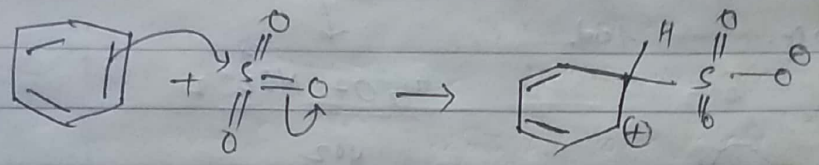




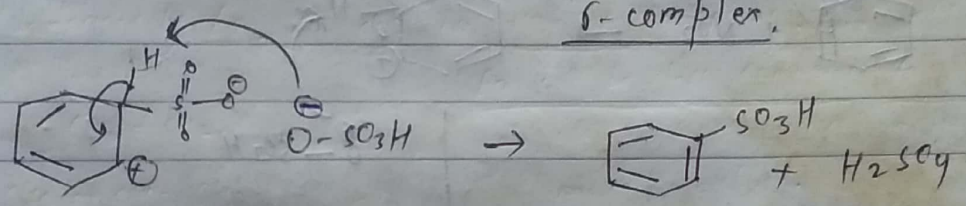
* Sulfonation :-

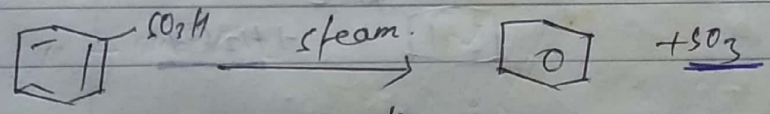


Mech- $2H_2SO_4 \rightarrow SO_3H^{\oplus} + HSO_4^{\ominus} + H_3O^{+}$



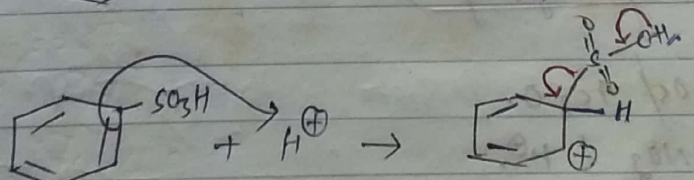
σ-complex.



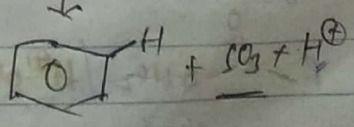
* 

De sulfonation

Mech-

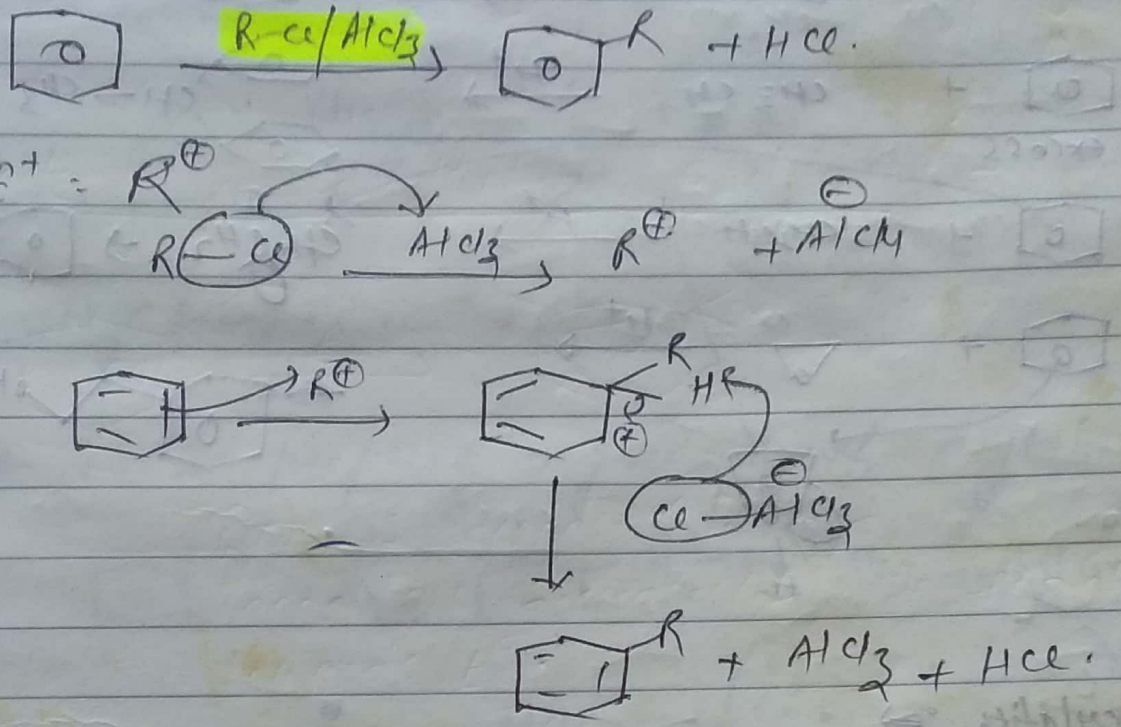


→ as -SO3H is very good leaving gp.

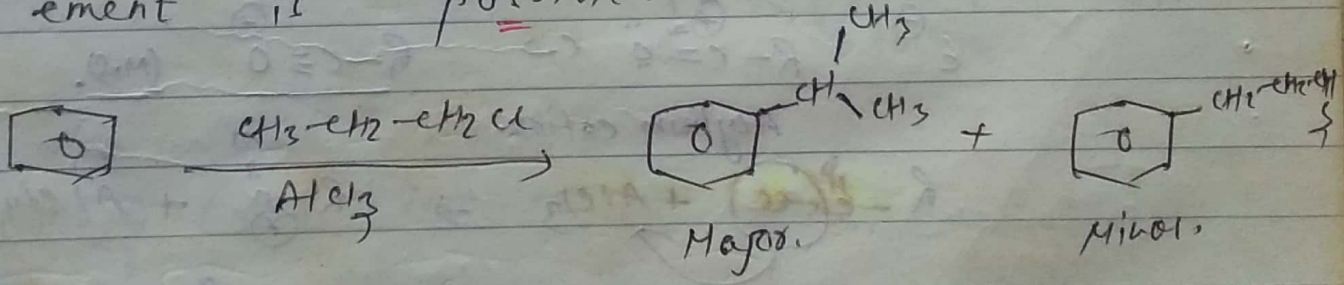


De sulfonation is reverse of sulfonation. Both occurs through σ-complex. Hence sulfonation is strongly reversible because -SO3H gp. is very good leaving gp.

* Friedel crafts alkylation:-



- $AlCl_3$ is the catalyst.
- $R^{\oplus}$ is electrophile. ∴ Carbonium ion rearrangement is possible.



(HB) It is not good rx^n for making n-alkyl benzenes.

⇒ Properties:-

① Addition of HX

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

Mech:-

$CH_3-CH=CH_2 \xrightarrow{rds} CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^-} CH_3-\underset{Br}{CH}-CH_3$

- Electrophilic addition.
- M'Rule is followed.
- Carbocation is intermediate.

∴ Rearrangement is possible

* $CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow{HCl}$

$CH_3-\underset{CH_3}{\underset{Br}{C}H}-CH_2-CH_2$ + $CH_3-\underset{CH_3}{\underset{Cl}{C}H}-CH-CH_3$.

(Major)

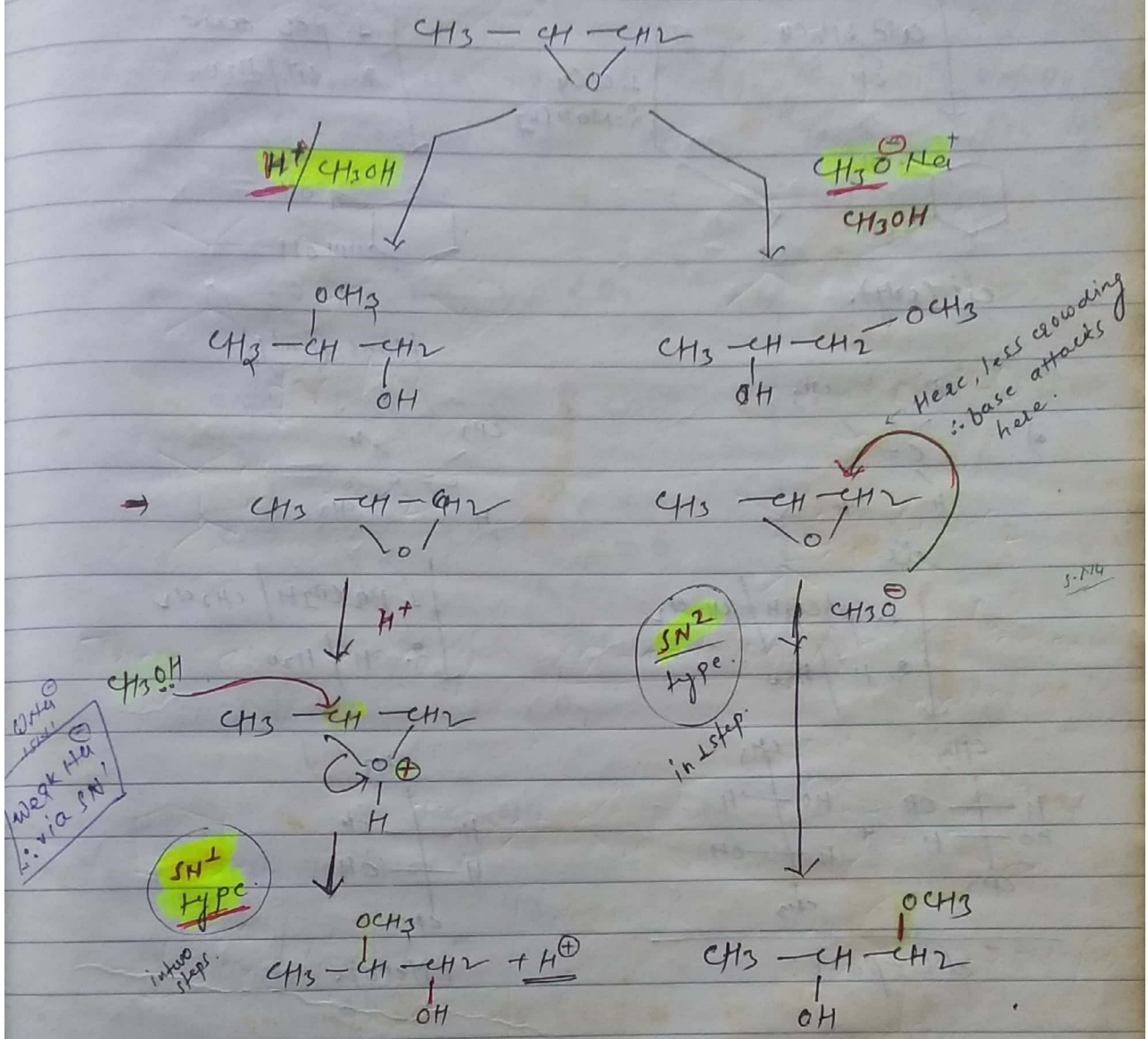
Mech:-

* Reactivity of HX:-

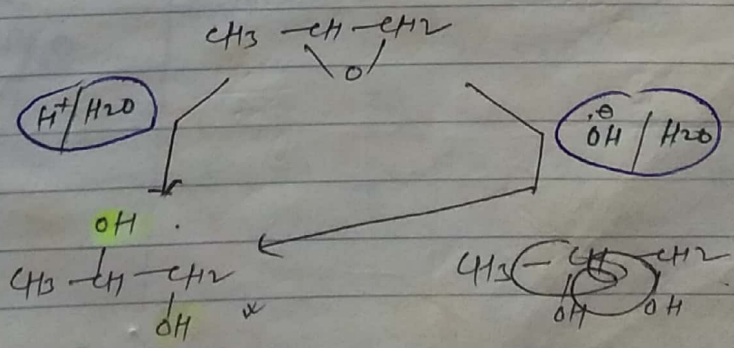
HI > HBr > HCl > HF.

HI आसानी से H^+ दे, तो rds के लिए जरूरी है।

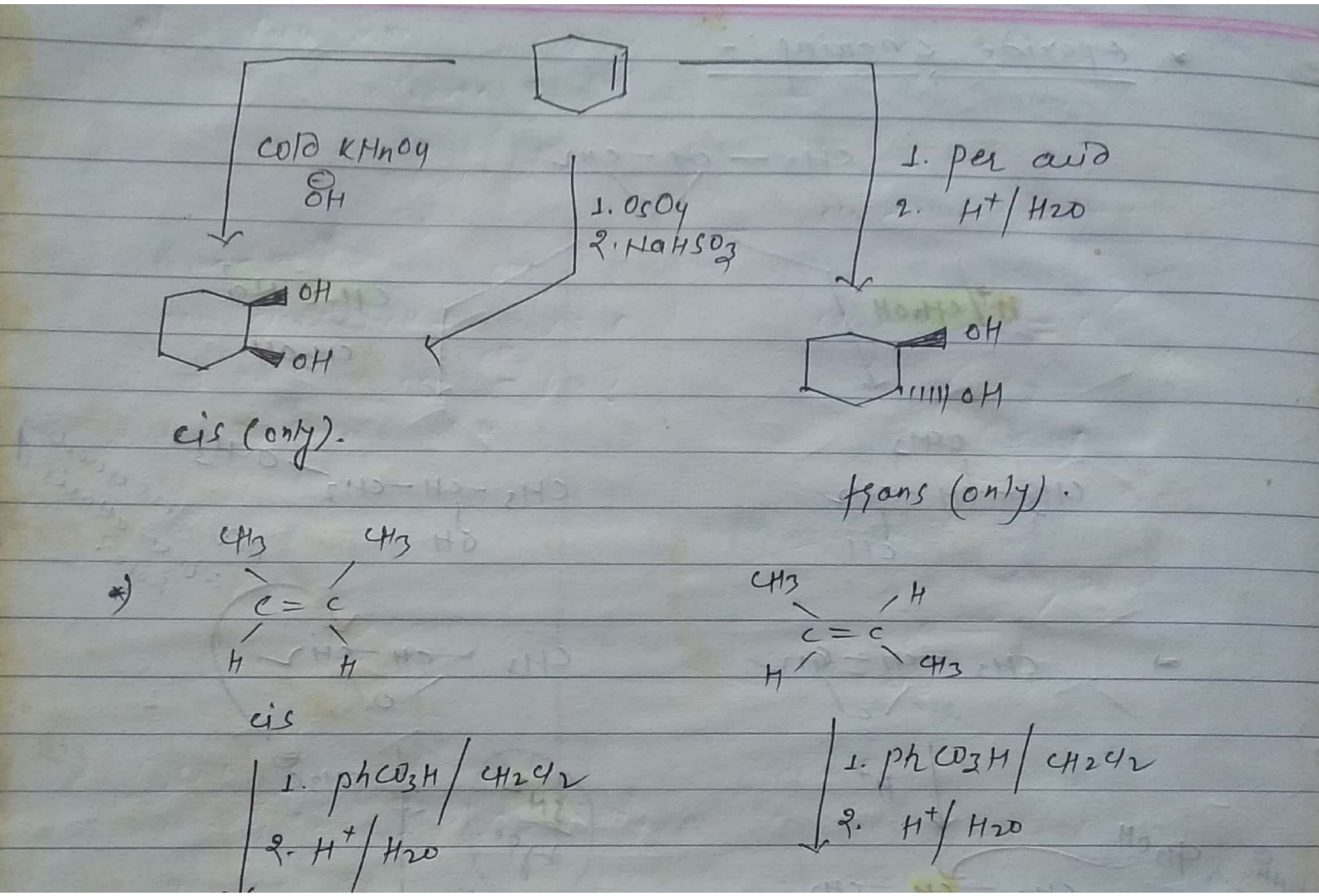
* Epoxide opening :-



Acid - catalysed is S_N1 type and
base - catalysed is S_N2 type.



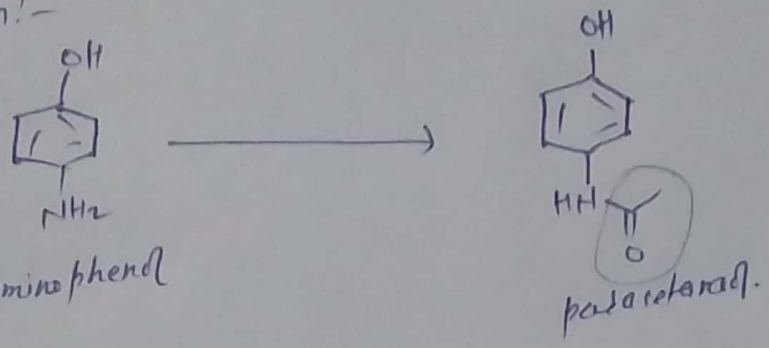
Hydroxylation via epoxidation is an anti addition.



⊛ Synthesis of paracetamol.

Paracetamol can be synthesized from p-aminophenol.

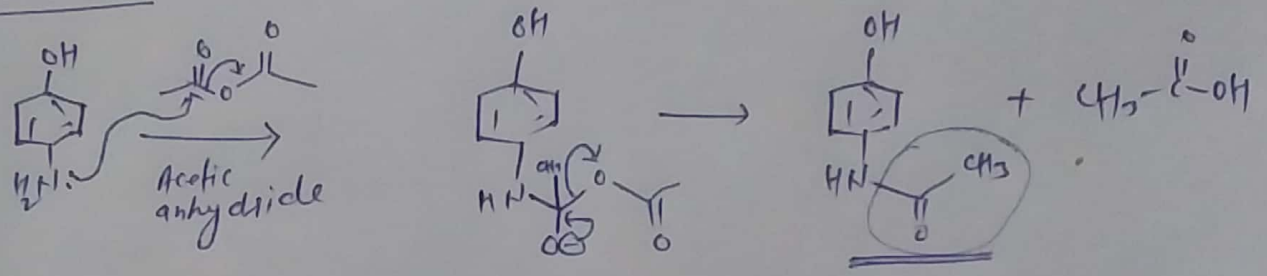
Reaction:-



p-aminophenol

paracetamol.

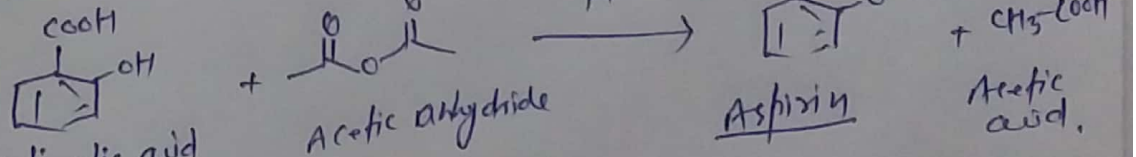
Mechanism:-



Uses:- It is antipyretic and analgesic
- used as medicine/drug. when you have fever
- But now it's banned in developed countries due to other side effects.

⊛ Synthesis of Aspirin:-

Reaction:-



Mechi:-