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Class: S. Y. B. Sc, Paper-II course-302
Sem.-III (First term )
Name of Paper: Inorganic and organic Chemistry
According to the new revised syllabus of Savitribai
Phule University from June 2020
Name of Teacher: Prof. Kolekar S.S.
Topic-Alkyl and Aryl halides

## Nucleophilic Substitution Reaction of order two. i.e. $SN^2$

It is nucleophilic substitution reaction follows second order because the rate of reaction depends upon the concentration of both methyl bromide and hydroxyl ion gives inversion product, The polar solvent decreases rate of $SN^2$and strong nucleophile favour the reaction. The reactivity sequence is primary carbocation > secondary carbocation> tertiary carbocation.

**e.g. Methyl bromide undergoes hydrolysis aq. NaOH to gives methyl alcohol.**

**Kinetics-** The kinetics study shows that the rate of the reaction is proportional to concentration of substrate and nucleophile (i.e. it is second order kinetics and follows the bimolecular reaction)

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$$\textbf{Rate} \;\; \alpha \;\; C_{\text{Methyl bromide}} \times C_{OH^-}$$

$$\textbf{Rate} = K_2 \; C_{\text{Methyl bromide}} \times C_{OH^-}$$

$K_2$ is called as rate constant of second order reaction.

Since the rate of the reaction is dependent only on the slow step known as rate determining step. The departure of leaving group and attack of nucleophile is simultaneous. The C-Br bond start breaking at the same time when the C-OH bond start form. The bond breaking is endothermic and the bond formation is exothermic., the energy given out in bond formation is utilized for bond breaking process.

Methyl bromide undergoes hydrolysis aq. NaOH to gives methyl alcohol.

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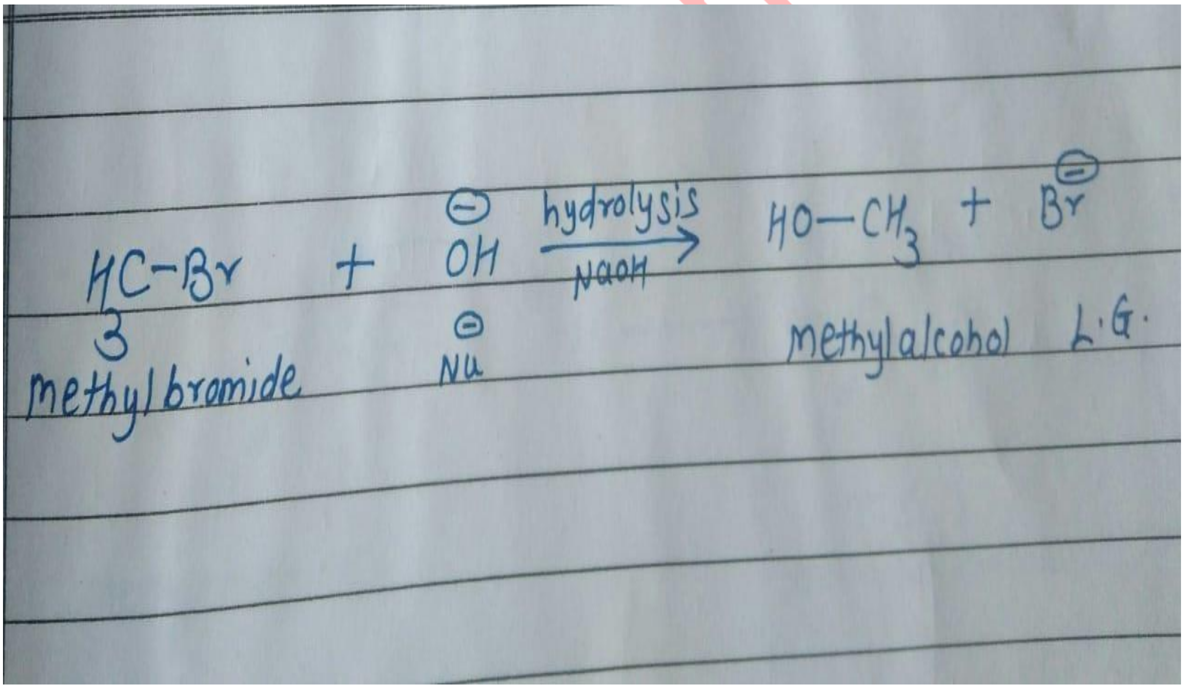
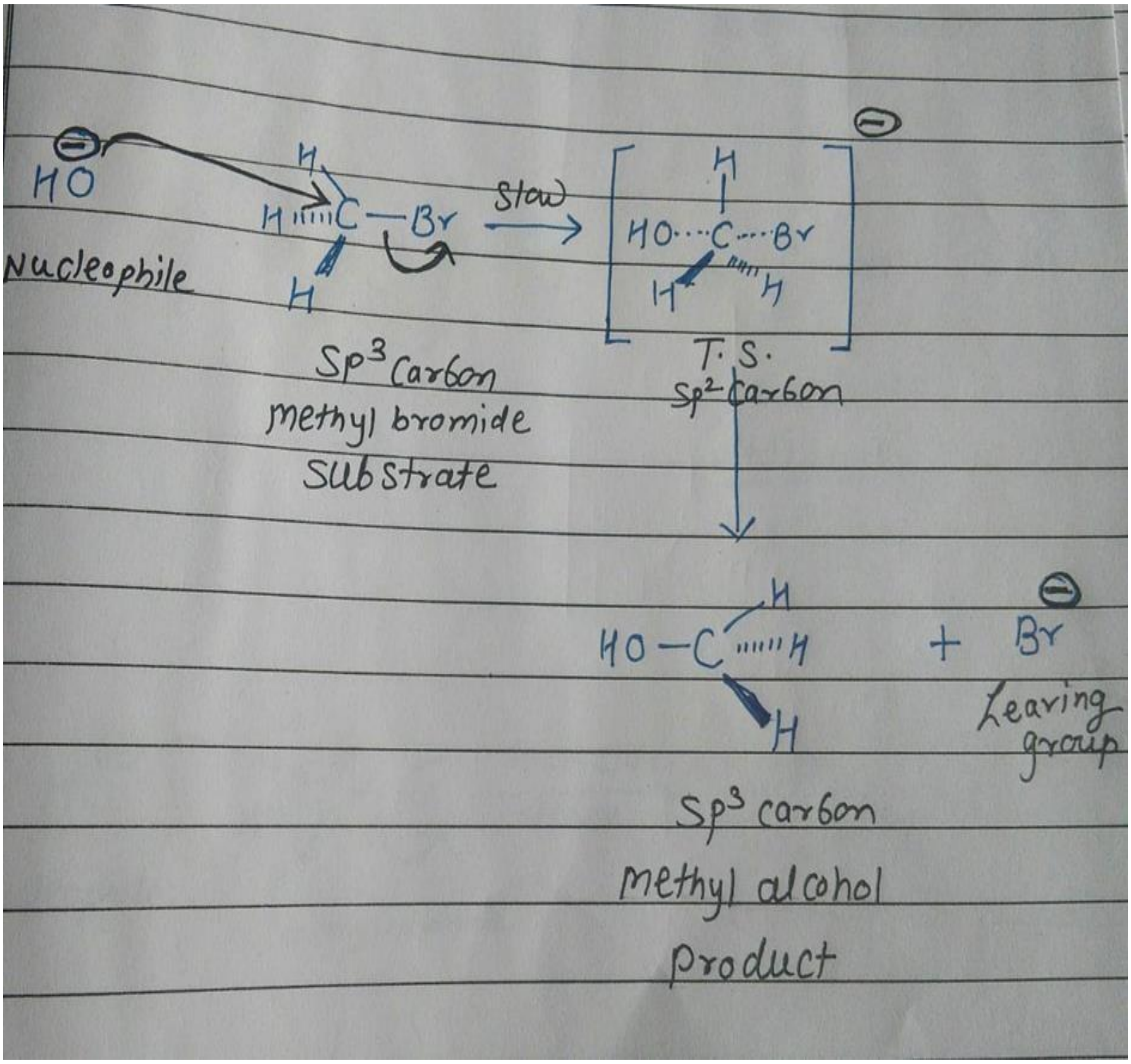


**proposed mechanism-**

X is leaving group like halogen may bromide, chloride and nucleophile is $OH^-$

e.g. The methyl bromide undergoes hydrolysis aq. NaOH to gives methyl alcohol.



In SN$^2$reaction the T.S, the carbon atom has five bonded to five groups. i.e. three hydrogen atoms-Br and -OH.

The –Br and -OH are located as far apart as possible and three hydrogens, carbon lie in the same plane with bond angle 120$^{o.}$ The nucleophile and leaving group are in plane perpendicular to the three hydrogen atoms. The T.S. having higher energy and breaks to give product. The C-Br bond start breaking at the same time when the C-OH bond start forming. The bond breaking is endothermic and the bond formation is exothermic. ,the energy given out in bond formation process is utilized for bond breaking process

In T.S. hybridization of carbon changes from sp3 to sp2. This mechanism SN$^2$ is term as bimolecular as in rate determining step collision of two species methyl bromide and OH$^-$ is take place.

In SN$^2$ reaction the departure of leaving group like –Br and attack of nucleophile OH$^-$is simultaneous. The C-Br bond start breaking at the same time when the C-OH bond start forming. The bond breaking and the bond formation are concerted.

**The SN$^2$ Reaction -Stereochemistry**

In SN$^2$ reaction the T.S, the carbon atom has five bonded to five groups. i.e. three hydrogen atoms, -Br and -OH. The -Br and -OH are located as far apart as possible and three hydrogens, carbon lie in the same plane with bond angle 120$^o$The nucleophile and leaving group are in plane perpendicular to the three hydrogen atoms. (having higher energy)

In T.S. hybridization of carbon changes from sp3 to sp2 and breaks to give the product having hybridization with SP$^3$

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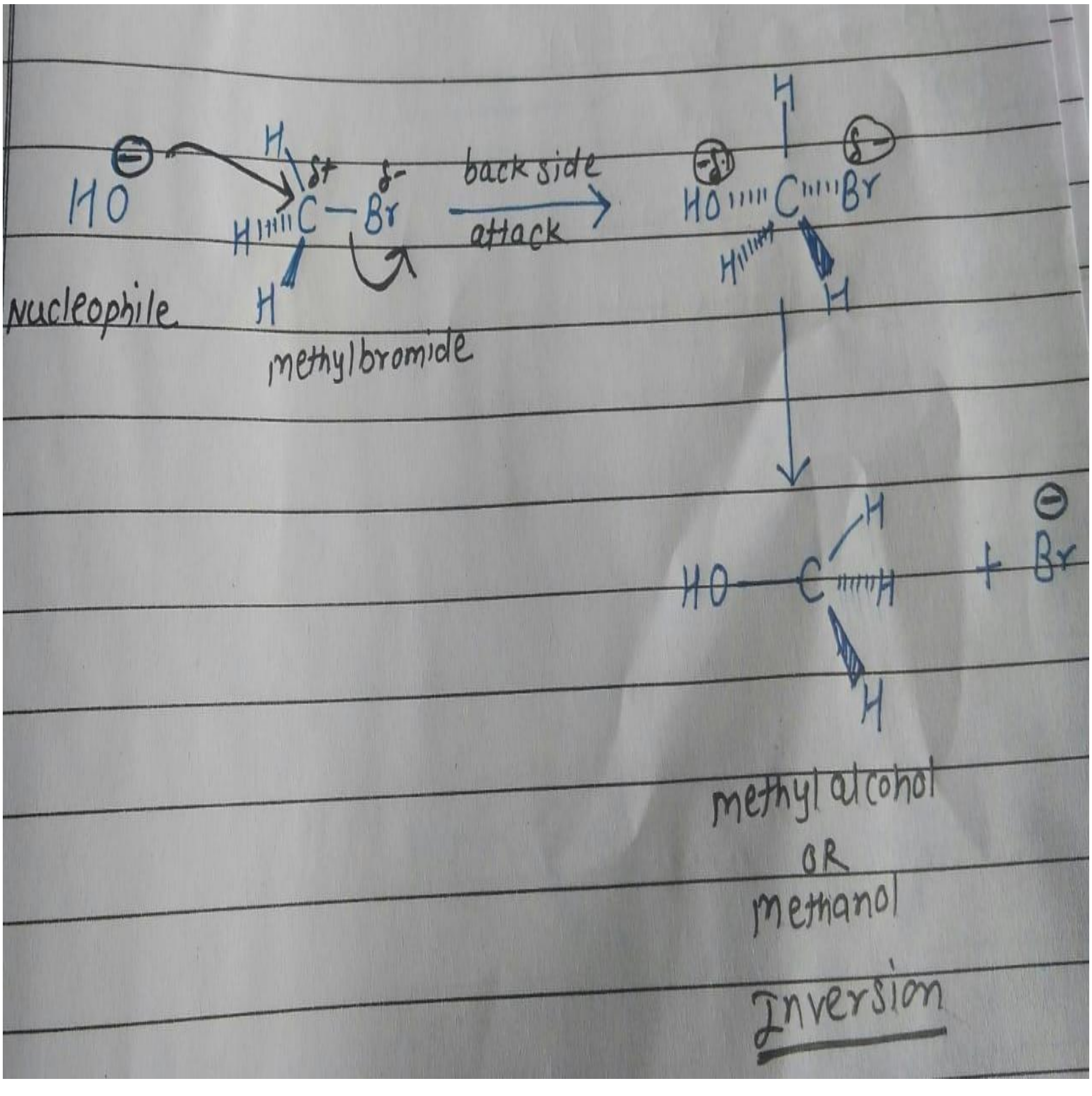
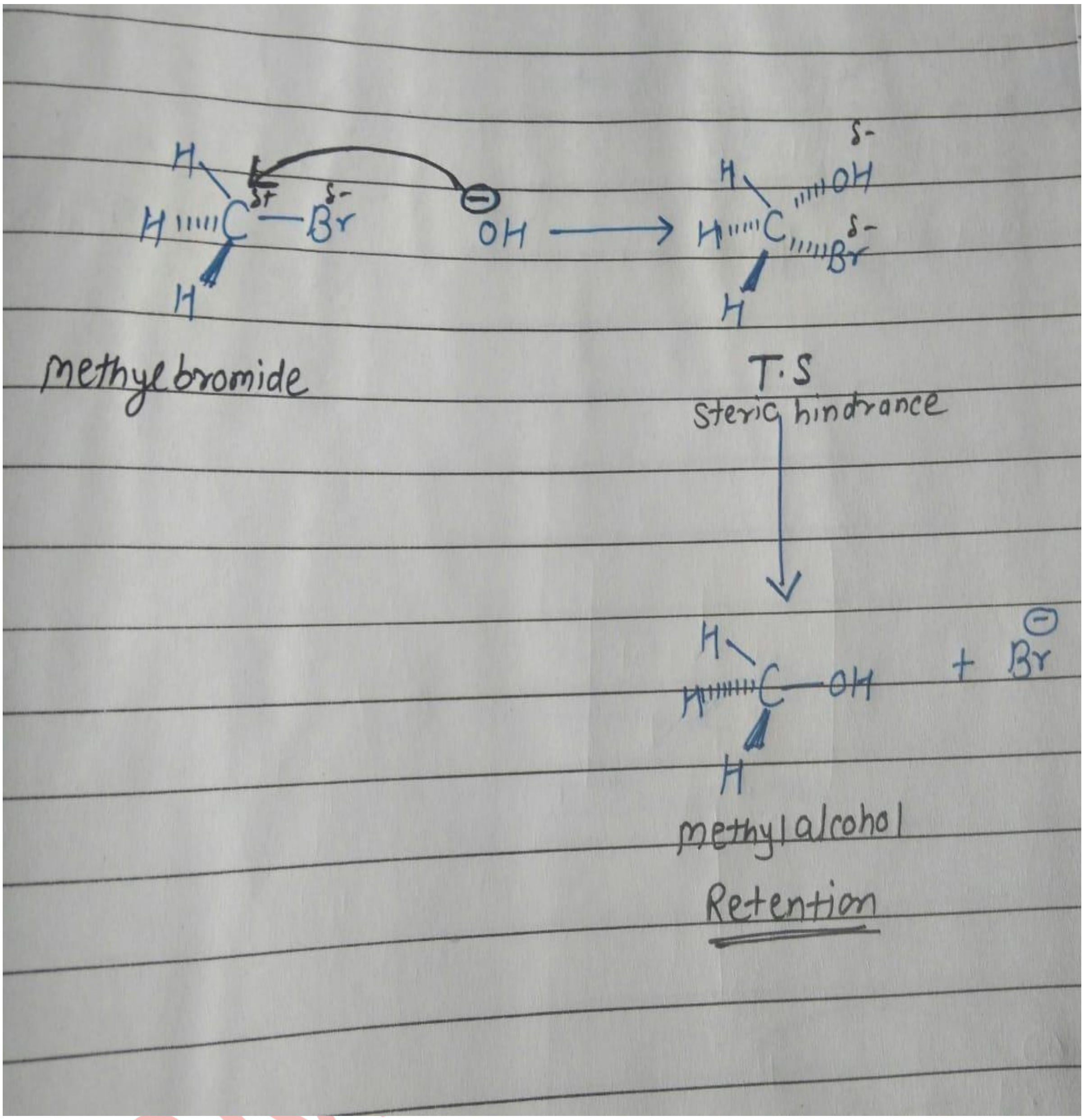
In $SN^2$the backside attack of nucleophile is preferred because of minimum steric interaction and require minimum energy.

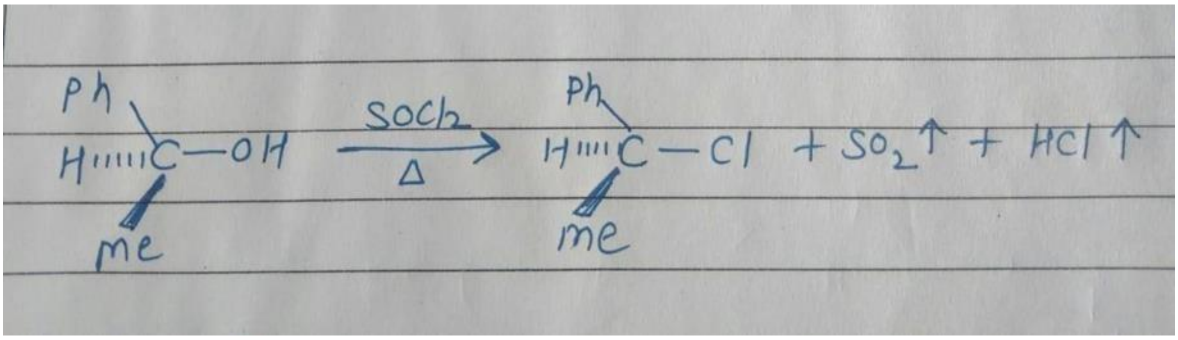
If nucleophile approaches from front side of C-Br bond it will have lot of steric interactions and dipole repulsion so back side attack of nucleophile of C-Br bond is take place gives product with inversion configuration.



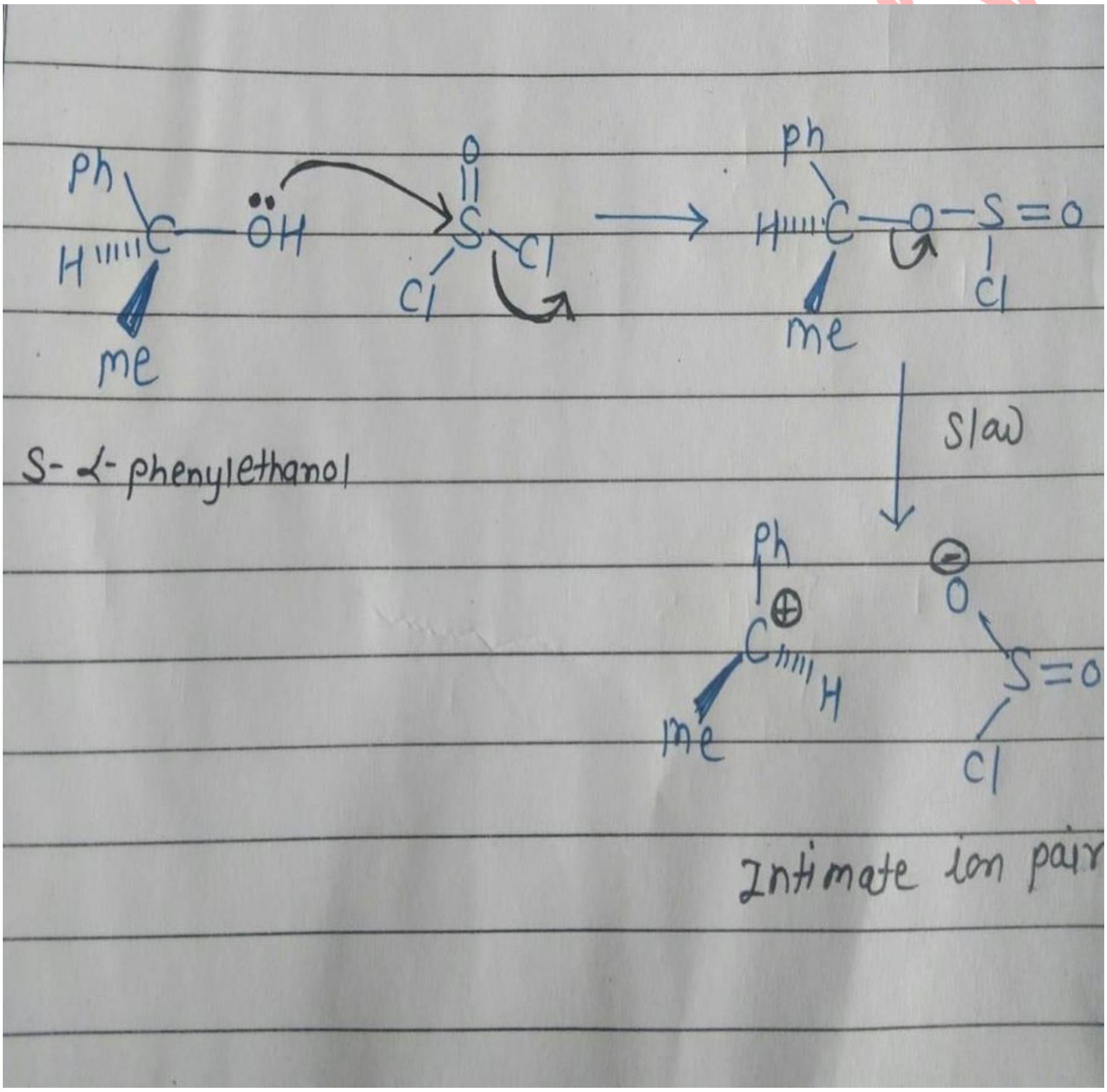


**Nucleophilic Substitution internal. i.e. SNi –**

It is substitution nucleophilic internal, when thionyl chloride allow to react with alcohol under anhydrous condition it gives alkyl chloride with retention configuration. when same reaction is carried out the presence of pyridine result in inversion of configuration



## Proposed Mechanism



## Elimination Vs Substitution

For elimination reaction – the substrate should have the good leaving group and reagent should be basic in character while for substitution reaction the substrate should have the good leaving group and reagent should be nucleophilic in character

All the elimination reaction can be compare with substitution reaction

**$SN^2$ and $E^2$ reaction**

When reagent is basic in character elimination is take place while when reagent is nucleophilic in character then substitution is take place

The % of elimination reaction increases as primary alkyl halide to secondary alkyl halide and secondary alkyl halide to tertiary alkyl halide

The substrate is more crowded elimination increases because if substrate is more crowded attack of nucleophile at $\alpha$-carbon atom from back side in $SN^2$ reaction becomes difficult. If substrate is crowded then there is no relief in steric strain as substitution take place while in elimination, hybridization changes from $SP^3$ to $SP^2$ so there is relief in steric strain

So for bimolecular substitution and elimination reaction more crowding in the substrate the % of elimination increases

2) Stability of alkene formed – The product form due to elimination reaction is alkene, if stability of the alkene increases the elimination reaction is preferred

3) Nature of leaving group – As the size of leaving group increases, the % of elimination increases

Highly crowded leaving group favor elimination over substitution reaction

4) Solvent polarity – The polarity of solvent decreases favor the elimination reaction.

Unimolecular reaction – $SN^1$ and $E^1$

For $SN^1$ and $E^1$ the rate determining step is slow step in which carbocation is formed as intermediate

1) The reagent acts as nucleophile then it is substitution reaction and
2) The reagent acts as base the it is elimination reaction.

The $SN^1$ and $E^1$ reaction if crowding increases, substrate changes from primary to secondary and secondary to tertiary. The rate of $E^1$ is greater than $SN^1$ because the intermediate obtain is carbocation s more stable due to steric interaction attack of nucleophile becomes less so rate of $SN^1$is slow while in $E^1$ abstraction of β hydrogen by the base is take place which is away from the carbocation so there is no steric interaction so rate of E1 is fast

The overall order of elimination and substitution reaction as follow $E^1>SN^1>E^2>SN^2$

According to the new revised choice based credit system syllabus of Savitribai Phule Pune University from June 2020, Text book of Inorganic and organic chemistry for S.Y. B.Sc. course (CH-302 ), Sem-II Manali Publication and google images