Neighbouring group participation (NGP):

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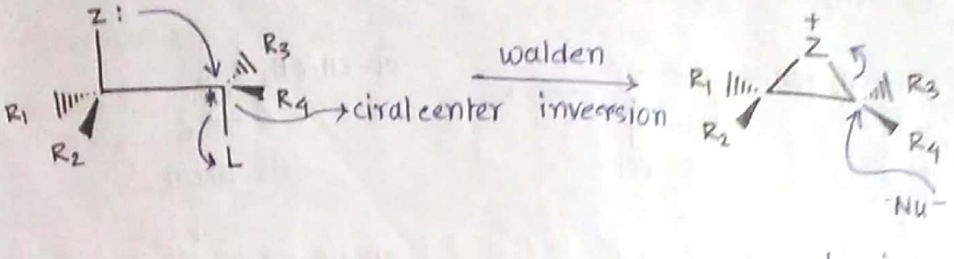
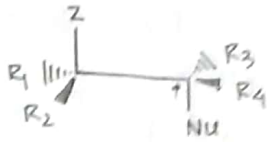
Sem-2 cc-4

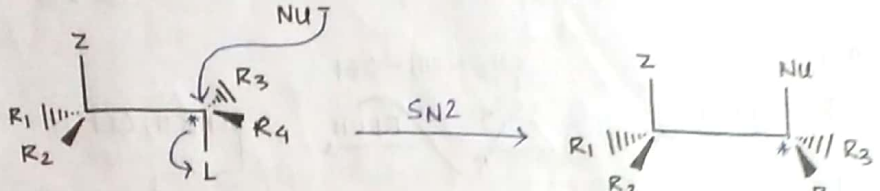


↓ inversion

Double inversion = Retension

Retension of the configuration at the ciral center.





NGP reaction is always faster than the normal S_N2 reaction due to the following reason ——

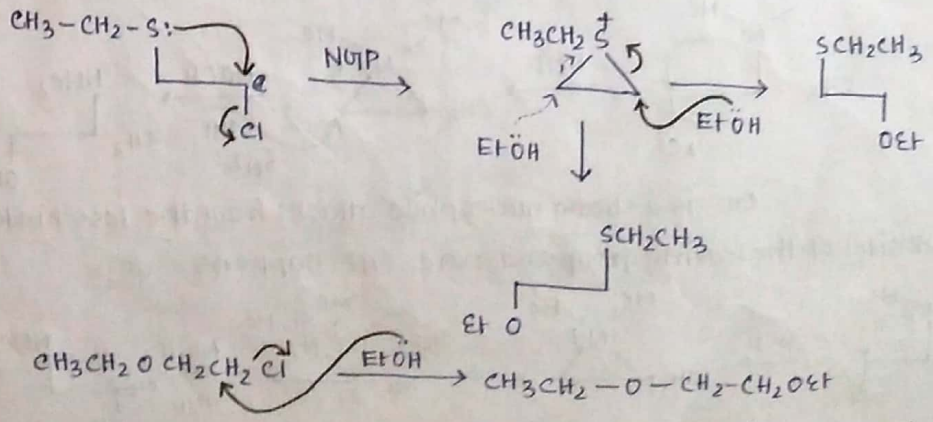
(i) The reason attack by 'Z' faster than the Nu^- (external Nu) is that the group is easily available. On order for nucleophile to react it must collide with the substrate but z is equi(easily) avaiable by the virtue of it's position.

(ii) Reaction between substrate and external nucleophile involves large decrease in entropy. Since, the reactants are less free in the transition state than the before. The reaction of z involves a much smalledr loss of entropy of the activation. That is why NGP reaction are faster than normal S_N2 reaction.

Example :

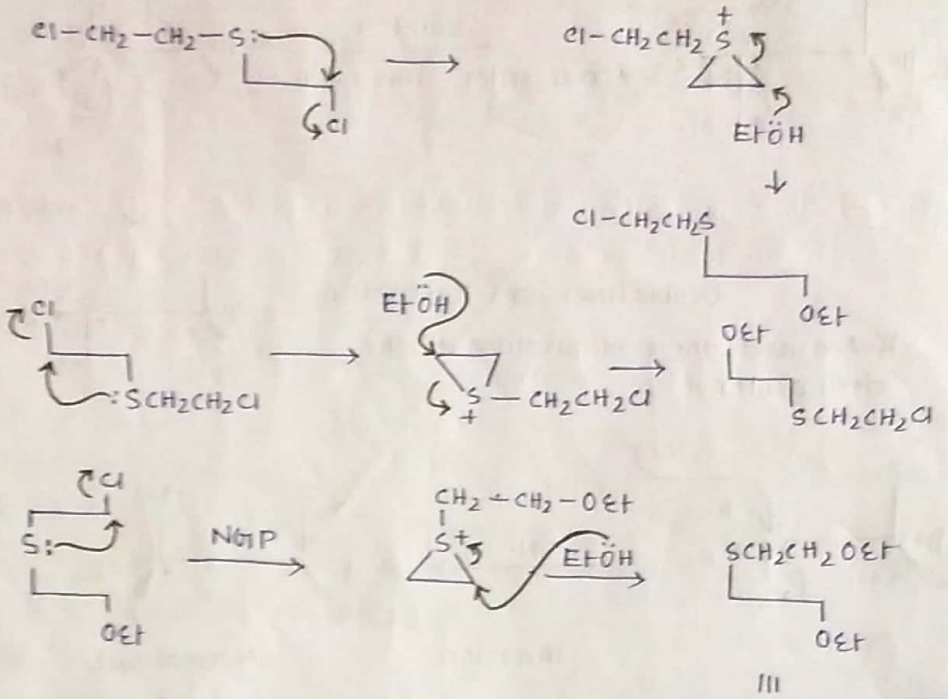
1. $CH_3-CH_2-S-CH_2-CH_2-Cl \xrightarrow{EtOH}$ fast

$CH_3-CH_2-O-CH_2-CH_2-Cl \xrightarrow{EtOH}$ slow



Due to greater electronegativity of 'O' atom than 'S' it cannot act as NGP.

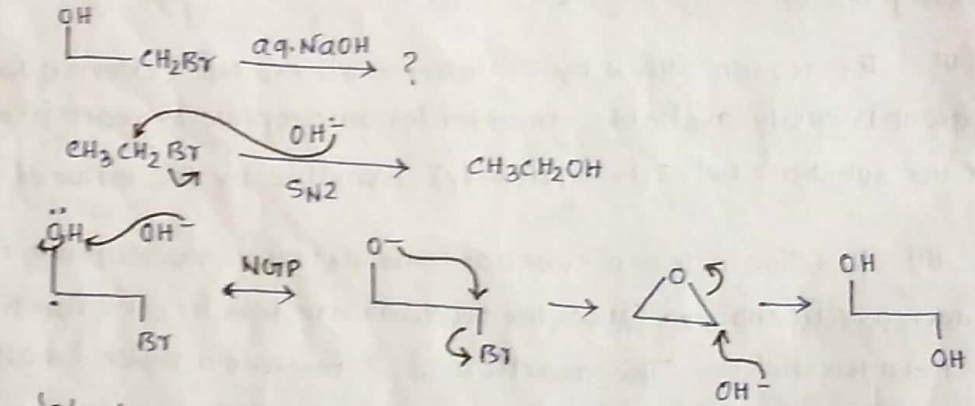
2. $Cl-CH_2-CH_2-S-CH_2-CH_2-Cl \xrightarrow{EtOH}$ very fast



III

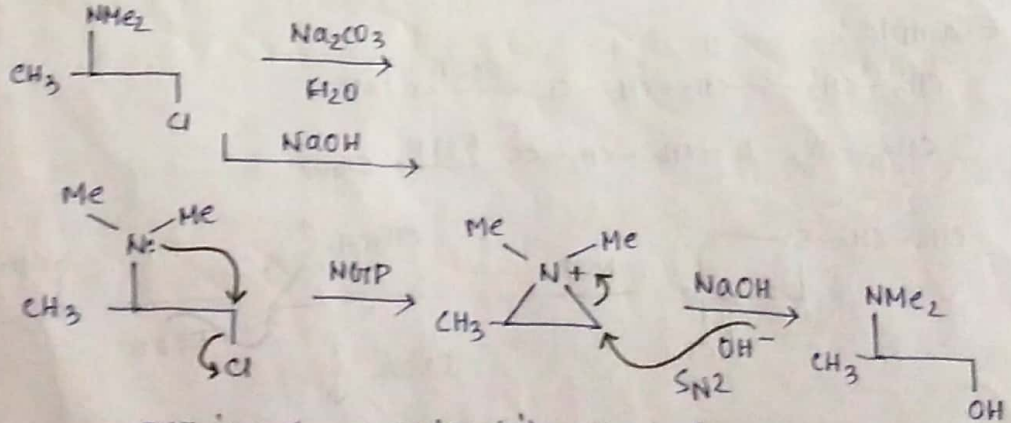
$EtO\,CH_2CH_2\,S\,CH_2CH_2OEt$.

3. $CH_3CH_2Br \xrightarrow{aq.NaOH}$?

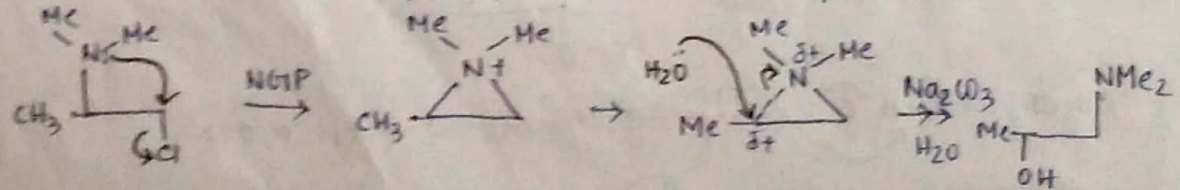


'O' acts as NGP

4. 'N' acts as NGP



OH^- is a strong nucleophile attacks from the less hindered side (back side) of the leaving group and pure S_N2 happens



Here T.S is loose S_N2 T.S and the partial '+'ve charge is stabilized by the

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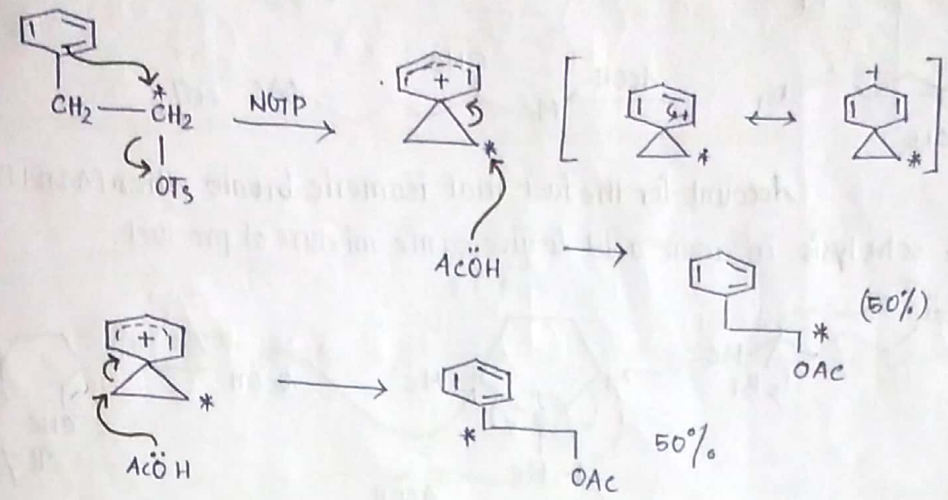
Sem-2 cc-4

+9 effect of the -Me group.

Phenyl group acts as NGP:

1.



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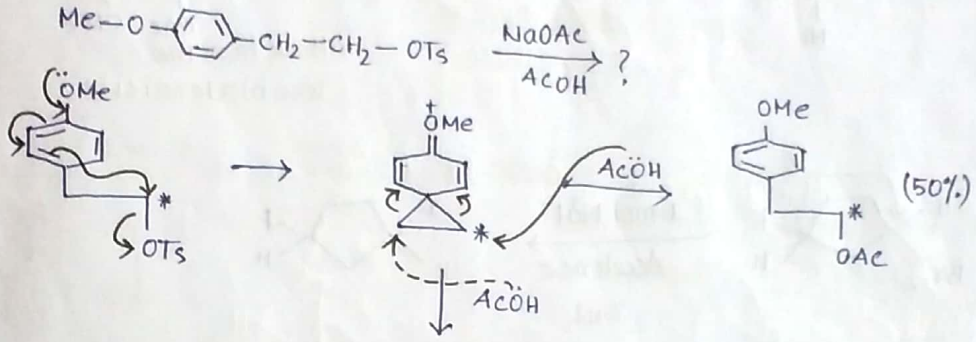

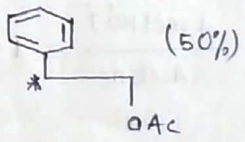

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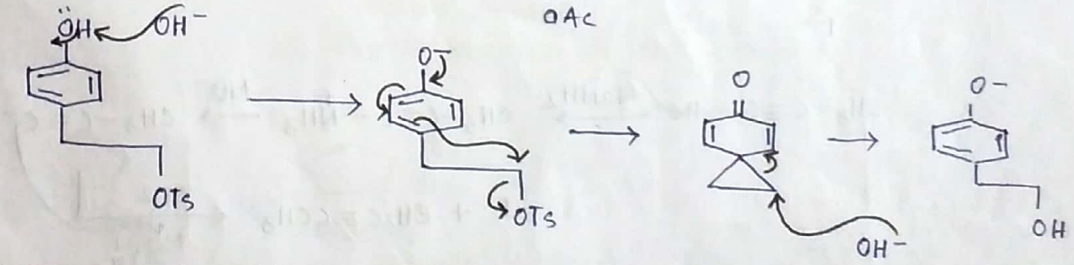
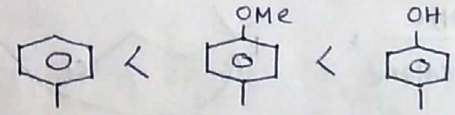
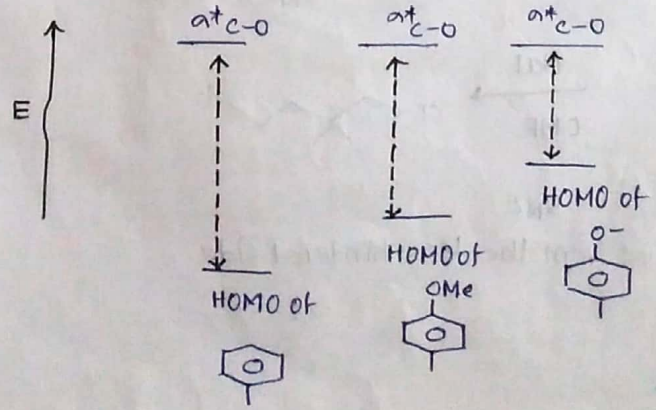


NGP Order: (reactivity increases)



→ +R effect increases



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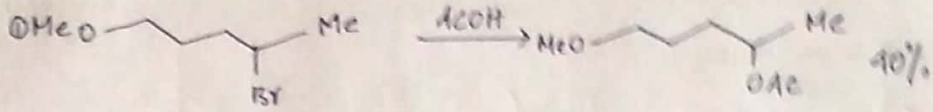
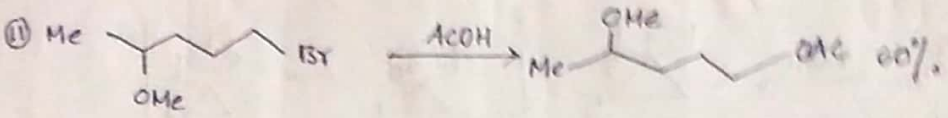
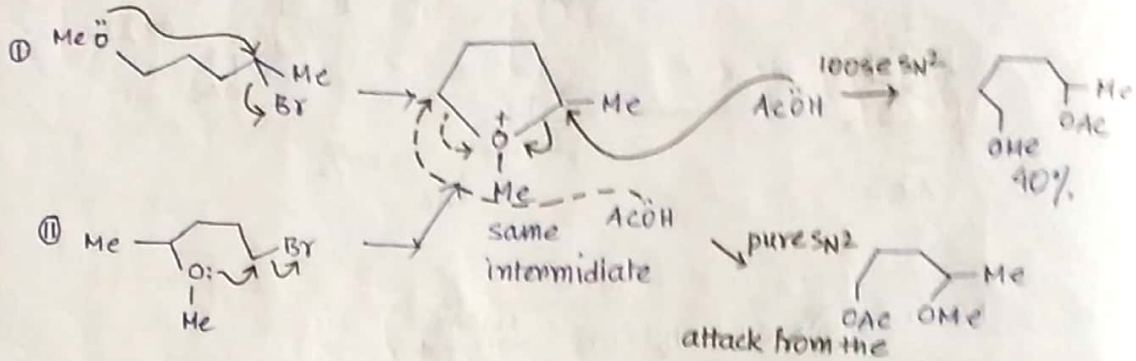


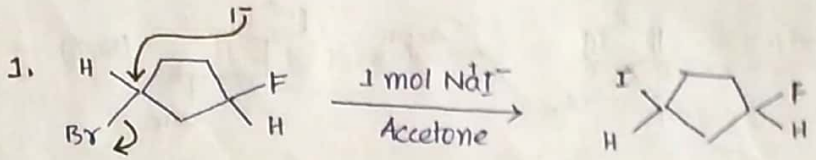
(II)



Account for the fact that isomeric bromo ether (A and B) undergoes solvolysis in acetic acid to give same mixture of product:



1.



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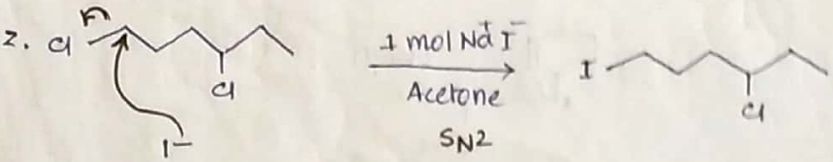

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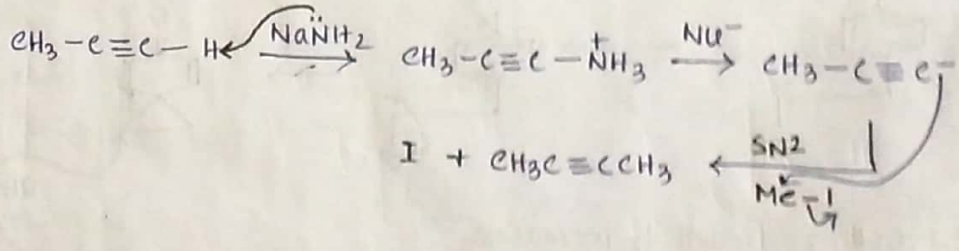

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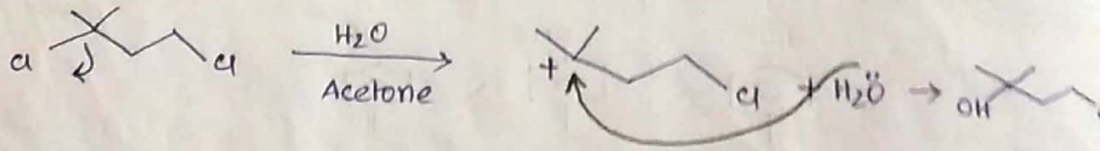
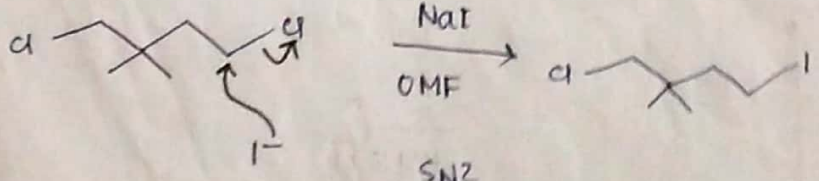


SN1 condition

5.



Nu⁻ attacks from the less hindered side.

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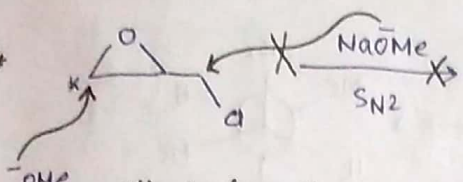
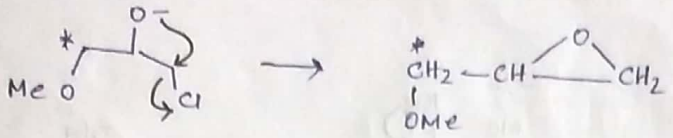
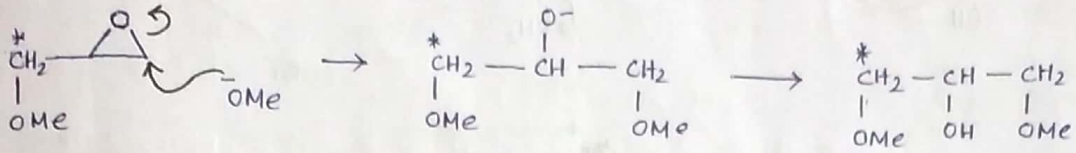


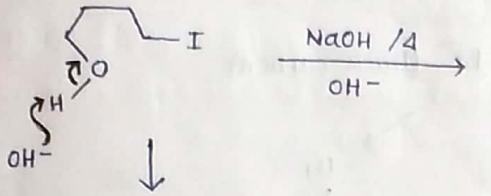
attacks from the less hindered side of the substrate.

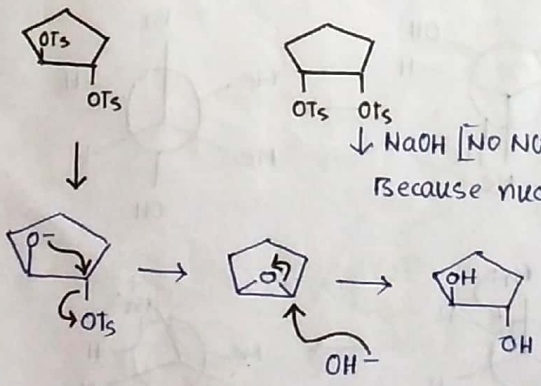


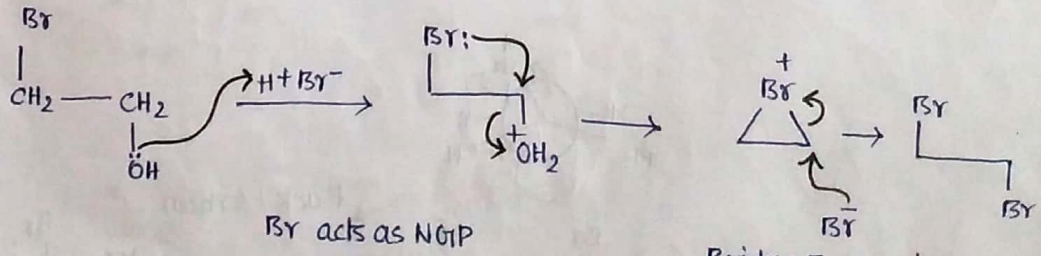
If we can use two mole NaOMe then the reaction will be —

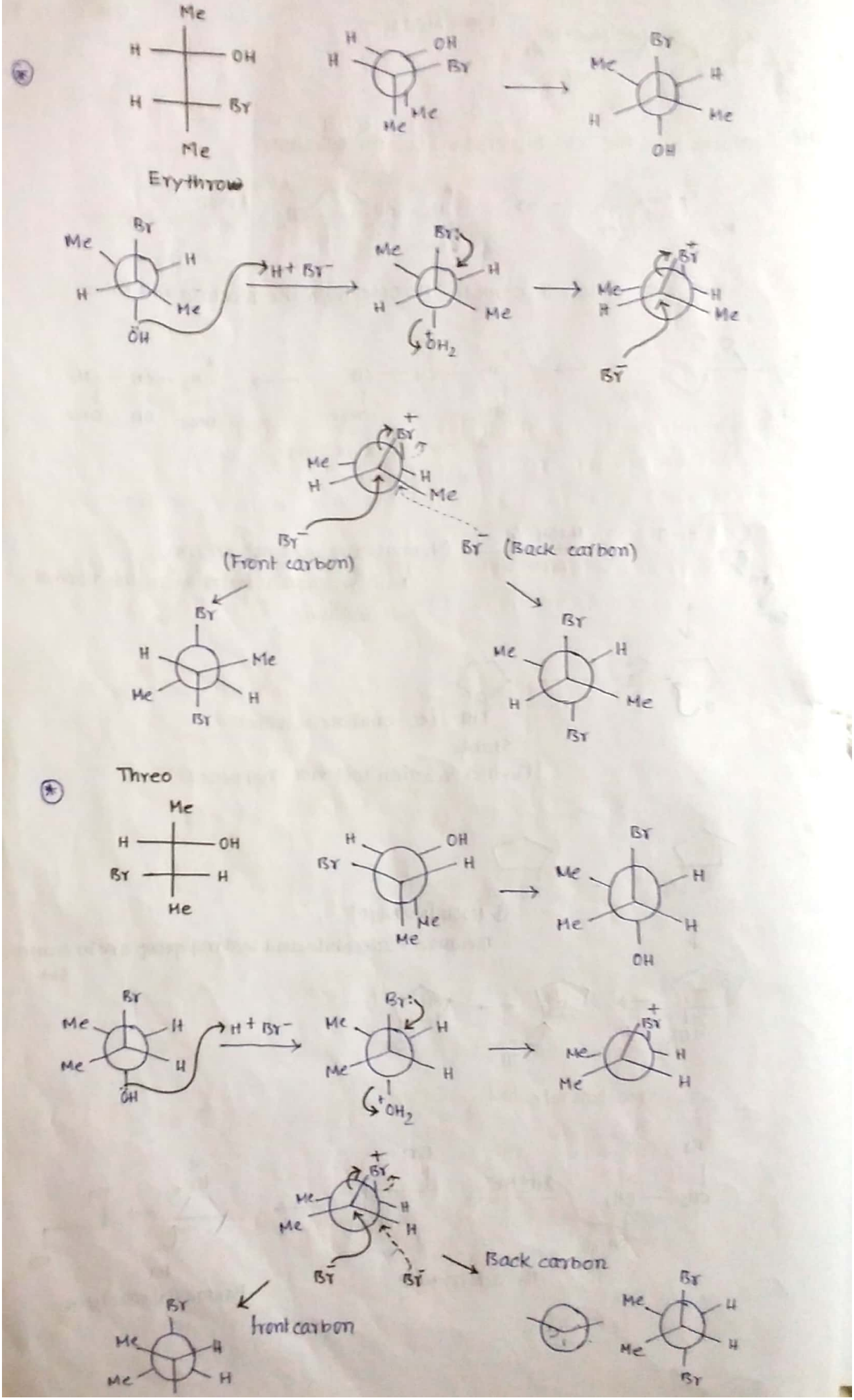


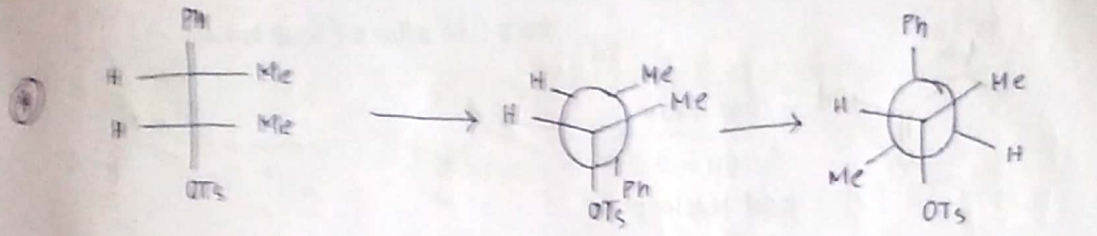
At first epoxide ring will cleavage

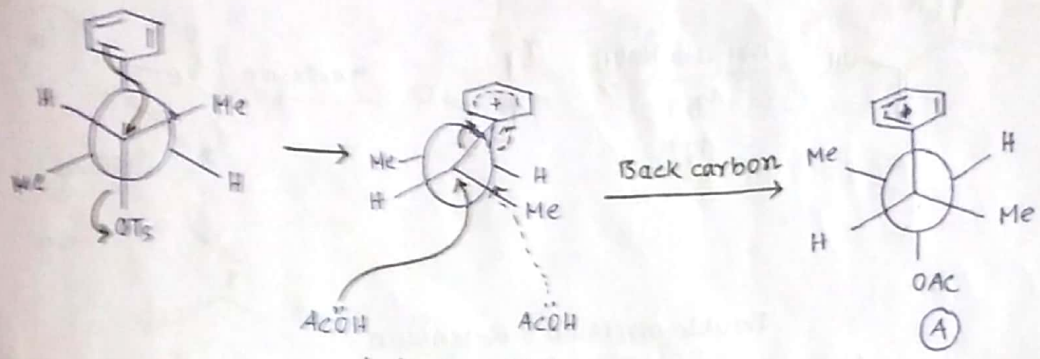






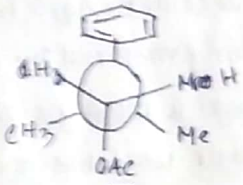






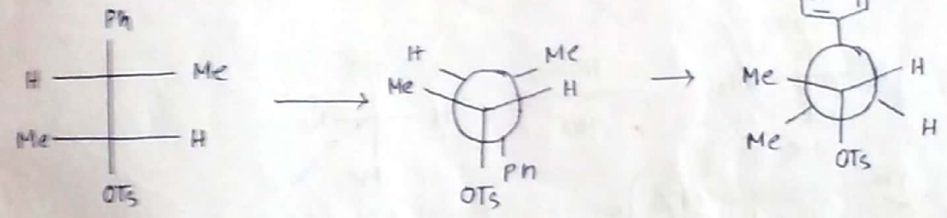
(A)

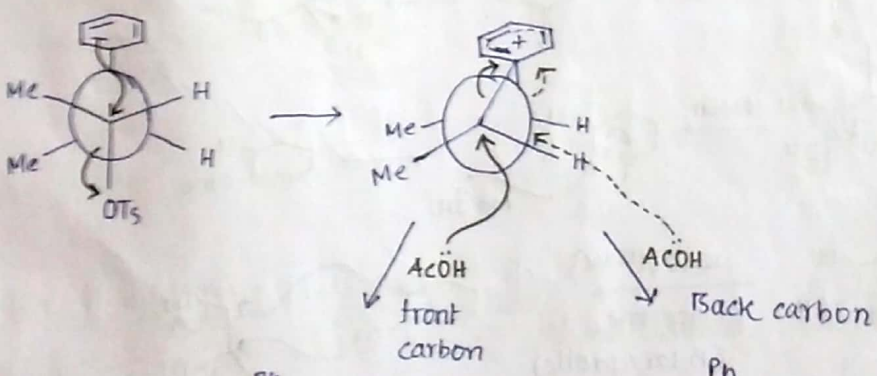
front carbon

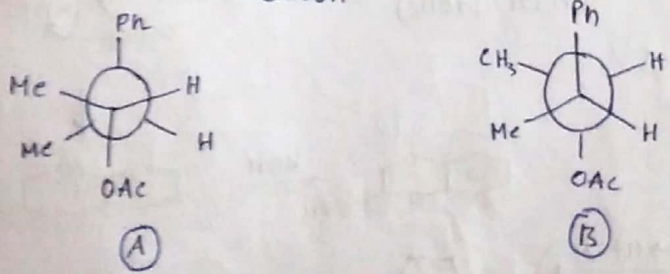


(B)

A and B are HOMOMER

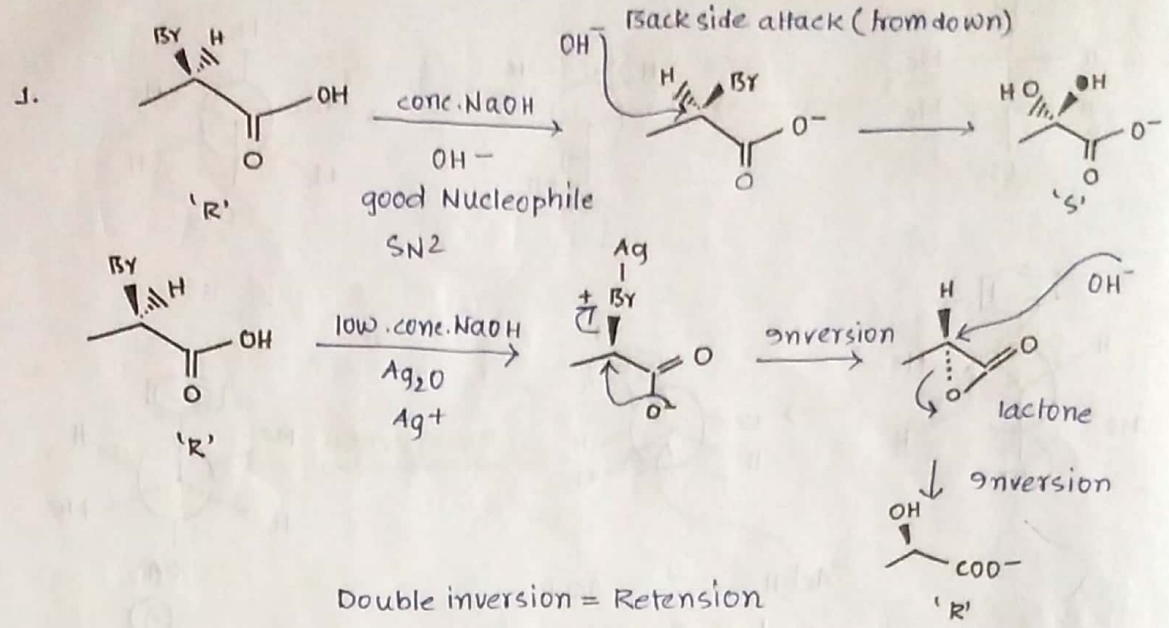






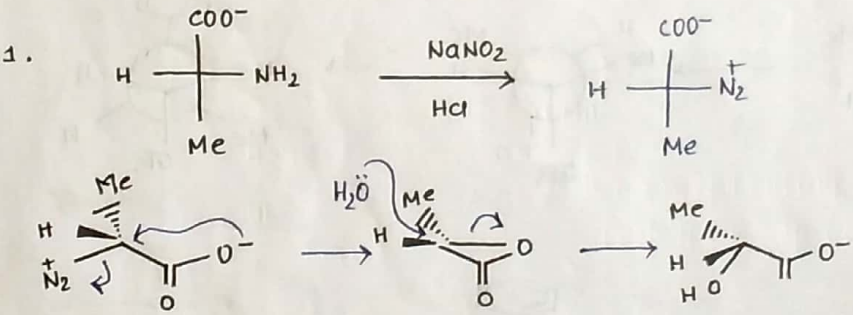
(A) (B)

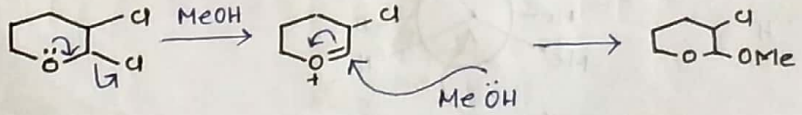
A and B are enantiomer.

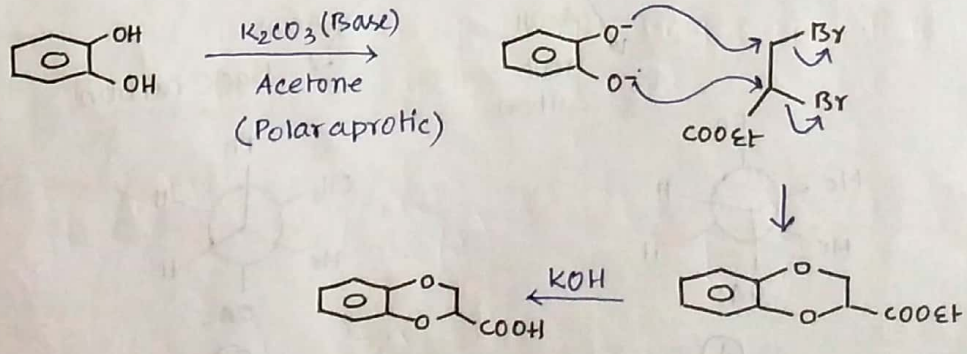
1. 

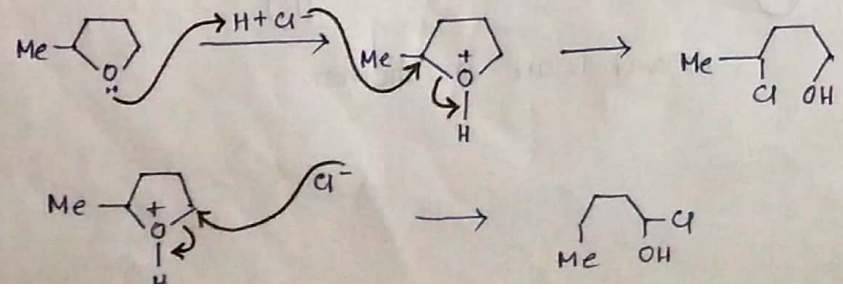
Double inversion = Retension

Ag_2O at low concentration of NaOH R acid is obtained. There is overall retension of configuration at the ciral center. Ag_2O is important because Ag_2O encourage the ionization of the starting meterial by acting as a halogen selective lewis acid but the trouble is that without neighbouring group participation the cation here would be rather unstable and CO_2^- acts as a NGIP in the departure of the Br^- and forming Lactone.

1. 

2. 

3. 

4. 

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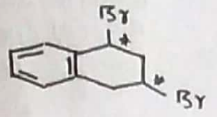
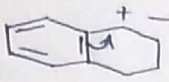
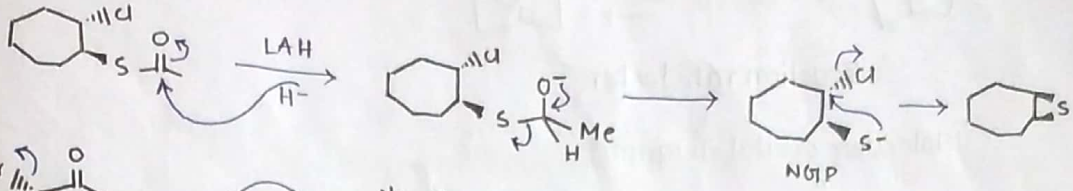
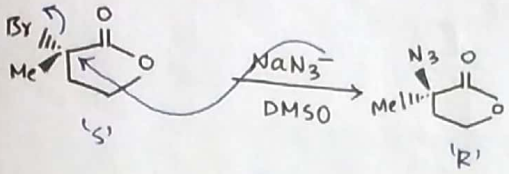
Sem-2 cc-9

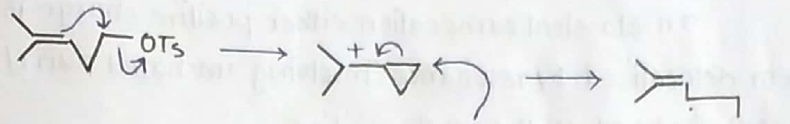
5.  — Which position is more reactive?

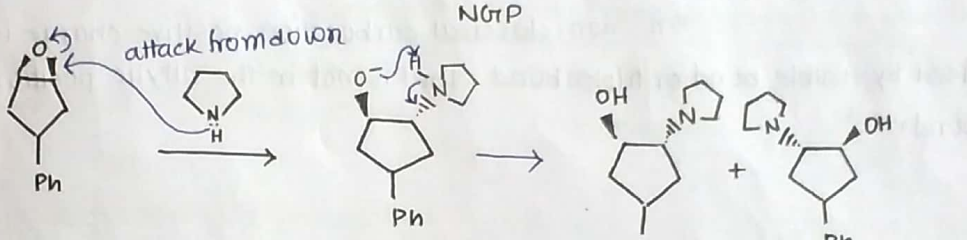
 → 2° Benzylic (reactive)

6. 

7. 

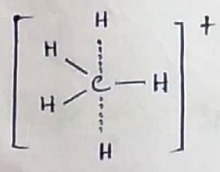
Pure S_N2

8. 

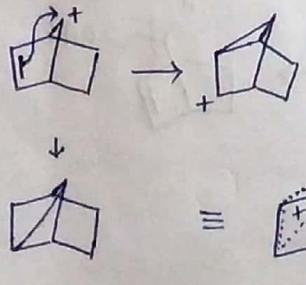
9. 

Enantiomer
Resimic mixture
Optically inactive

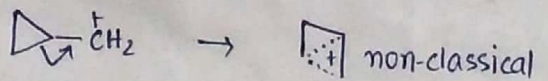
Non classical carbocation :



 non classical carbocation



 nonclassical carbocation

 non-classical

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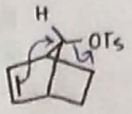
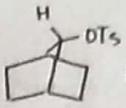
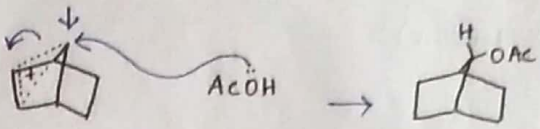
B.Sc(H) CHEM
Sem-2 CC-4

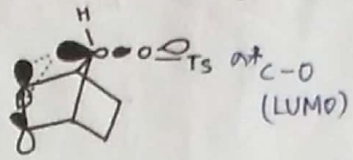



Normal S_N2



Reaction rate faster

Molecular orbital diagram:



π (HOMO)

In classical carbocation either positive charge is localised one carbon atom or delocalised by resonance involving unshared pair of electron or double bond or triple bond at the allylic position.

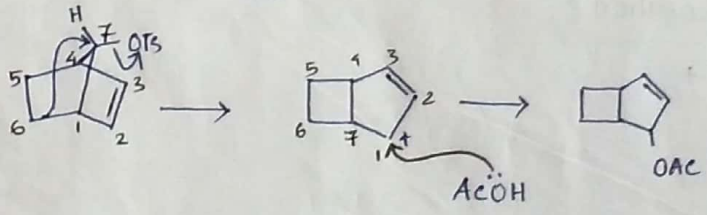
In non-classical carbocation positive charge is delocalised by double bond or triple bond, that is not in the allylic position or by σ - bond.

σ^* LUMO

π - bond

σ - bond

Better σ neighbouring group participation group.



Here σ bond acts a neighbouring group participating group NGP of π bond in greater than that of a bond.