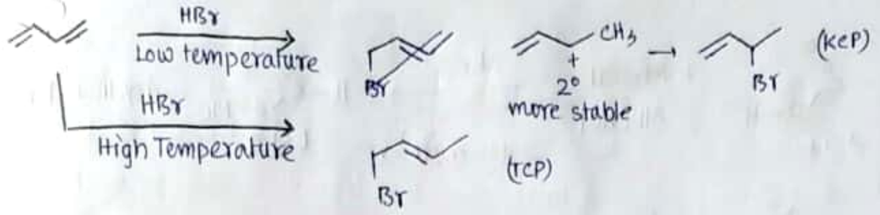
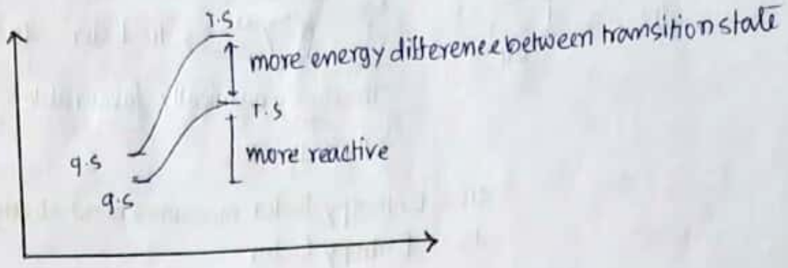
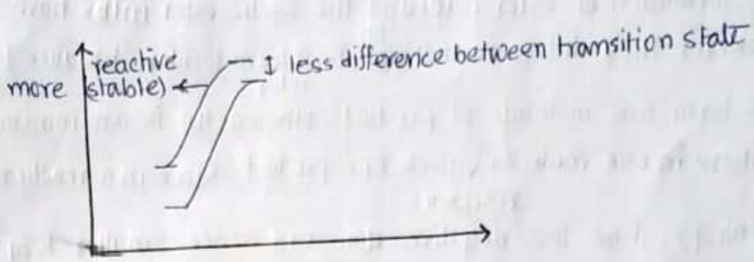
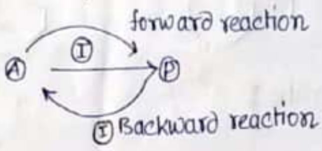
2.





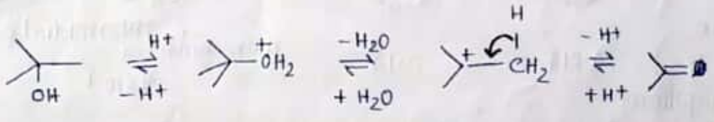


Microscopic reversibility principle:



In the course of a reaction the nuclei and electrons assume position that at each point correspond to the lowest free energy possible. If the

Example:

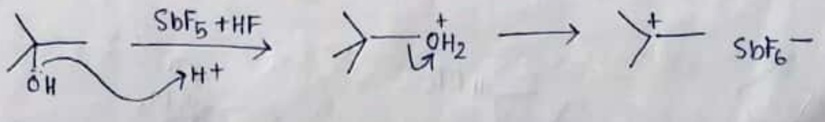


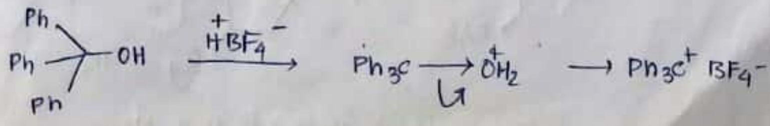
If the reaction is reversible, these position must be same in the reverse process. This means that the forward and the reverse reaction (same reaction condition) must proceed by the same mechanism. This is called Microscopic reversibility principle.

For example - If a reaction,

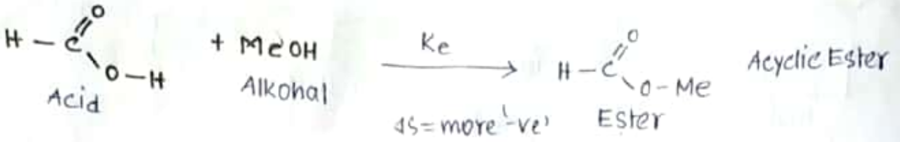
$$A \longrightarrow P$$

There is an intermidiate I, then I must also be an intermidiate in the reaction $P \longrightarrow A$.





(a)



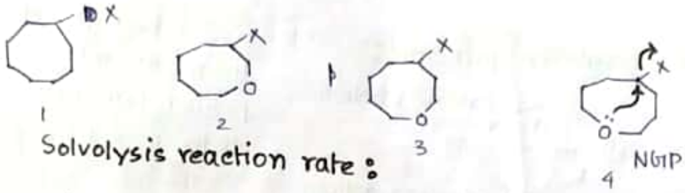
(b)

Thermodynamically favourable

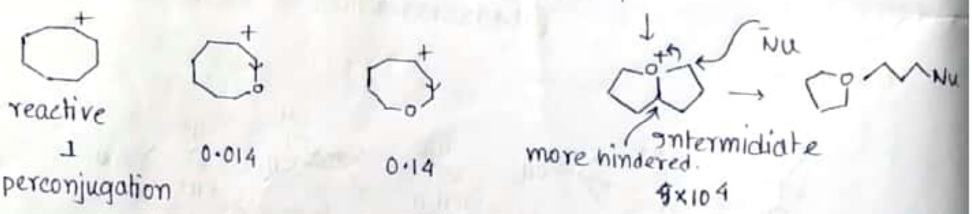
$\Delta G = \Delta H - T\Delta S$

ΔH = Enthalpy factor measures bond strength
ΔS = Entropy factor

Since, the change in the bonding in both the reaction are similar. The formation of ester in (a) and the cyclic ester in (b) have about the same ΔH. However, they differs in that (a) is ~~intra~~molecular because two molecules react to form one molecule of product. Whereas (b) is an intramolecular cyclaization where in one molecule gives one product. Since in a reaction a looses more entropy, it has less negative ΔG. and hence smaller Keq

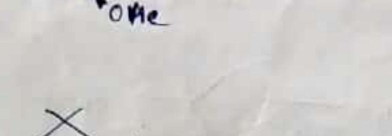


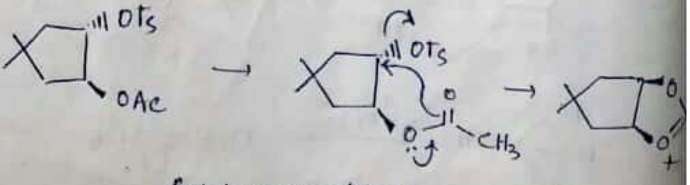
Solvolysis reaction rate :



4 > 1 > 3 > 2

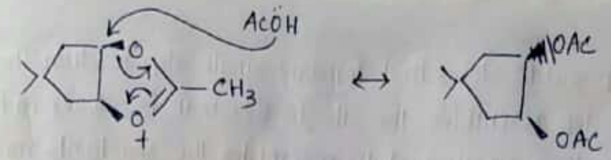
First three members expected to follows S_N1 solvolysis. The rate retardiation for the first three members can be attributed are due to the unfavourable 9nductive electron withdrawing effect of C–O bond. The last member undergoes solvolysis at a faster rate via NGP reaction.

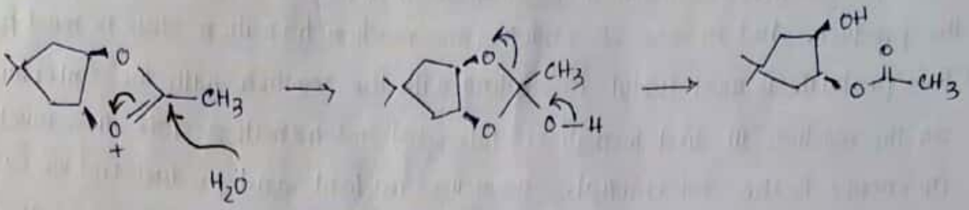




Acetate group acts as a NGP.

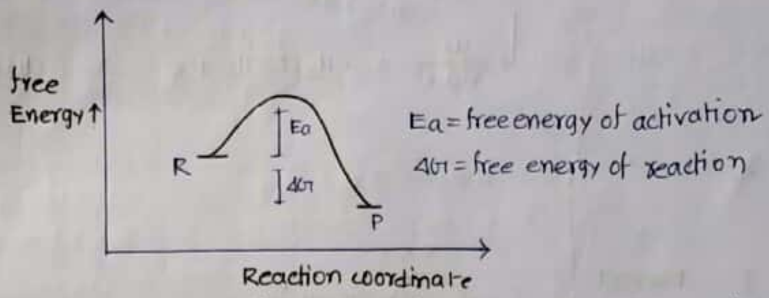
Rathin Jana
Organic Chem
Sem-2 CC-4





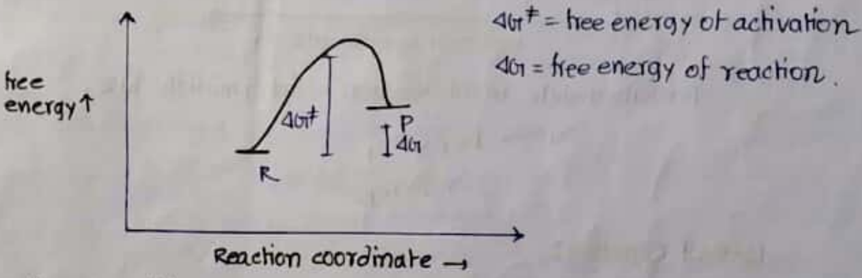
Hammond Postulate:

i.



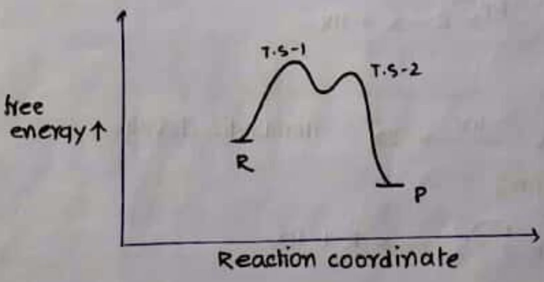
Here transition state is reactant like for exothermic reaction.

ii.



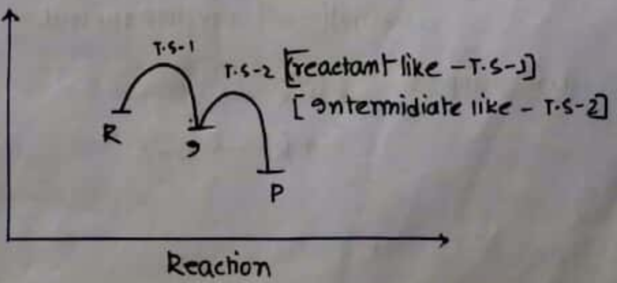
Here transition state is product like for endothermic reaction.

iii.



In this case Both the transition state are intermidiate like. This is true for unstable intermidiate.

iv.

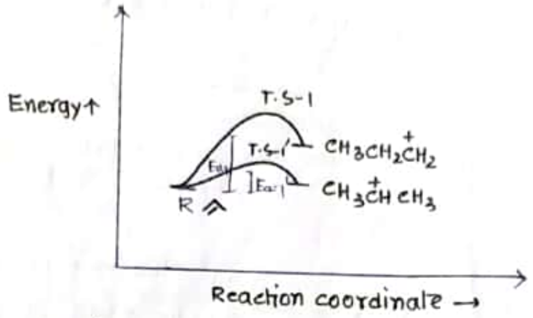


In this case intermidiate is highly stable. This is reactant like (T.S-1

Hammond postulate states that fop any single step reaction the geometr of a transition slate for that step resembles the site to which it is closer in free energ Thus for a exothermic reaction the transition state resembles the reactants more than the product. And in case of endothermic reaction transition state is ~~react~~ product lik This postulate is most useful in dealing with the reaction with the 9ntermidiate. In the reaction III first transition state and 2nd transition state lies much closer in energy to the 9ntermidiate. than the reactant and product and we can Predict that the geometry of the transition state is intermidiate like. than that of product.

$$CH_3-CH=CH_2 \xrightarrow[r.d.s]{HX} CH_3\overset{+}{C}HCH_3 + X^- \longrightarrow CH_3CH(Br)CH_3$$

$$\xrightarrow[r.d.s]{HX} CH_3CH_2\overset{+}{C}H_2 + X^- \longrightarrow CH_3CH_2CH_2Br$$



Transition state in this reaction is intermidiate like.

Since, $Ea_{1'} < Ea_1$

$ra_{1'} > ra_2$

Radical Reaction:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$R-H + X_2 \xrightarrow{h\nu} R-X + HX$$

chain initiation:

$$X-X \xrightarrow{h\nu} 2\dot{X}$$ Homolytic clevage

chain propagation:

$$R-H + X^{\cdot} \longrightarrow \dot{R} + HX$$

$$\dot{R} + X-X \longrightarrow RX + \dot{X}$$

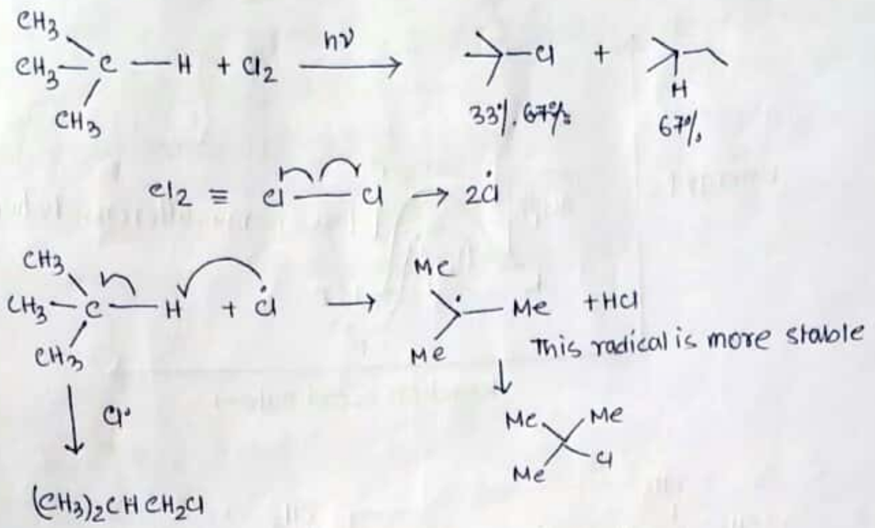
chain termination:

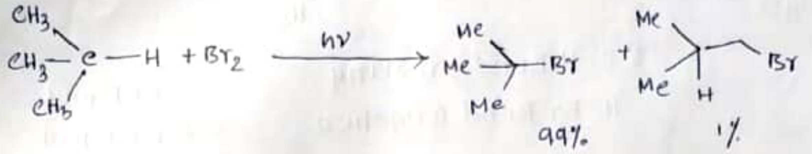
combination of any two radical.

For example: $\dot{X} + \dot{X} \longrightarrow X_2$

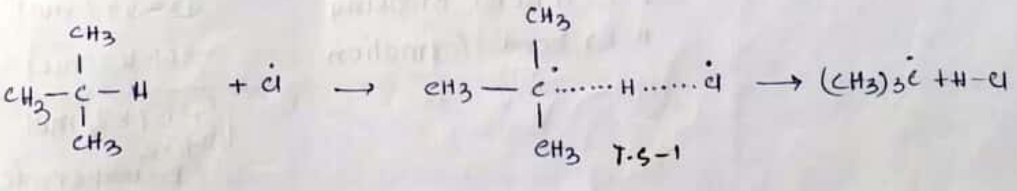
$\dot{X} + \dot{R} \longrightarrow R-X$

Bromination of alkane is more selective than the chlorination of alkane.





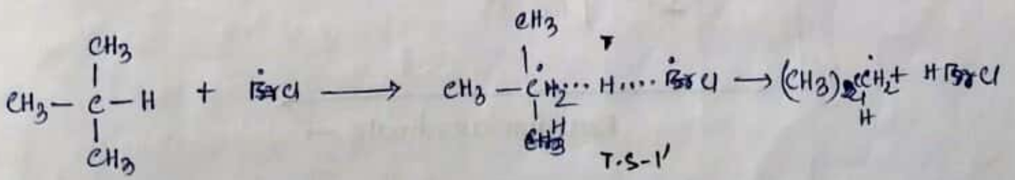
H—Cl Bond formation	−431 KJ/mol
H—Br Bond formation	−366 KJ/mol
Primary C—H Bond Breaking	+ 423 KJ/mol
3° C—H Bond Breaking	+ 397 KJ/mol



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + \dot{Cl} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\dot{C}}}\cdots\cdots H\cdots\cdots\dot{Cl} \longrightarrow (CH_3)_3\dot{C} + H-Cl$$

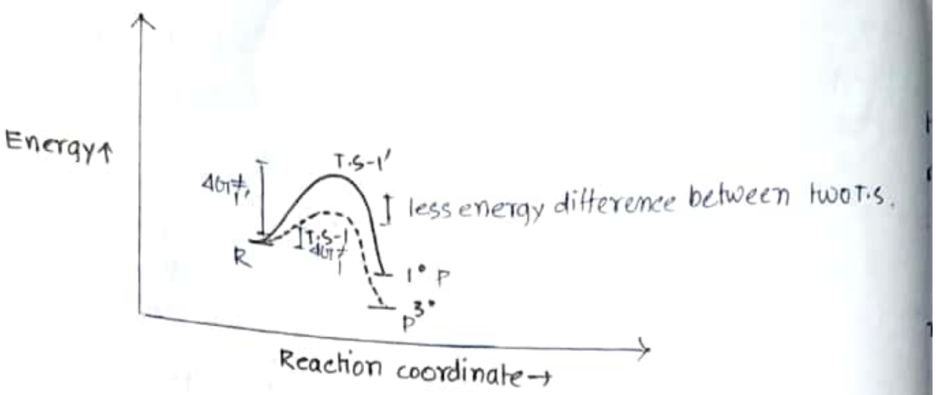
T.S-1

H—Cl ~~Bond Breaking~~ formation	−431 KJ/mol
3° C—H Bond Breaking	397 KJ/mol
	−34 KJ/mol for 3° C-H Bond Breaking

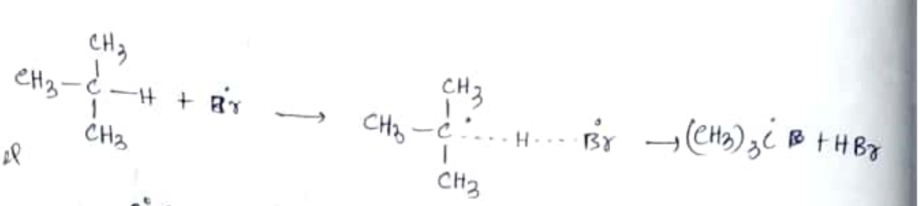


H—Cl Bond formation	−431 KJ/mol
1° C—H Bond formation	423 KJ/m
	−8 KJ mol

Exothermic curve:



2nd step



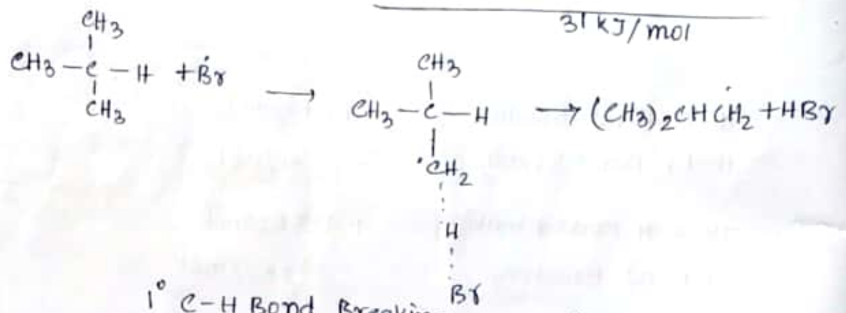
$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-H + \dot{Br} \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\dot{C}}}\cdots H\cdots \dot{Br} \longrightarrow (CH_3)_3\dot{C}\ \cancel{B} + HBr}$$

3° C—H Bond breaking 397 KJ/mol

H-Br Bond formation - 366 KJ/mol

31 KJ/mol

1st step



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-H + \dot{Br} \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle \dot{C}H_2\cdots H\cdots Br}{C}}-H \longrightarrow (CH_3)_2CH\dot{C}H_2 + HBr}$$

1° C-H Bond Breaking 423 KJ/mol

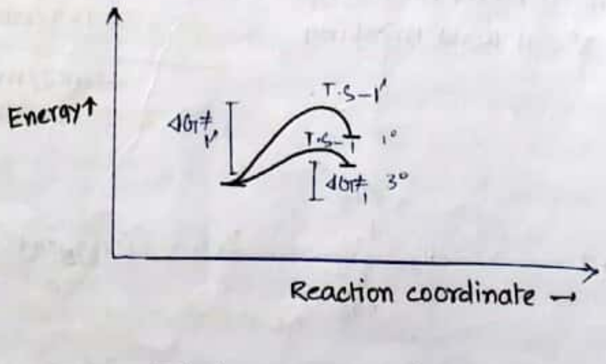
H-Br bond formation - -366 KJ/mol

(+) 57 KJ/mol

'+'ve

Endothermic.

Endothermic curve:



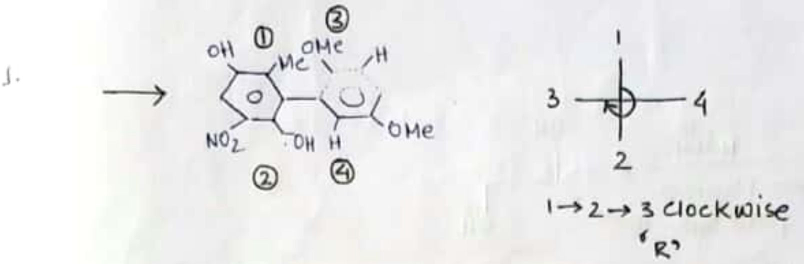
This is an example of how the Hammond Postulate apply to the real chemistry. Because the product of the first step of bromination are higher in energy than the starting meterial. The transition state must be similar in structure and energy to that product radical. The difference in energies of the primary and tartiary product radical should therefore be markedly ~~diffected~~ reflected in the transition state.

$\Delta G^{\neq}_{1'}$ is larger than the $\Delta G^{\neq}_{1}$

For chlorination reaction the product are slidely lower in energy than the starting meterial. So, the transition state for the two possible reaction both resembled the starting meterial more than the product radical. So, energy difference in the products are less pronouced than the transition state

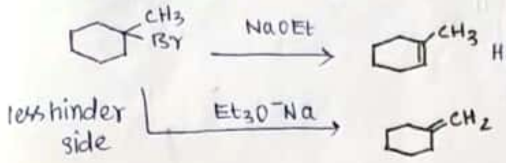
That is why bromination reaction is moreselective than the chlorination. Here product is depends up the statistical factor also.

1.

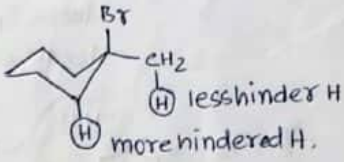


1→2→3 clockwise
'R'

2.

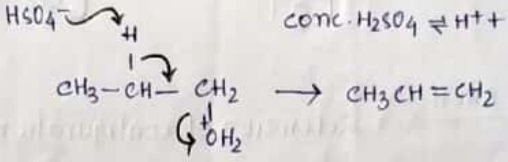


Here seytzer product predominent

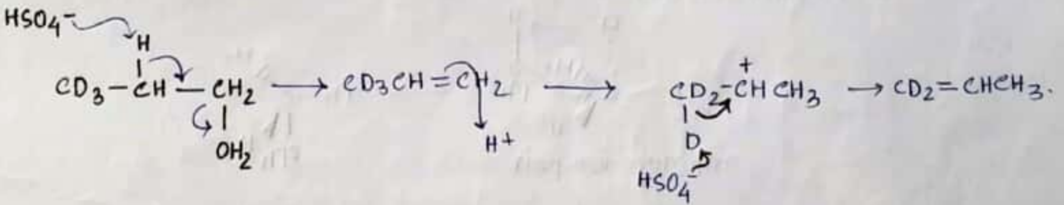


3. $CD_3CH_2CH_2OH \xrightarrow{conc.\ H_2SO_4} CD_3CH=CH_2$

$conc.\ H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$



$CD_3CH_2CH_2OH \xrightarrow{conc.\ H_2SO_4} CD_3CH=CH_2 + CD_2=CH-CH_3$



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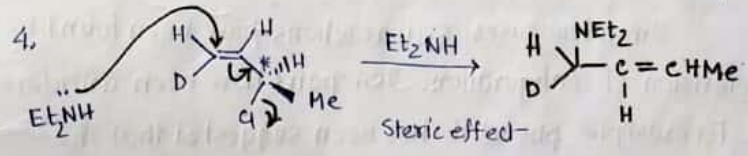
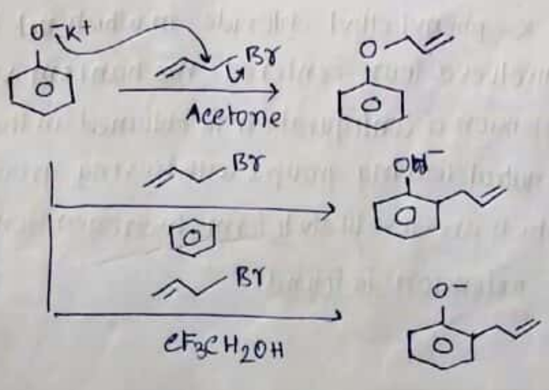
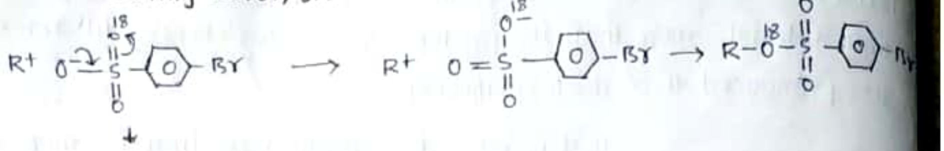


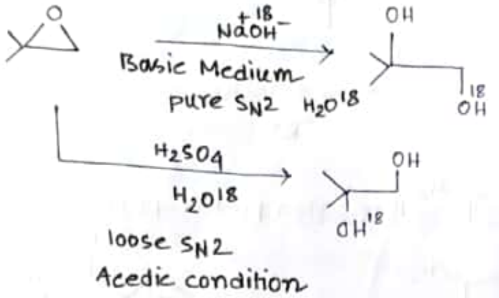


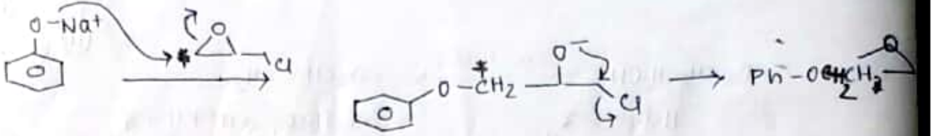
5.

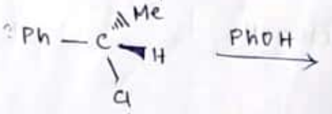
5. 

During solvolysis



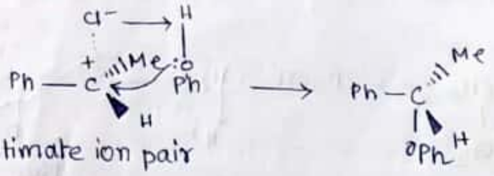
6. 

7. 

8. 

Retension of configuration

α-Ph ethyl chloride



Intimate ion pair

9. In a few cases S_N1 reactions have been found to proceed with partial retension of configuration. Ion pairs have been considered to explain some of this. For example ~~(pheno)~~ it has been suggested that the phenolysis of optically active α-phenyl ethyl chloride in which net retension of configuration is obtained involves a four centered mechanism via the formation of ion pair. Net retension of configuration is obtained in the system only with the chloride or nutral leaving group, with leaving group bearing a positive charge which are less likely to form hydrogen bonding with the solvent molecule, no retension is found.