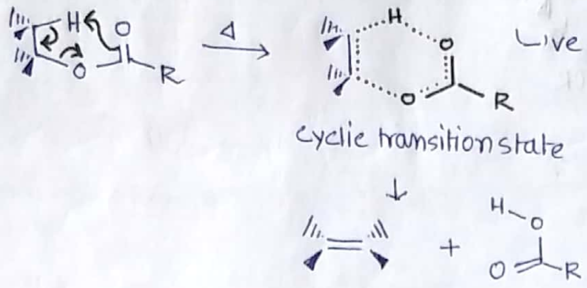
part-3

Rathin Jana
organic Chem
Sem-2 CC-4

Ei (Internal Elimination reaction)

Pyrolysis of Ester:

1.

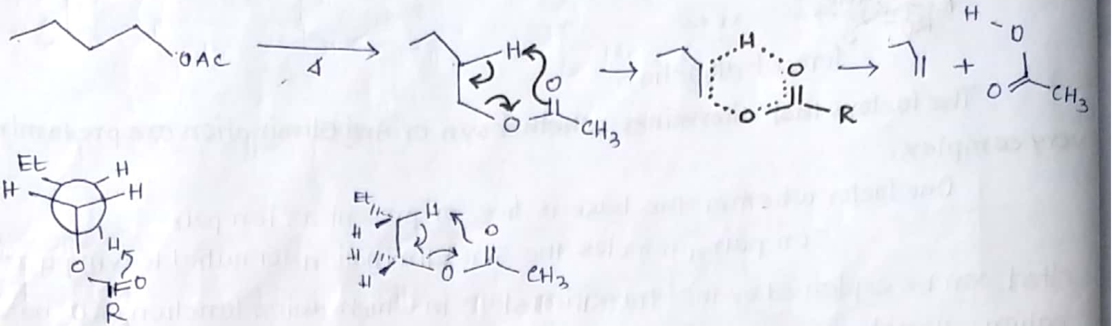


-ive entropy of activation

cyclic transition state

leaving group acts as a base.

2.



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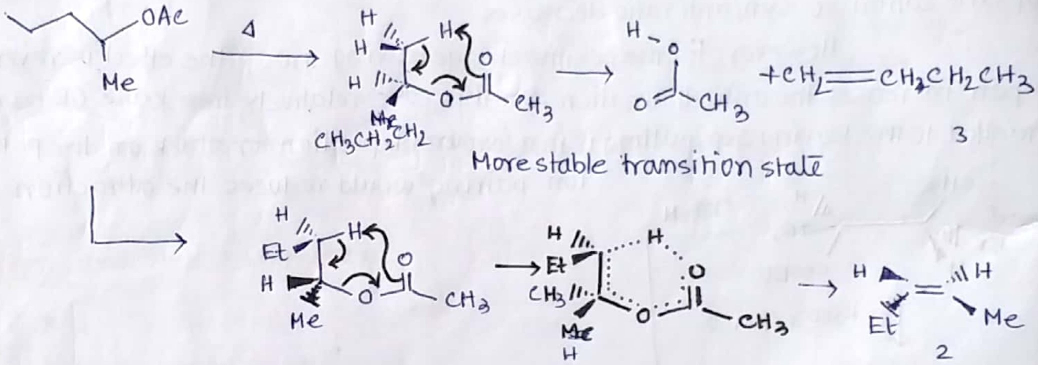
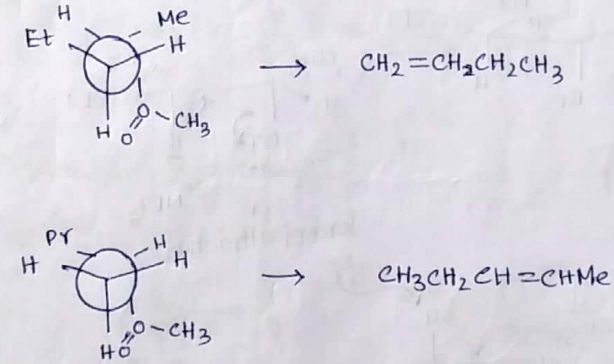
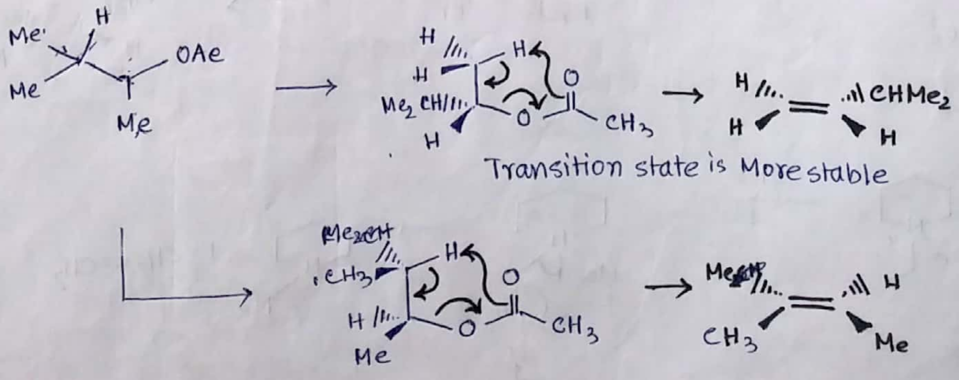


More stable transition state



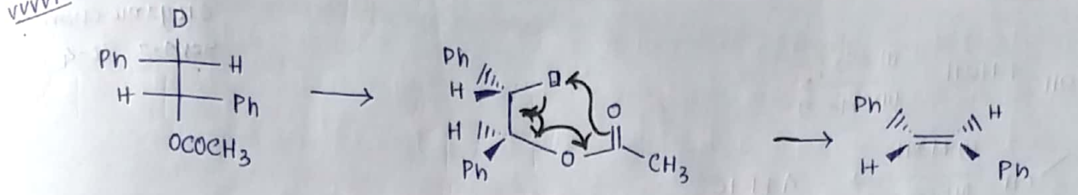
Product ratio = 3:2

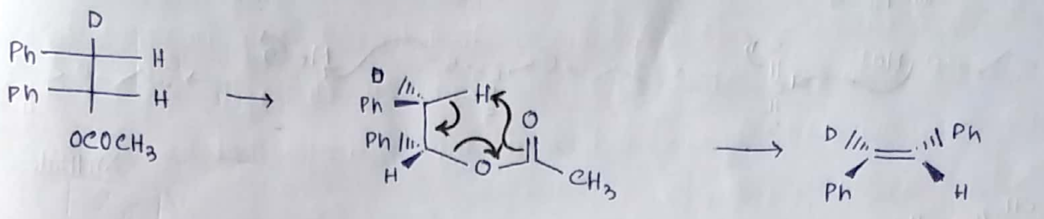
4.



Transition state is More stable

VVVI





Pyrolysis of Xnthate :

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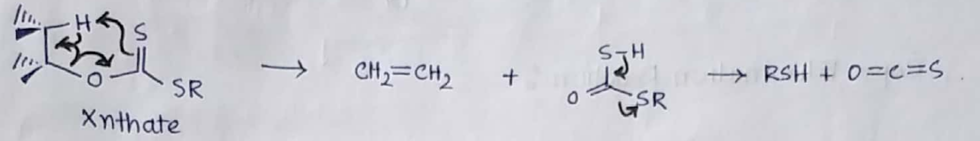

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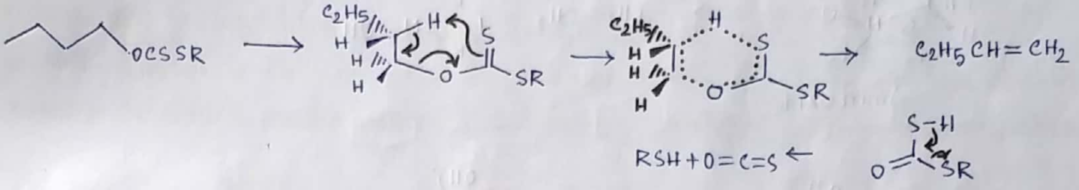

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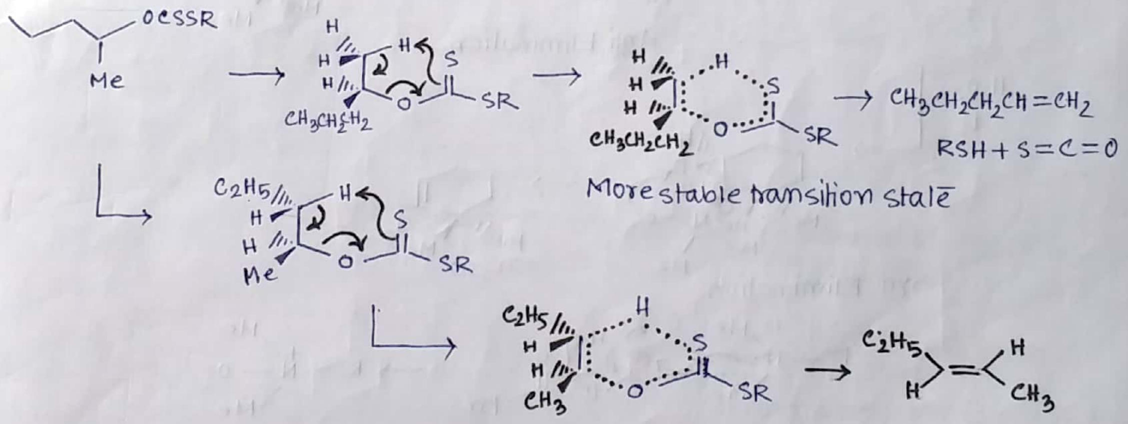
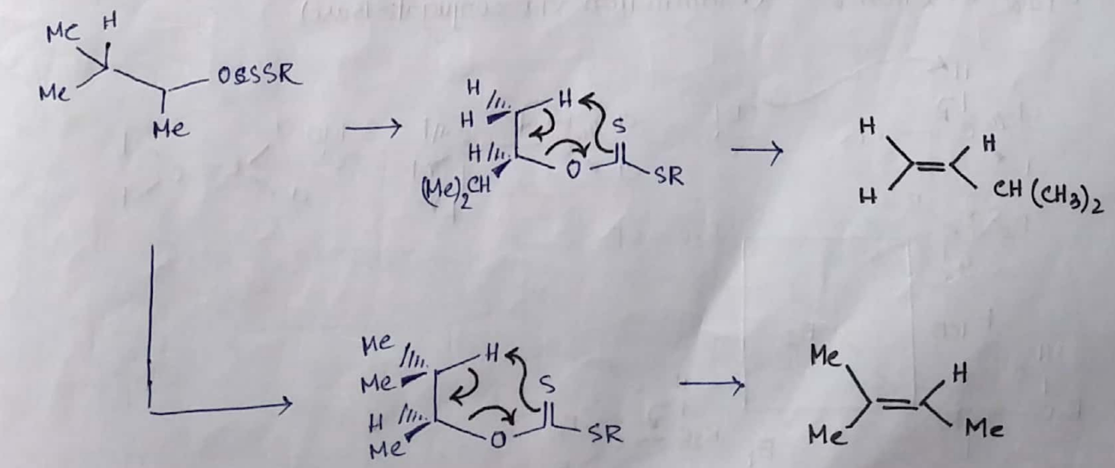


More stable transition state

4.



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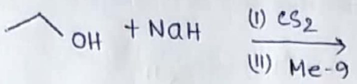
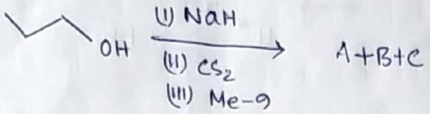
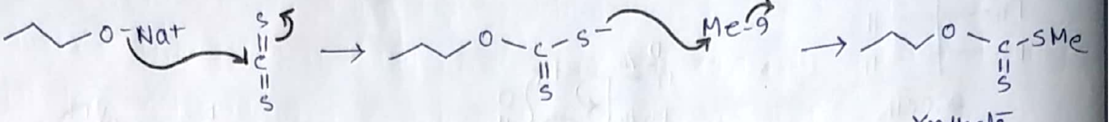
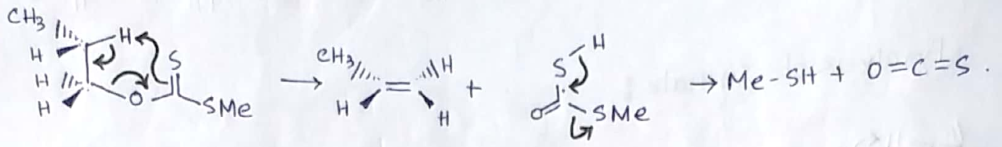


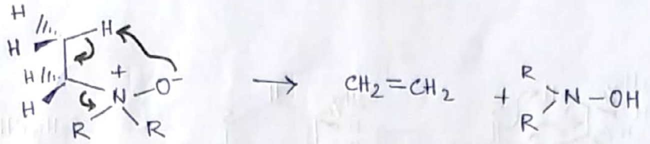




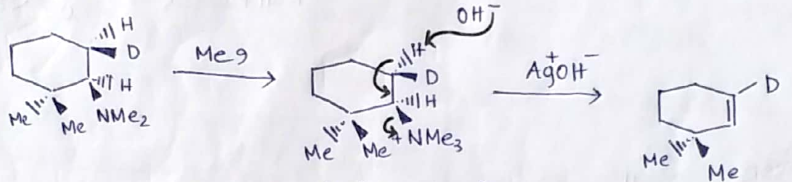
Xnthalē



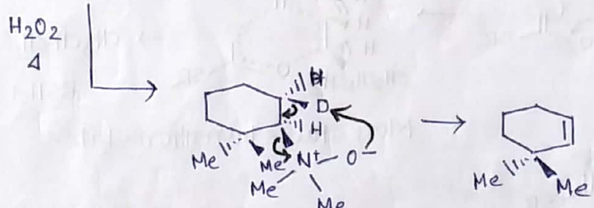
Cope Elimination Reaction :



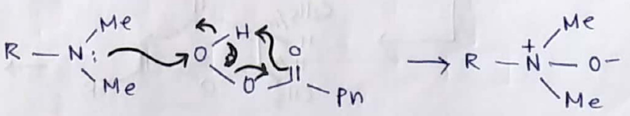
Amin oxide



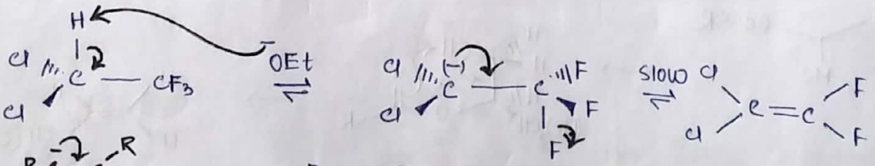
Anti Elimination

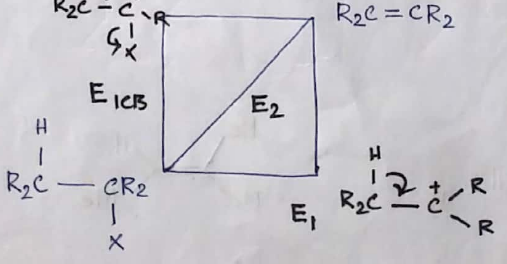


Syn Elimination



E1cb Reaction : (Elimination via conjugate Base)

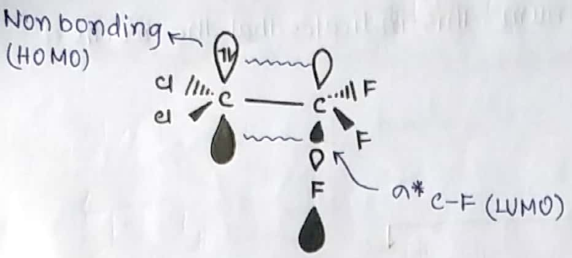




E1cB reaction depends upon the following factor —

(I) Acidity of the β-H atom.
(II) Bad leaving group.
(III) Stability of the conjugate base.
(IV) solvent polarity.

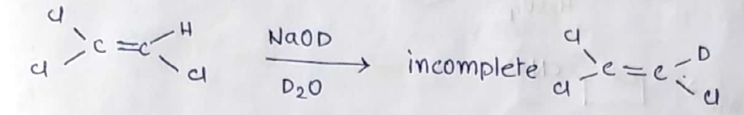
Molecular Orbital diagram :



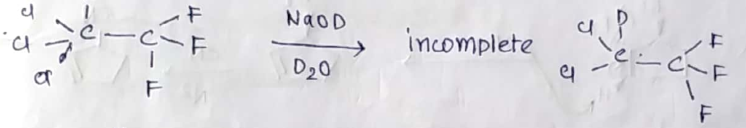
V.U 2017

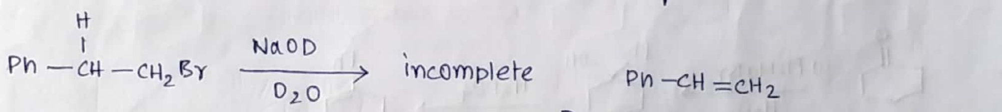
R₂C

Reaction of $CCl_2=CHCl$ with NaOD in D_2O affords $Cl-C\equiv C-Cl$
When the reaction is stopped before completion of the recovered alkenes contains deutorium. Suggest a mechanism of this reaction consistent with this observation.

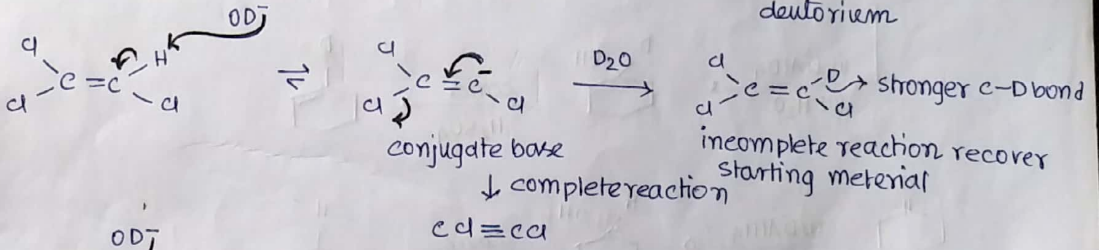


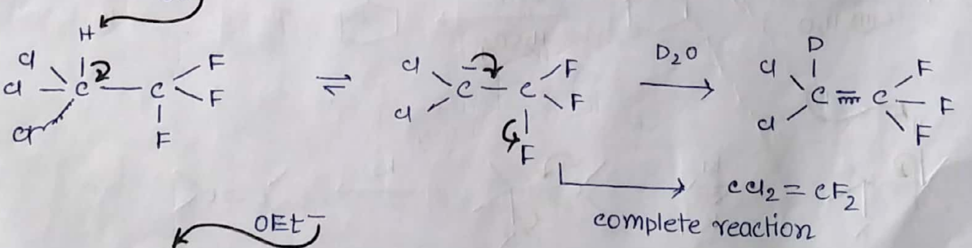
Recover starting Meterial contain deutorium

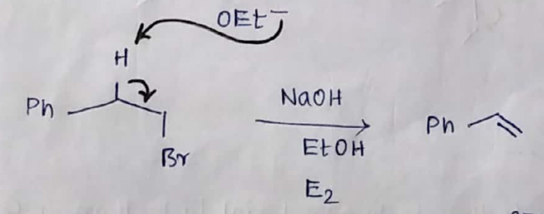


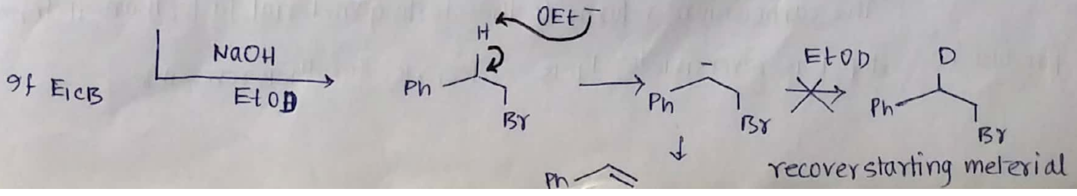


Recover starting meterial contain no deutorium

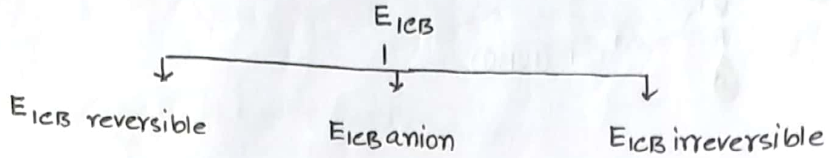




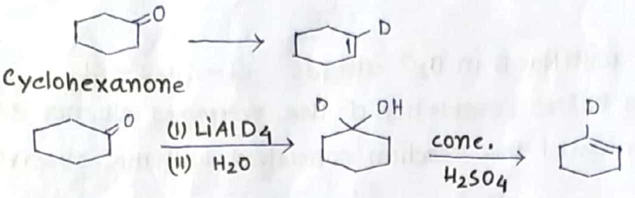




First step of the E1cB mechanism involves a reversible exchange of proton between substrate and base. In that case of D is present on the solvent molecule then the recover starting meterial should have D. This is found to be the case in the treatment of $Cl_2-CH-CF_3$ with NaOEt and EtOD to give $CH_2CCl_2=CF_2$. When the reaction is stopped before completion of the reaction there is a D-incorporation in the recover starting meterial. But in case of $ph-CH_2-CH_2Br$ the recover starting meterial does not contain any deutorium. This indicates that the reaction follows E_2 mechanism pathway.



1.



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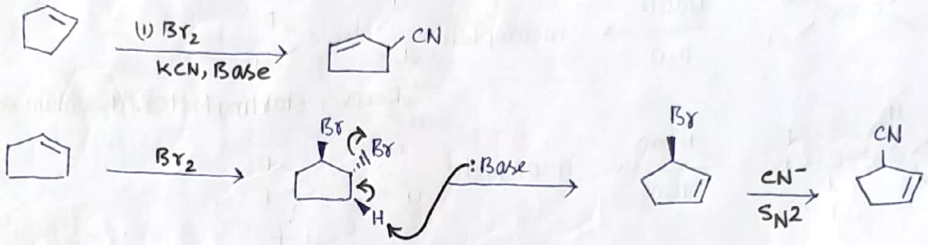

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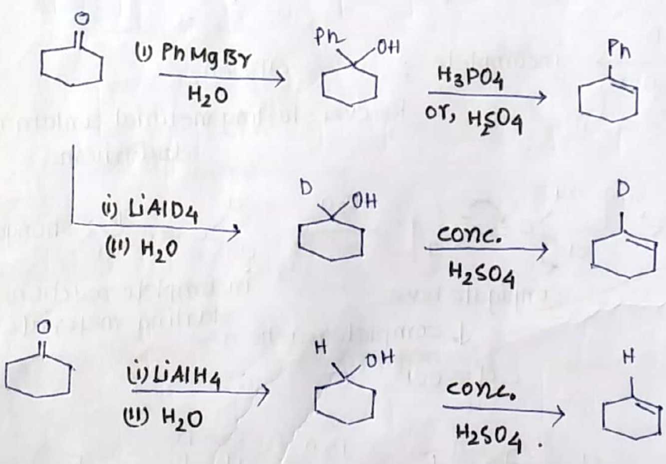
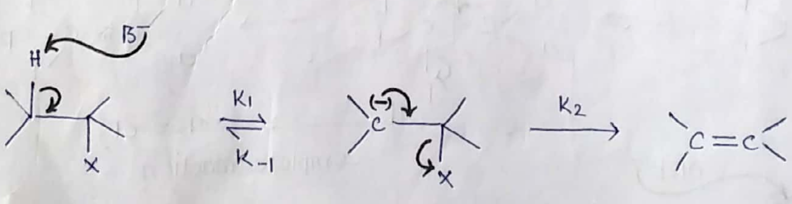
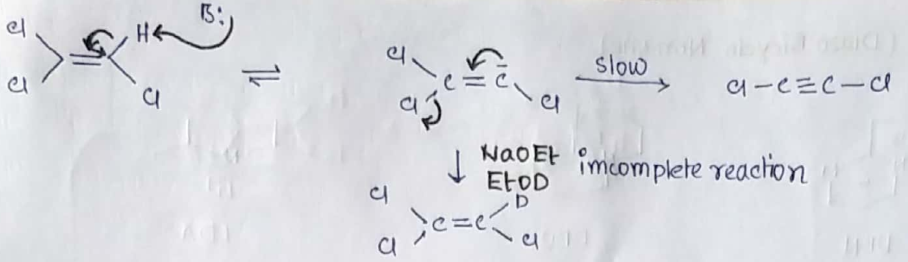




E1cB reversible :

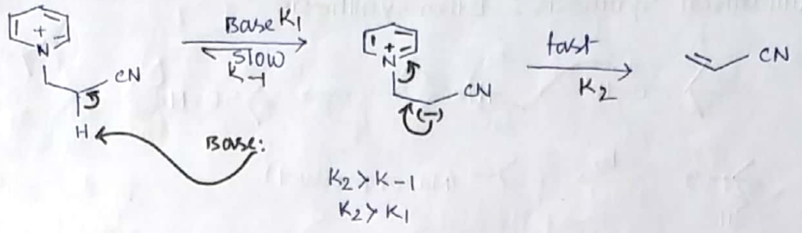
$K_1, K_{-1} > K_2$

The carboanion returns to the starting meterial fasterthan it forms product i.e step 1 is reversiblefor E1cB $K_{-1} > K_2$ for E1cB reversible.



E1cB irreversible:

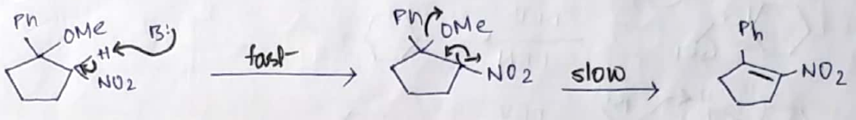
Step I is slow and the formation of product is faster than the return of the carboanion to the starting meterial i.e. last step is irreversible step.



E1cB anion:

Step 1 is rapid and the carbocation is slowly converted to the product. This occurs only with the more stable carbanion. In this case the step 1 is irreversible.

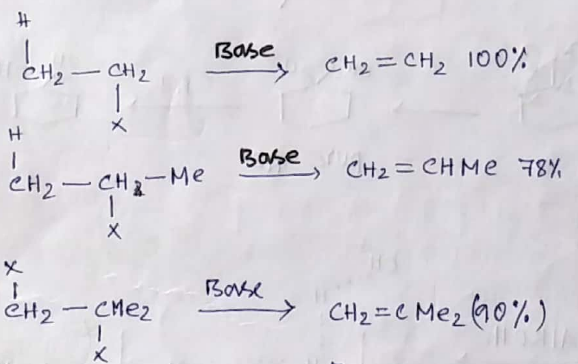
Example –



Elimination vs substitution reaction:

Effect of the substrate:

Strong basic condition favours E_2 elimination reaction.

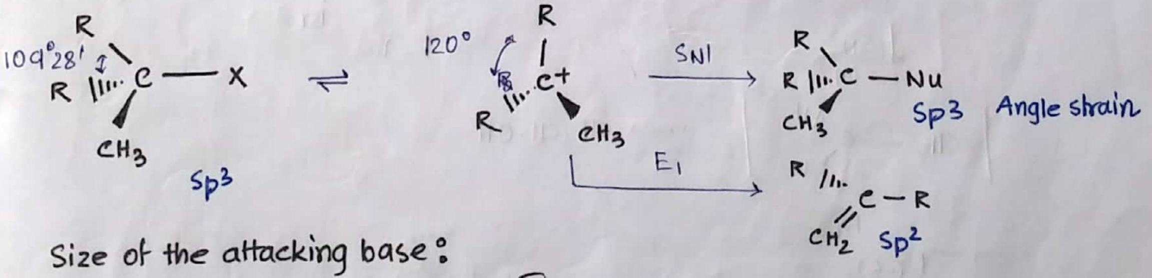


$$\overset{H}{\overset{|}{C}H_2}-\underset{X}{\underset{|}{C}H_2} \xrightarrow{Base} CH_2=CH_2 \; 100\%$$

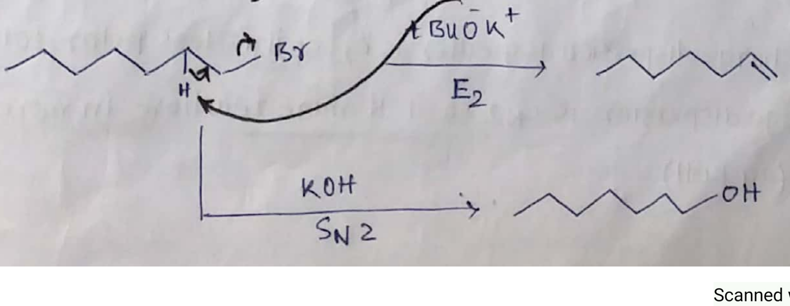
$$\overset{H}{\overset{|}{C}H_2}-\underset{X}{\underset{|}{C}H}-Me \xrightarrow{Base} CH_2=CHMe \; 78\%$$

$$\overset{X}{\overset{|}{C}H_2}-\underset{X}{\underset{|}{C}Me_2} \xrightarrow{Base} CH_2=CMe_2 \; (90\%)$$

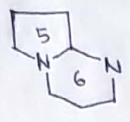
Branching increases $\frac{E_2}{S_N2}$ increases.



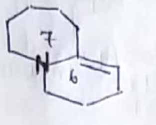
Size of the attacking base:



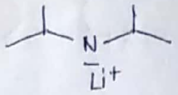
DBN (Diazo Bicyclo Nonane)



DBN



DBU

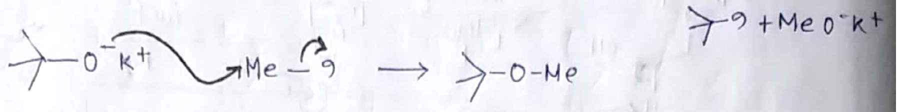


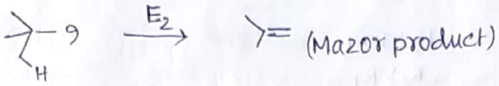
LDA

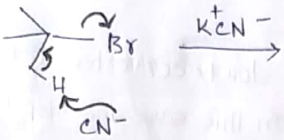
DBU (Diazo Bicyclo undacane).

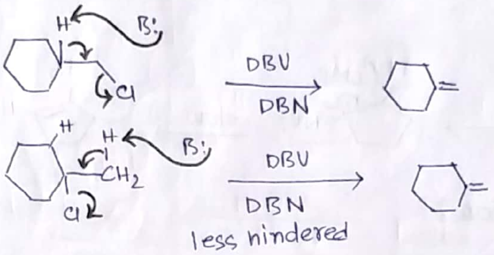
Strong organic base non nucleophilic base.

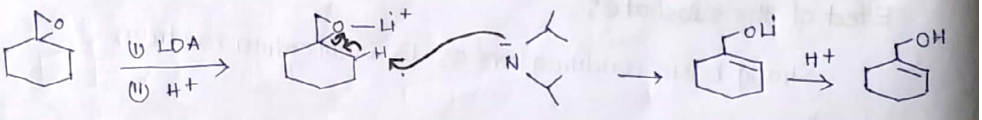
Williamson Synthesis : Ethar synthesis

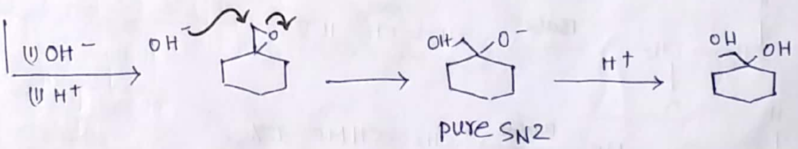




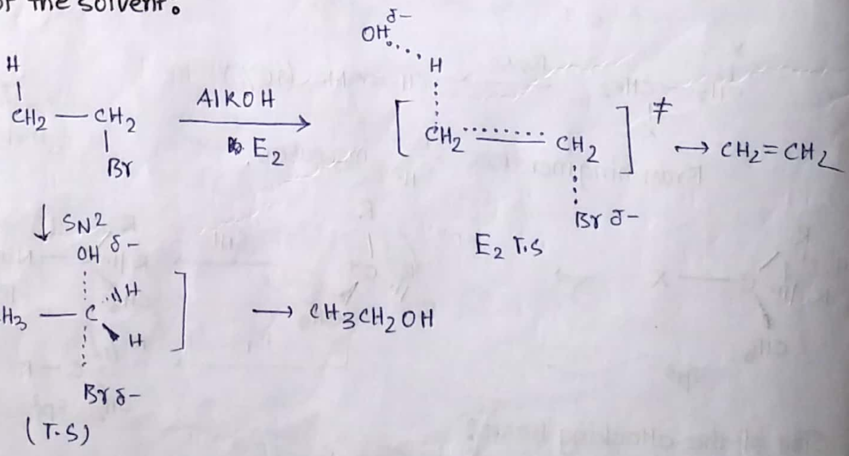








Effect of the solvent:



Charge dispersion isgreater is E_2 so it is less polar solvent alk

There is less charge dispersion is S_N2 so it is more reactiove in more polar solvent (aq KOH)

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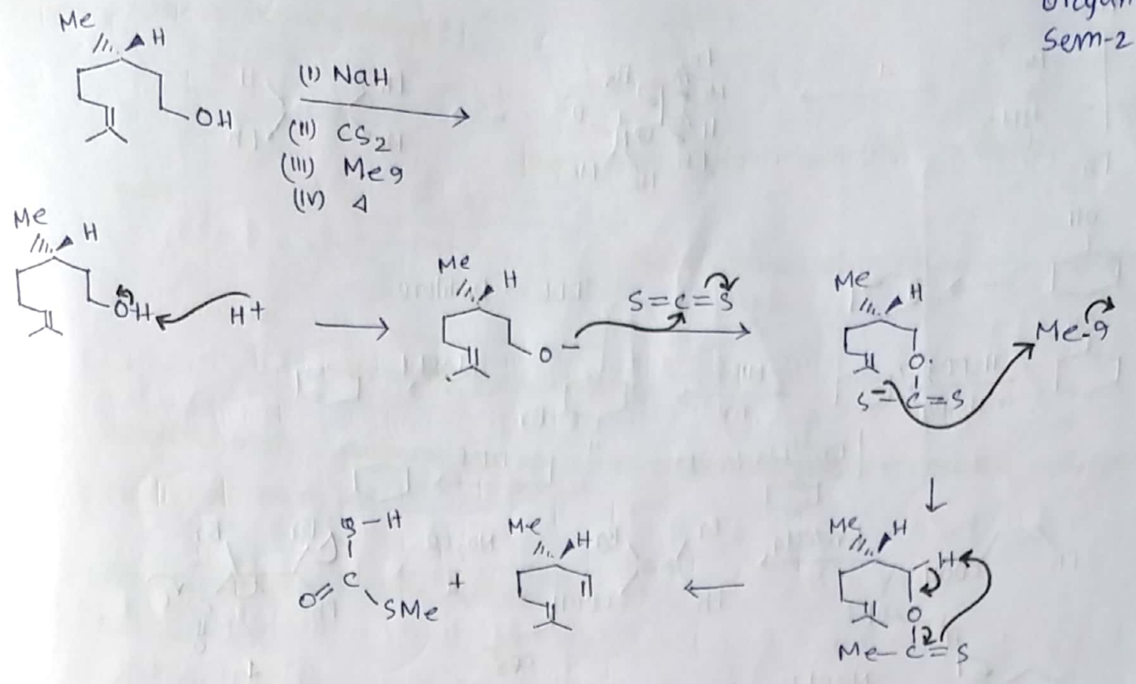
Organic Chem
Sem-2 CC-4



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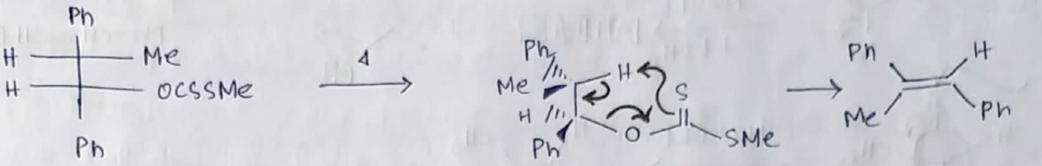

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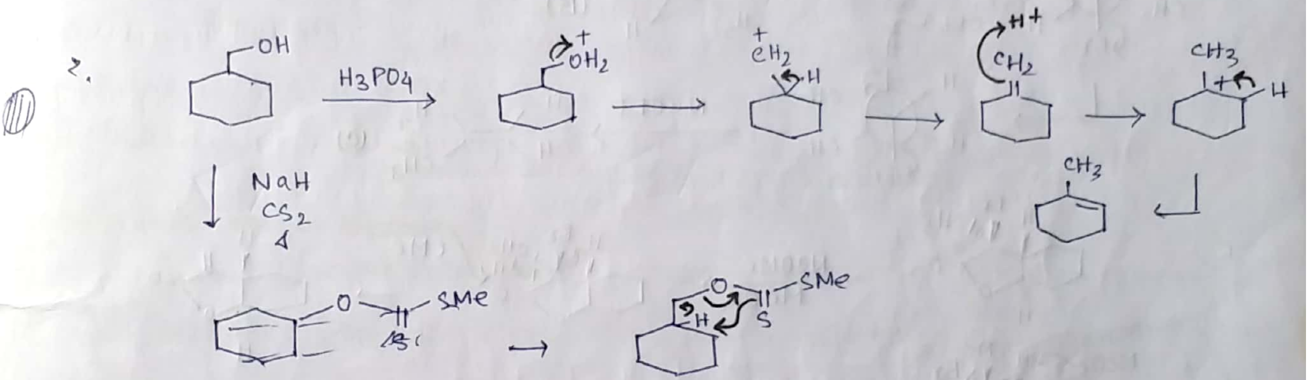

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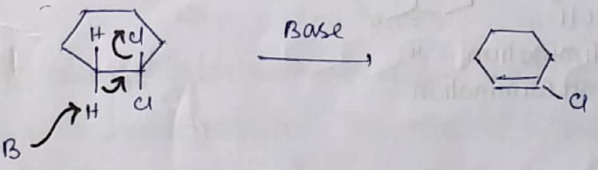

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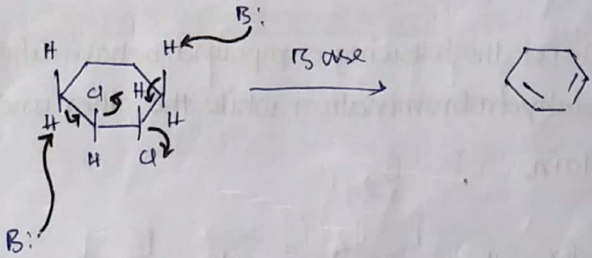

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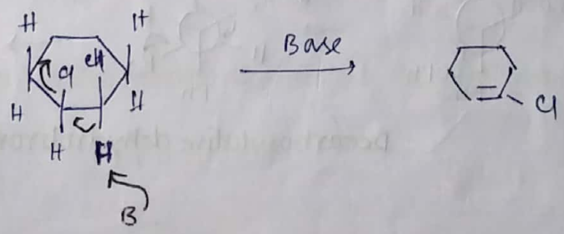

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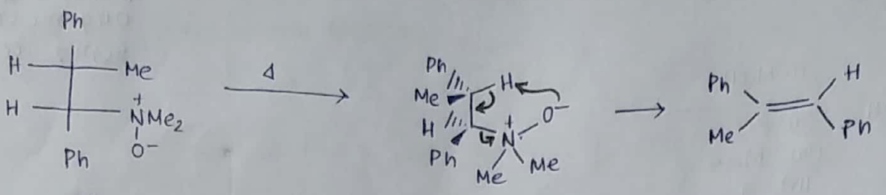

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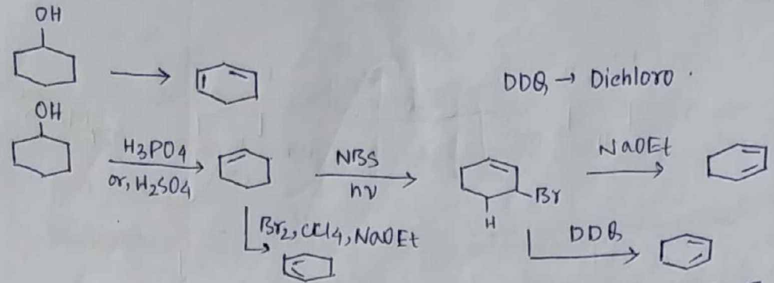
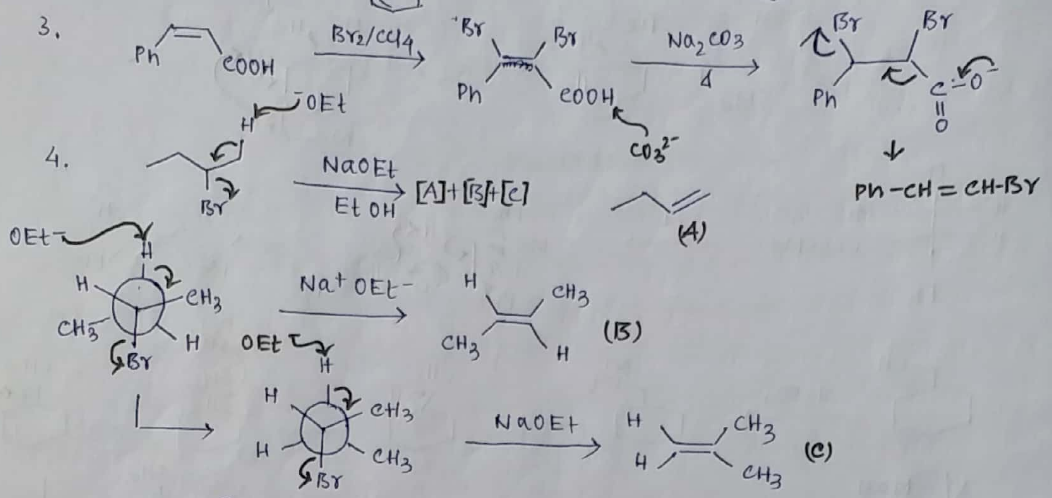
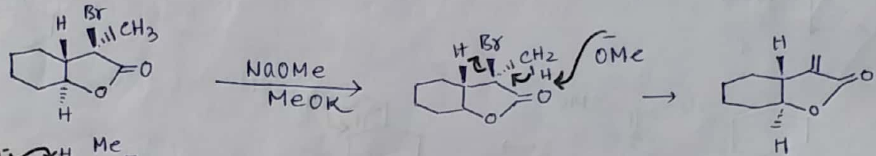

DDQ → Dichloro

3.

4.


(A) (B) (C)

5.



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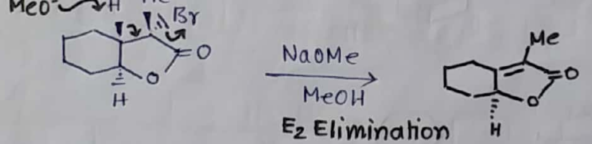
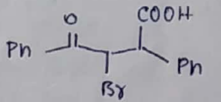
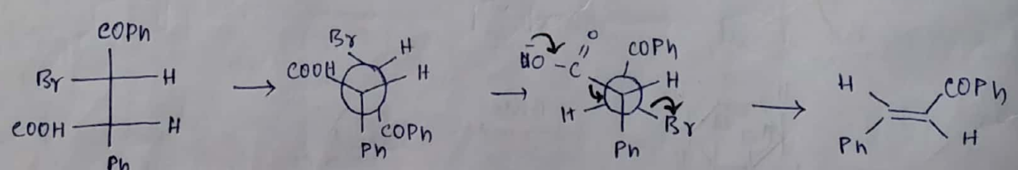


E₂ Elimination
Anti Elimination

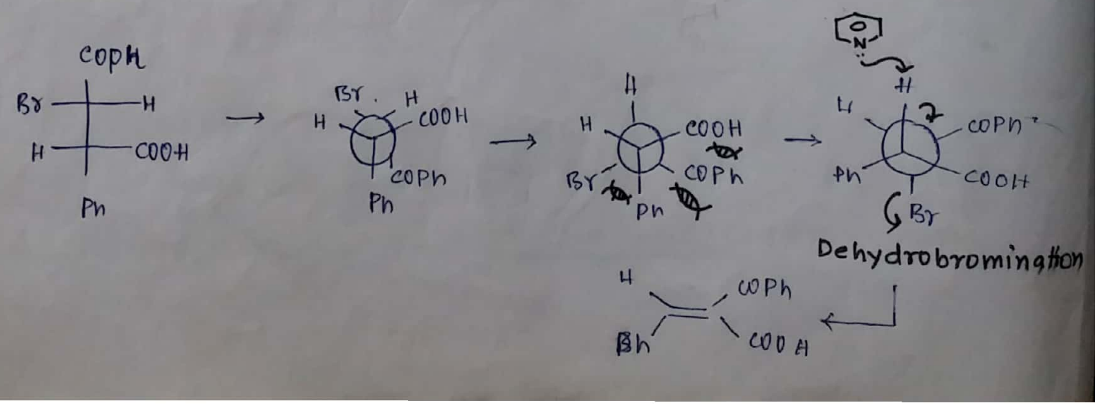
7.



Two diastreomer of the following compound behave differently. One undergoes decarboxylative dehydrobromination while the other undergoes simple dehybromination. —Explain.

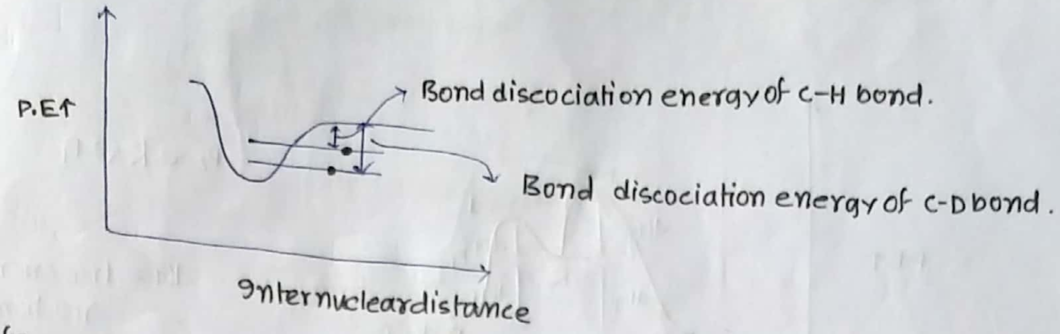


Decarboxylative dehydrobromination



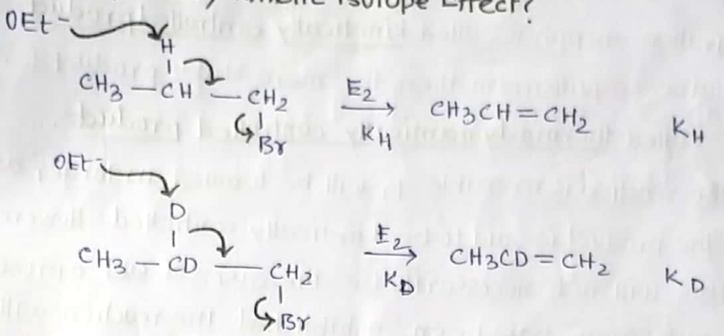
Dehydrobromingtion

Primary kinetic isotope Effect :



Ground state vivrational energy of C-D bond is ~~greater~~ lower because reduced mass of C-D is greater than -H.

What is primary kinetic isotope Effect?

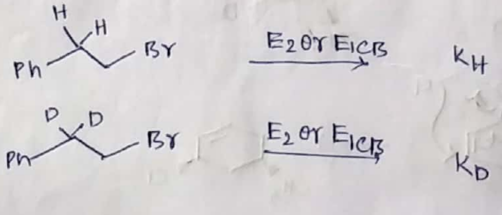


$\frac{K_H}{K_D} = 3-8$ Shows primary kinetic isotope effect-

C-D bond is stronger because :

The ground state vibration energy (or zero point vibration energy) of a bond depends on the mass of the atoms and is lower when the reduced mass is higher. That is why C-D bond is stronger than the C-H bond.

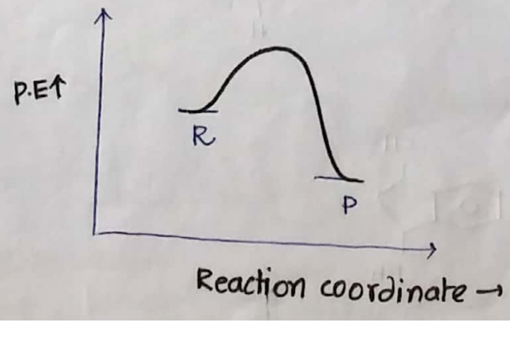
When a C-H breaking is involved in the rate determining step of a reaction a compound in which that hydrogen is replaced by it's isotope deutorium will react more slowly in the same reaction. This effect of isopictopic substitution on the reation rate is called <u>primary kinetic isotope effect</u>.



$\frac{K_H}{K_D} = (3-8)$

It shows primary kinetic isotope effect-

KCP and TCP (Kinetically controlled Product And Thermodynamically controlled product) :



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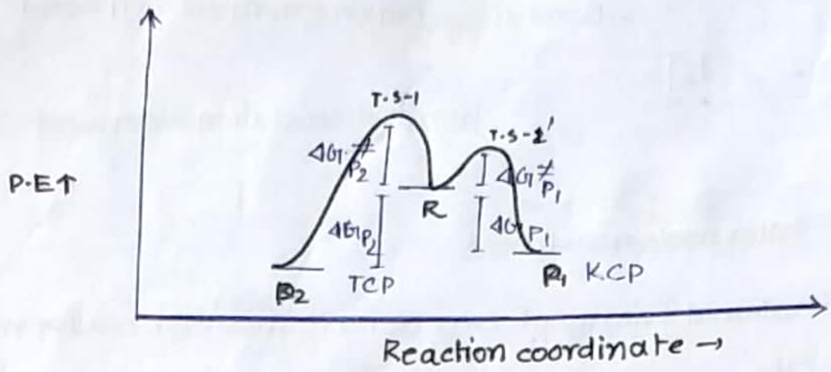

$P_2 \rightleftharpoons R \rightleftharpoons P_1$

ΔG = free energy of the reaction

When in a reaction more than one product are formed which produced at a faster rate (lower activation energy) is called **kinetically controlled product**. If the reaction is allowed to attained equilibrium then the more stable product form predominently. This is called **thermodynamically controlled product**.

If neither the reaction is reversible P_1 will be formed in larger amount because it is form faster. The product is said to be kinetically controlled. However, if the reactions are reversible this will not necessarily be the case. If such a process is stopped well before the equillibrium has been established the reaction will be kinetically controlled. However, if the reaction is permitted to approach equilibrium the predominent product will be P_2 (Thermodynamically controlled).