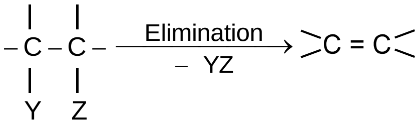
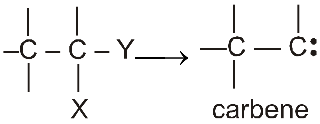
Organic Reaction Mechanisms-IV

Elimination reactions:

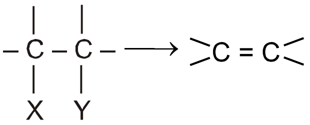
In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of π bond.



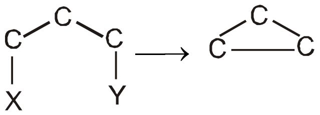
α-elimination : When two groups are lost from the same carbon atom to give a carbene (or nitrene). This is also called 1,1-elimination.



β-elimination : When two groups are lost from adjacent atoms so that a new π bond is formed. This is also called 1,2-elimination.



γ–elimination : It is also called 1,3-elimination, In this a three membered ring is formed.



Type of β-elimination reactions : There are three types of elimination reactions

(I) E1 (II) E2 (III) E1cB

Section (A) : Unimolecular eliminaiton reaction (E1)

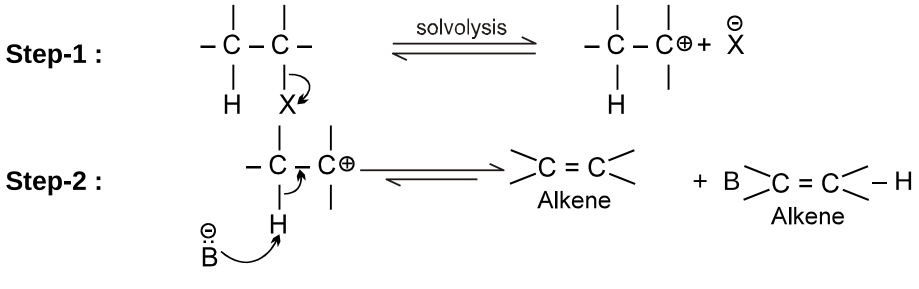
Proton and leaving group depart in two different step.

(a) First step : Slow step involves ionisation to form carbocation

(b) Second step : Abstraction of proton

(1) E1 Reaction of Alkyl halides :

Mechanism :



Characteristics of E1 reaction :

(i) It is unimolecular, two step process.

(ii) It is a first order reaction.

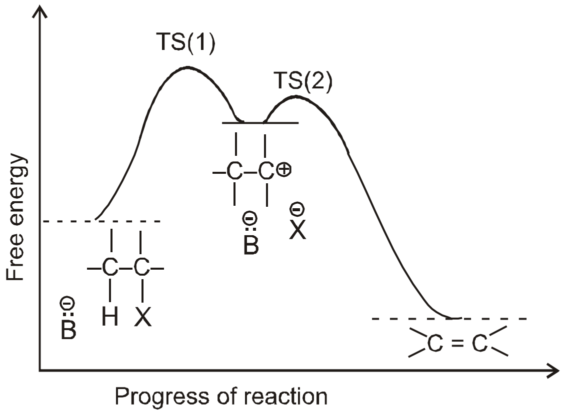
(iii) Reaction intermediate is carbocation, so rearrangment is possible

(iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

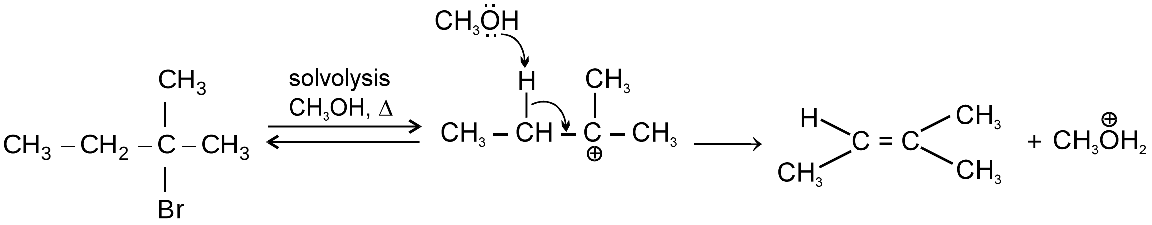
Rate of E1 = 3° Alcohol > 2° Alcohol > 1° Alcohol.
Rate of reaction $\propto$ stability of carbocation

(v) Kinetics : Rate $\propto$ [Alkyl halide]
Rate = k [Alkyl halide]

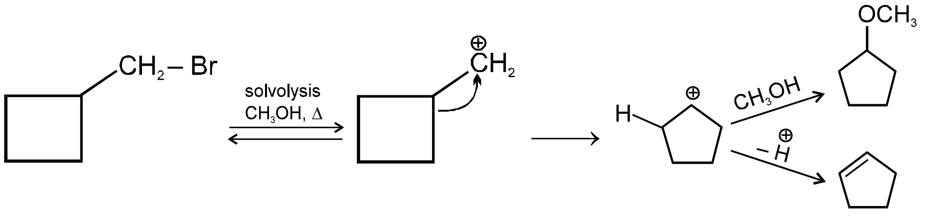
(vi) Energetics : The free energy diagram for the E1 reaction is similar to that for the S_N1 reaction.



Ex-1.



Ex-2.

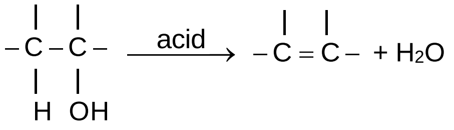


(2) E1 Reaction of Alcohols :

Dehydration requires an acidic catalyst to protonate the hydroxyl group of the alcohol and convert it to a good leaving group. Loss of water, followed by loss of proton, gives the alkene. An equilibrium is established between reactants and products. For E1 mechanism reagents are :

(i) H_3PO_4/Δ

(ii) H_2SO_4 / 160°

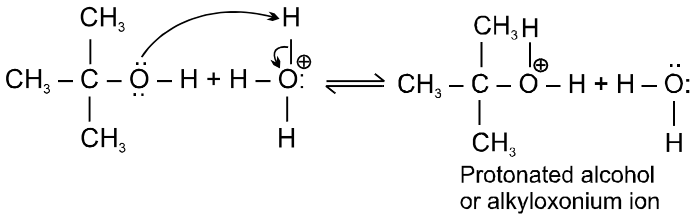


$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \xrightarrow{\text{acid}} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

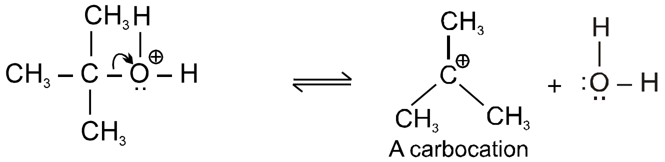
(Rearrangement may occur)

Mechanism :

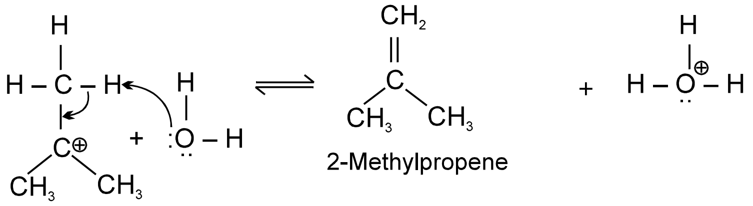
Step-1 :



Step-2 :



Step-3 :



Remarks :

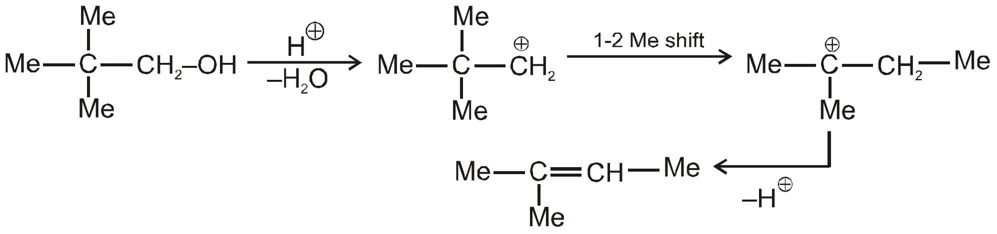
In first step, an acid-base reaction a proton is rapidly transferred from the acid to one of the unshared electon pairs of the alcohol.

In second step the carbon oxygen bond breaks. The leaving group is water molecule.

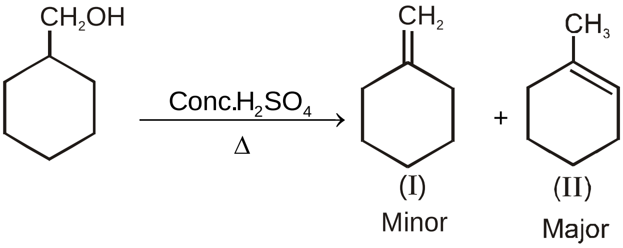
Finally, in third step the carbocation transfers a proton to a molecule of water. The result is the formation of a hydronium ion and an alkene.

Reactivity of ROH : 3° > 2° > 1°

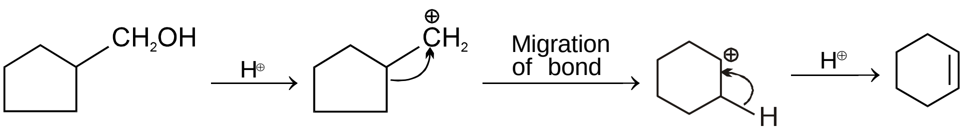
Ex-3.



Ex-4.



Ex-5.



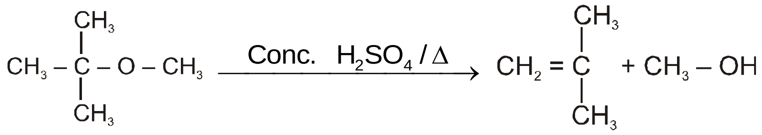
(3) E1 Reaction of Ether :

Elimination is not a favourable reaction for ether, but however few reactions have been observed.

E1 Elimination takes place via formation of stable carbocation.

Ether undergoes dehydration reaction in the presence of conc. H_2SO_4 / Δ .

Ex-6.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 \xrightarrow{\text{Conc. } H_2SO_4/\Delta} CH_2=\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} + CH_3-OH$$

Section (B) : Bimolecular elimination reaction (E2)

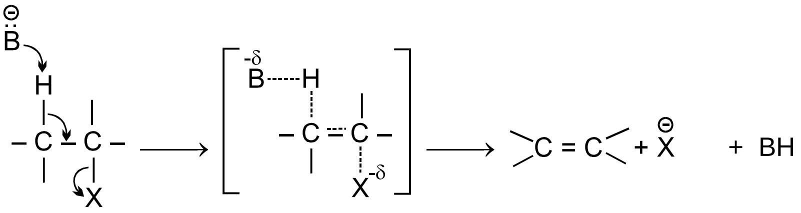
(1) E2 Reaction of Alkyl halide :

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene. Dehydrohalogenation can take place by E1 and E2 mechanism.

Reagent

(i) Hot alcoholic solution of KOH or EtO^- / EtOH (ii) $NaNH_2$ (iii) t-BuO^-K^+ in t-BuOH

Mechanism :



Transition state

Characteristics of E2 reaction :

1. This is a single step, bimolecular reaction
2. It is a second order reaction
3. Kinetics → Rate $\propto$ [R – X] [Base]

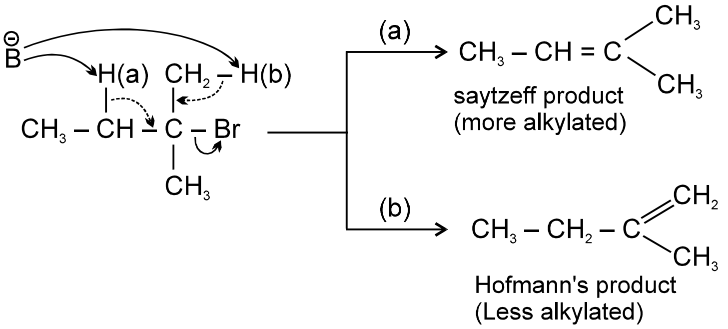
$$\text{Rate} = k\,[R-X]\,[\overset{\ominus}{B}]$$

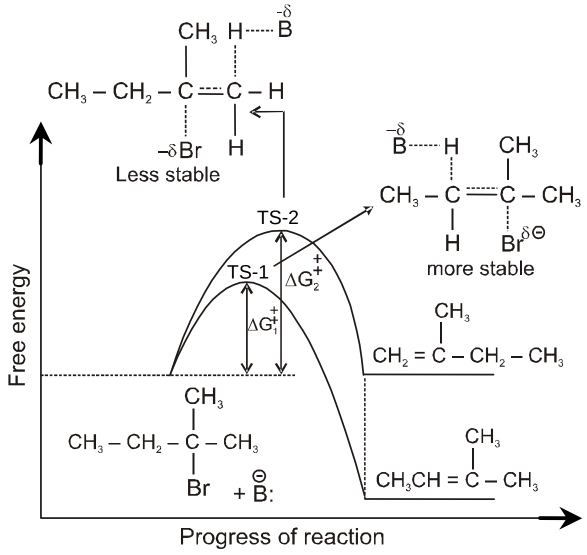
4. Rearrangment is not possible
5. For the lower energy of activation, transition state must be stable
6. E2 follows a concerted mechanism
7. The orientation of proton & leaving group should be antiperiplanar.
8. Here β–H is eliminated by base hence called **β elimination**
9. Positional orientation of elimination → In most E1 and E2 eliminations where there are two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule.

Reactivity towards E2 → R–I > R–Br > R–Cl > R–F

Rate of E2 reaction = 3° Alkylhalide > 2° Alkylhalide > 1° Alkylhalide

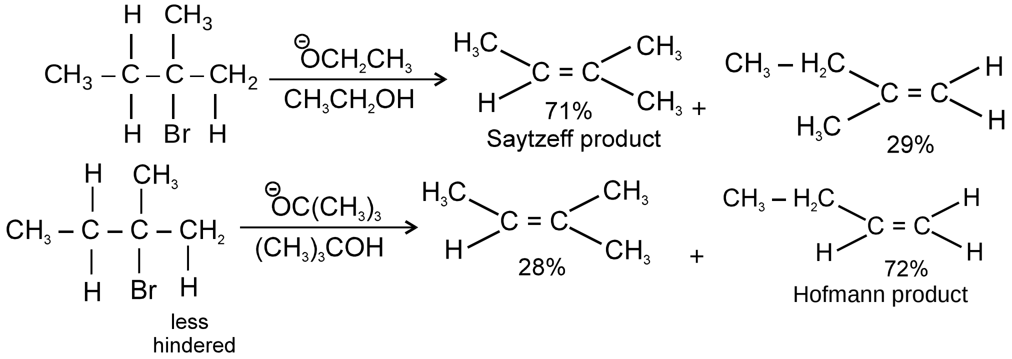
Ex-7. Dehydrohalogenation of 2-bromo-2-methylbutane can yield two products.



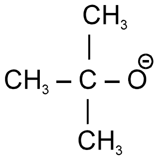


Formation of the Hoffmann product

Bulky bases can also accomplish dehydrohalogenations that do not follow the Saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hofmann product.

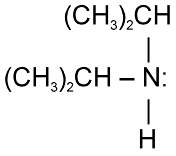


Bulky base :



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\ominus}{O}$

t-Butoxide

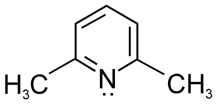


$(CH_3)_2CH-\overset{(CH_3)_2CH}{\underset{H}{N}}:$

Di-isopropylamine

$(CH_3CH_2)_3N:$

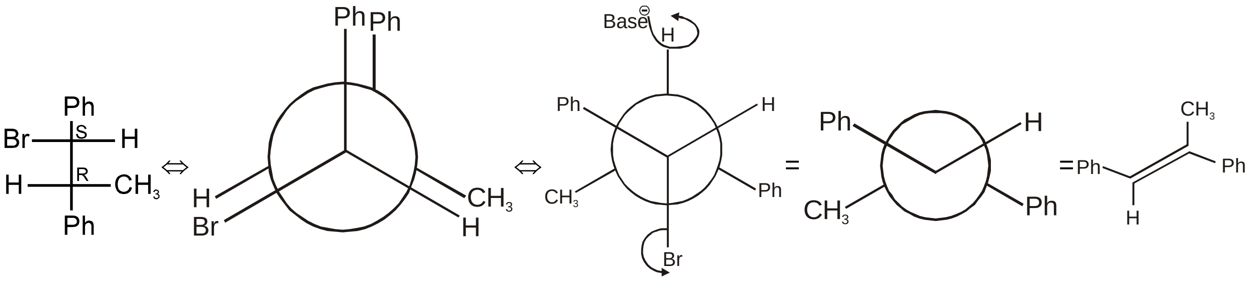
Triethylamine

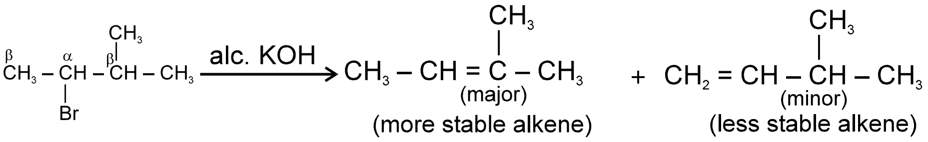


2, 6-dimethyl pyridine

Stereospecific E2 reactions

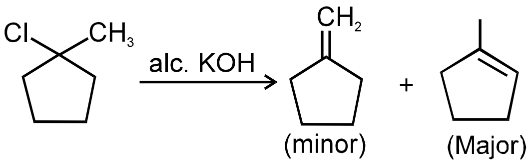
The E2 is stereospecific because it normally goes through an anti periplanar transition state. The products are alkenes.



Ex-8. 

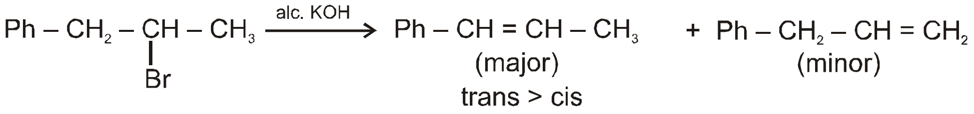
$$\overset{\beta}{CH_3}-\underset{Br}{\overset{\alpha}{CH}}-\overset{CH_3}{\overset{\beta}{CH}}-CH_3 \xrightarrow{\text{alc. KOH}} CH_3-CH=\overset{CH_3}{C}-CH_3 + CH_2=CH-\overset{CH_3}{CH}-CH_3$$

(major) (more stable alkene) (minor) (less stable alkene)

Ex-9. 

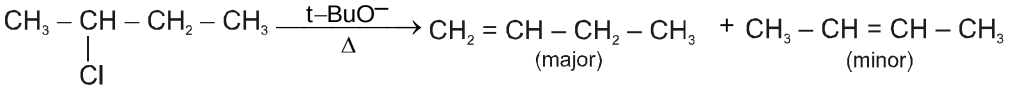
alc. KOH

(minor) (Major)

Ex-10. 

$$Ph-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow{\text{alc. KOH}} Ph-CH=CH-CH_3 + Ph-CH_2-CH=CH_2$$

(major) trans > cis (minor)

Ex-11. 

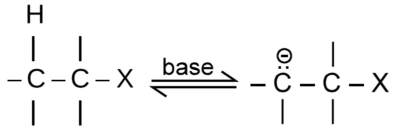
$$CH_3-\underset{Cl}{CH}-CH_2-CH_3 \xrightarrow[\Delta]{t\text{–}BuO^-} CH_2=CH-CH_2-CH_3 + CH_3-CH=CH-CH_3$$

(major) (minor)

Section (C) : Unimolecular elimination by conjugate base (E1cB)

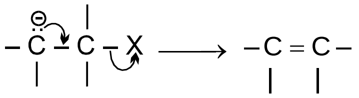
In the E1 cB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism :

Step-1 : 

$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}-X \underset{}{\overset{\text{base}}{\rightleftharpoons}} -\underset{|}{\overset{\ominus}{\ddot{C}}}-\underset{|}{\overset{|}{C}}-X$$

(conjugate base)

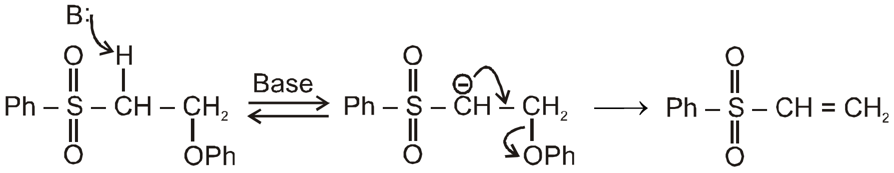
Step-2 : 

$$-\underset{|}{\overset{\ominus}{C}}-\underset{|}{\overset{|}{C}}-X \longrightarrow -\underset{|}{C}=\underset{|}{C}-$$

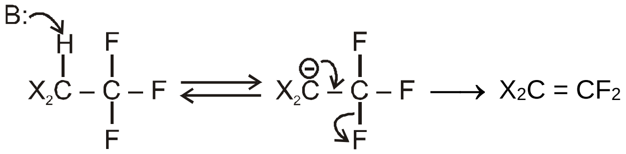
Remarks :

First step consists of the removal of a proton ($\overset{\oplus}{H}$) by a base generating a carbanion.
In second step carbanion looses a leaving group to form alkene**.**

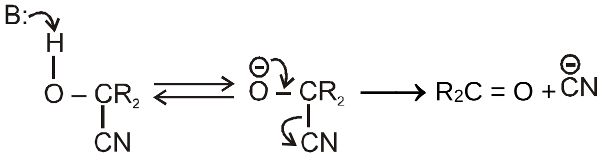
Condition: For the E1cB, (i) substrate must be containing acidic hydrogens and (ii) poor leaving groups.

Ex-12. 

$$Ph-\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{H}{CH}-\underset{OPh}{CH_2} \overset{\text{Base}}{\rightleftharpoons} Ph-\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{\ominus}{CH}-\underset{OPh}{CH_2} \longrightarrow Ph-\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}-CH=CH_2$$

Ex-13. 

$$X_2\overset{H}{C}-\underset{F}{\overset{F}{C}}-F \rightleftharpoons X_2\overset{\ominus}{C}-\underset{F}{\overset{F}{C}}-F \longrightarrow X_2C=CF_2$$

Ex-14. 

$$\overset{H}{O}-\underset{CN}{CR_2} \rightleftharpoons \overset{\ominus}{O}-\underset{CN}{CR_2} \longrightarrow R_2C=O+\overset{\ominus}{C}N$$