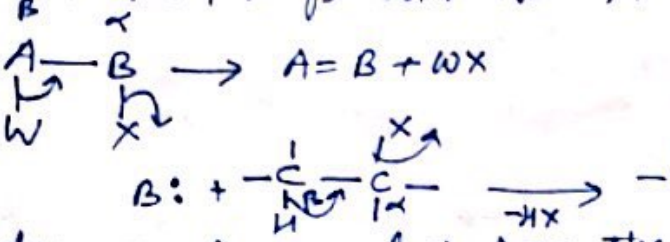
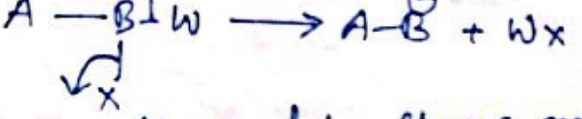
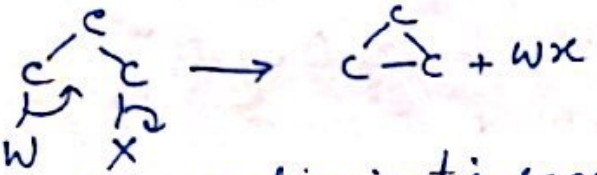
When two groups are lost from adjacent atoms to form a new double or triple bond compound, the reaction is called Elimination reaction. If proton is lost from β-carbon atom it is known as β-eliminations reactions.



If two groups are lost from the same atom, it is called α-elimination. It leads to the formation of a carbone or nitrene.



While in γ- elimination, three membered ring is formed.



Another type of elimination reaction involves expulsion of a fragment, from within a chain, such reactions are called Extrusion Reactions

$$X-Y-Z \longrightarrow X-Z + Y$$

Among all these eliminations, β-elimination reactions are of prime importance.

β-Elimination Reactions

These are divided into three categories – (I) E2 (II) E1CB (III) E1

β-elimination reactions occur mostly in solution form while other types of eliminations take place in gaseous phase.

(I) E2-mechanism — (Bimolecular Elimination Reaction)

In these reactions, rate of elimination depends upon the concentration of substrate and that of nucleophile, and the reaction is of 2nd order.

Like S_N2 reactions, E_2 reaction too, is a one step process

(1) meso 1,2 dibromo 1,2 diphenyl ethane

(2) (±) 1,2 dibromo 1,2 diphenyl ethane

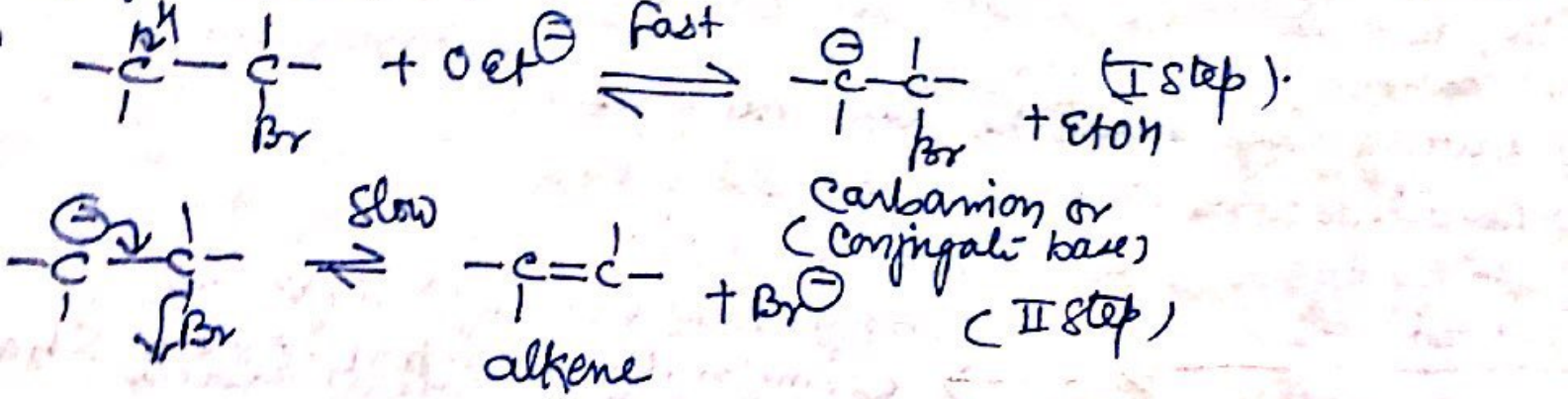
(±) 2-bromo stilbene

(trans) 2-bromo stilbene

This stereospecific reaction indicates - anti - elimination.

(2) E1CB-mechanism. (Elimination, Unimolecular form (conjugate base)

The second order elimination reaction may also proceed in two steps like E1. In this mechanism — (1) Base removes hydrogen in the first step to form an intermediate carbanion (2) In the second step, the intermediate carbanion looses the leaving group. It is slow and rate determining step. The rate of this reaction depends upon the concentration of the carbanion (Conjugate base) so this mechanism is called E1CB mechanism (Elimination, Unimolecular form conjugate base)



CB mechanism is not common for E2 reactions.

e carbanion mechanism occurs only, where the carbanion y the substrate is stabilized and the leaving group is poor leaving group.

An important example, where E1CB mechanism

In E_2 reaction, when all β-hydrogens are not equal, major product will be most highly substituted alkene, i.e. one containing largest number of alkyl groups bonded to the double bond. This is known as Saytzeff Rule.

Relative stabilities in alkyl halids in an E2 reaction:

Tertiary > Secondary > Primary

In most of the dehydrohalogenation reactions the major products are the Saytzeff products, but sometimes the least substituted alkenes is the major product, and this is known as Hoffmann elimination. It occurs when (i) the base is bulky (ii) when the leaving group is a poor leaving group such as F, $\overset{\oplus}{N}R_3$ and SR_2 (iii) steric hinderance at β-carbon (iv) when alkyl halide contains one or more than one double bond

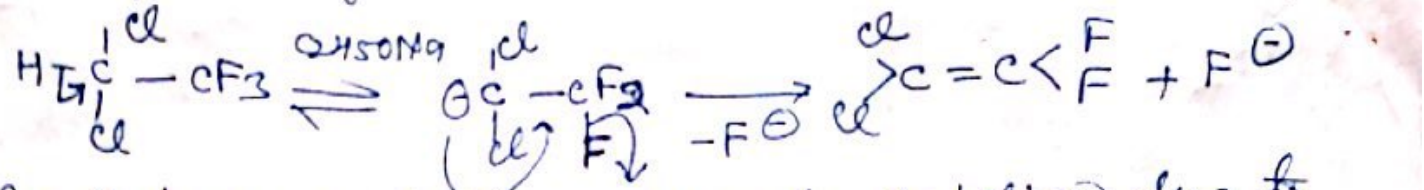
$$CH_3-CH_2-\underset{F}{CH}-CH_3 + CH_3O^{\ominus} \longrightarrow \underset{70\%}{CH_3CH_2-CH=CH_2} + \underset{30\%}{CH_3-CH=CH-CH_3}$$

1) Kinetic Isotope effect.

An experimental evidence that is helpful in determining the mechanism of a reaction is a kinetic Isotope effect which is used to demonstrate that a C-H bond is broken in rate determining step. During elimination of $\overset{\oplus}{H}Br^{\ominus}$ from 1-bromo 2 phenyl methane (K_H) was found to be 7 times K_D. proving that H-containing compound undergoes elimination faster than the deuterium containing compound. proving that (C-H) or (C-D) bond is broken in the rate determining step.

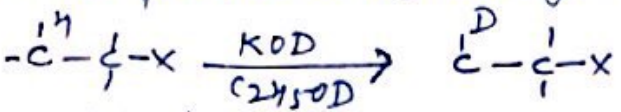
2) E1CB-mechanism →

in the presence of C_2H_5ONa.



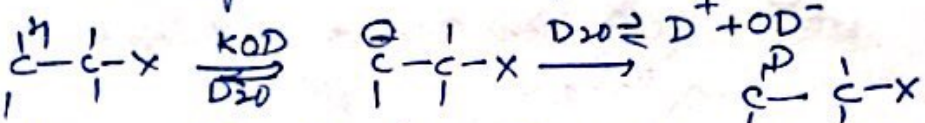
In this case, carbanion is strongly stabilized due to -I effect of halogens., because beside $F^{\ominus}$ is a poor leaving group.

The use of deuterium labelling can help to distinguish E1CB from E2 mechanism. If an E2, reaction is carried out in an solvent which can act as a source of deuterium, and the reaction is interrupted before completion, the substance does not contain D. This happens because there is no way by which D can be incorporated into starting material.



Any reaction which involves carbanion will produce the substrate containing Deuterium e.g.

E1CB.



This also confirms that the first step is reversible step.

Characteristics of E1CB mech. (1) These reactions are limited to the substrates, which can stabilise the carbanion intermediate i.e. β carbon should contain >C=O, NO_2, CN, or sulphonyl groups.

(2) Leaving group should be poor leaving group

(3) Reaction occurs in presence of a strong base

(4) β-hydrogen should be highly acidic

(5) Product formation occurs generally by Hofmann's rule.

(3) E1-mechanism (2nd invited) Elimination Reaction - by P.K. Sharma

In these reactions, rate of reaction is dependent only on the concentration of the substrate and is independent of the conc^n of the nucleophile. Like SN1, E1 reactions also occur in two steps - (1) In first step, slow ionization of alkyl halide produces carbocation (which is a rate determining step)