14.1 Introduction

Elimination reactions are formally the reverse of addition reactions and *consist in removing the two groups* (generally, one being a proton) *from one or two carbon* atoms of a molecule to form an unillustrated linkage or center, e.g.,*

$$RCH_2CH_2X \xrightarrow{OH^-} RCH{=}CH_2 + H_2O + X^-$$

Elimination reactions are classified under two general headings.

(A) 1, 2-(β)-Elimination : *When the two groups or atoms are removed from the two adjacent carbon atoms, the process is known as β-elimination.* This is the most common and important type and hence, most of our discussion will be concerned with this type. The carbon atom from which Y (atom or group other than hydrogen) is lost is usually designated as the 1-(α-) carbon and that losing H as the 2-(β-) carbon ; however, in the older αβ-terminology, the α- is usually omitted and the reactions are thus, referred to simply as β-eliminations. The most familiar examples of β-elimination are (*i*) base-induced elimination of hydrogen halide from alkyl halides (generally bromides), (*ii*) acid-catalysed dehydration of alcohols, and (*iii*) Hofmann degradation of quaternary alkyl ammonium hydroxides.

(*i*) $$RCH_2CH_2Br \xrightarrow{OH^-} RCH{=}CH_2 + H_2O + Br^-$$

(*ii*) $$RCH_2CH_2OH \xrightarrow{H^+} RCH{=}CH_2 + H_3O^+$$

(*iii*) $$RCH_2CH_2\overset{+}{N}Me_3\overset{-}{O}H \longrightarrow RCH{=}CH_2 + H_2O + NMe_3$$

(B) 1, 1-(α-) Elimination : *When the two groups are eliminated from the same carbon atom, the process is known as α-elimination.* However, only a small number of examples of this type are known. The most important being the base-catalysed elimination of HCl from alkyl chloride. For example,

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{B:} CH_3CH_2CH{=}CH_2$$

* **Some eliminationa reactions are also known in which the two groups are eliminated from the two different adjacent atoms, *viz.* a carbon atom and a hetero atom, *e.g.*,**

$$\underset{\text{Benzaldoxime acetate}}{C_6H_5{-}CH{=}NOAc} \xrightarrow{-AcOH} \underset{\text{Phenyl cyanide}}{C_6H_5\,C{\equiv}N}$$

$$R{-}\overset{\overset{\Large H}{|}}{\underset{\underset{\Large CN}{|}}{C}}{-}OH \xrightarrow{-HCN} RCHO$$

But these reactions have not been studied in detail.

14.2 Mechanism of β-Elimination

Depending upon the structure of alkyl halide and some other factors, the reaction can take place either by E2 (elimination, biomolecular) or by El (elimination, unimolecular) mechanism.

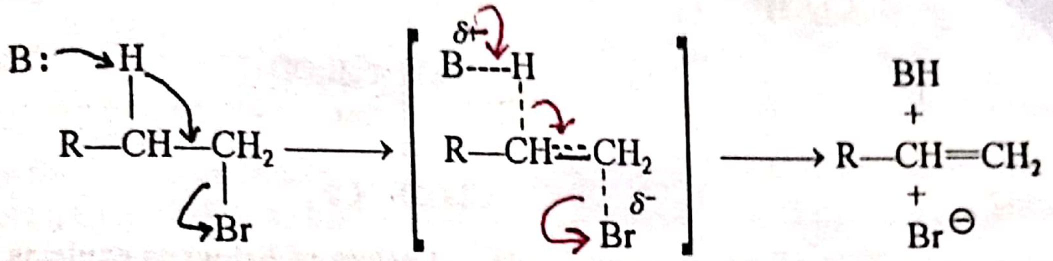
1. The E2 mechanism. Kinetic studies reveal that the rate of the base-induced elimination of HBr from the alkyl bromides is proportional to the concentration of both of the reactants, *i.e.*, alkyl halide as well as base. In other words,

$$CH_3CH_2Br + \bar{O}C_2H_5 \longrightarrow CH_2{=}CH_2 + C_2H_5OH + Br^-$$

$$\text{Rate} = k\,[CH_3CH_2Br]\,[\bar{O}C_2H_5]$$

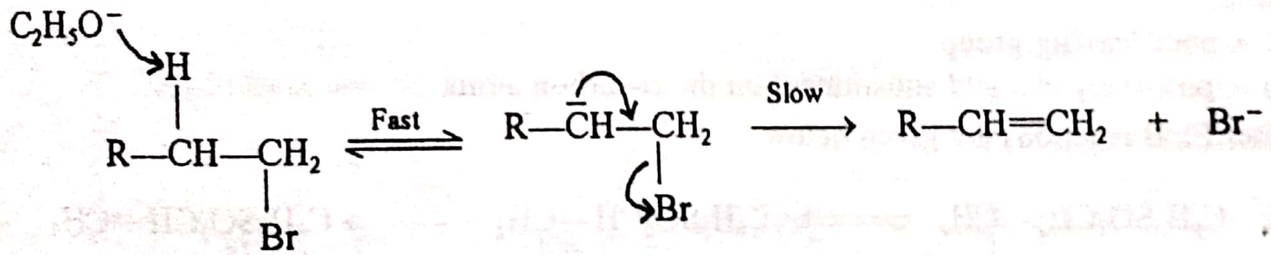
Two alternative mechanisms can be proposed on the basis of this kinetic evidence.

One-step process. This consists in the attack of a nucleophile (base) on the β-carbon atom followed by a simultaneous loss of a halide ion from the α-carbon atom.



Since the reaction is a one-step process which involves two molecules, the mechanism is designated as E2.

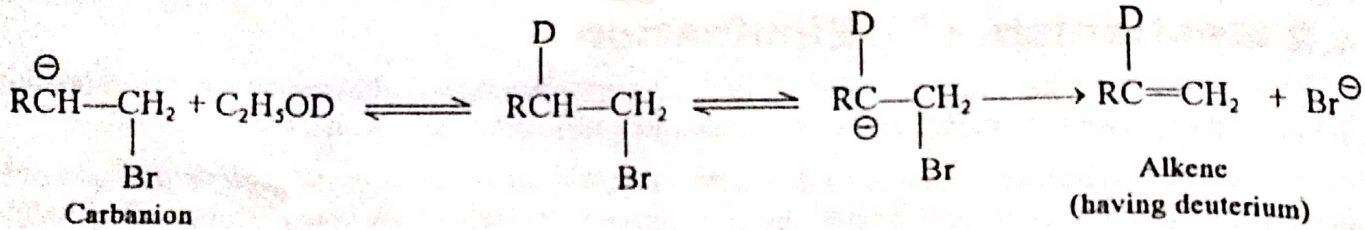
Two-step process. In this mechanism, the reaction takes place in two distinct steps. The first step involves rapid removal of a proton from the α-carbon forming a carbanion which then loses the halide ion in the second rate-determining step.



Note that this mechanism although involves two steps, the overall rate of reaction is limited to the slower second step and hence, *the rate of reaction depends only on the concentration of the carbanion.* Now since carbanion is the conjugate base of the alkyl halide* and its conversion to alkene involves only one molecule, the mechanism is designated as **ElcB mechanism** (*elimination unimolecular, conjugate base*).

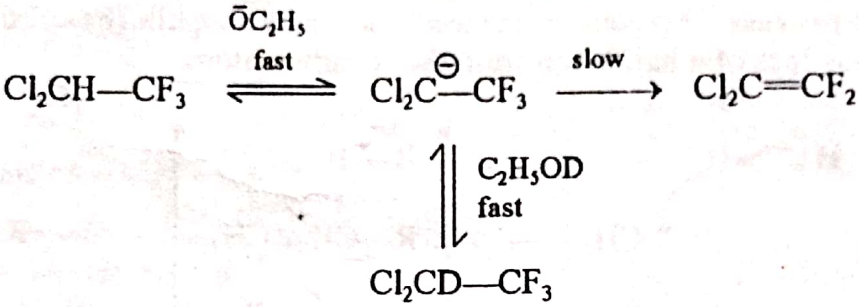
The actual path adopted by a reaction can be established by isotopic labelling experiments. In the two-step process (ElcB mechanism), since the first step is reversible when such reaction is carried out in presence of C_2H_5OD instead of C_2H_5OH, the intermediate carbanion (conjugate base of the alkyl halide) should pick up deuterium and hence, the product must contain labelled hydrogen (deuterium).

* α-Hydrogen of alkyl halides are acidic in nature and hence, such halides are examples of *carbon acid* (extremely weak acids).



Thus, 2-phenyl ethyl bromide ($C_6H_5CH_2CH_2Br$) when treated with C_2H_5OD, no deuterated styrene ($C_6H_5CD{=}CH_2$) is formed which shows that the reaction exclusively takes place *via* E2 mechanism and not through ElcB mechanism.

Reactions proceeding by ElcB pathway are exceedingly rare. However, elimination of HF from $X_2CH.CF_3$ (when X = halogen) certainly involves ElcB mechanism. For example,



Note that a stronger C—F bond coupled with —I effect of halogens explains the formation of carbanion before elimination. In general, the formation of carbanion and hence, the ElcB mechanism is favoured by the following facts.

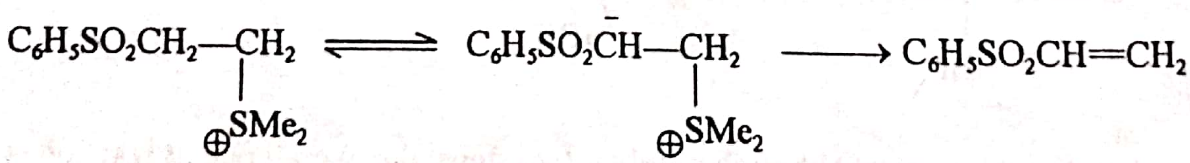
(a) Presence of electronegative halogen atoms on the β-carbon to make the β-hydrogen more acidic.

(b) Stabilisation of the carbanion through electron withdrawal by the halogen atoms on the carbanion carbon atom.

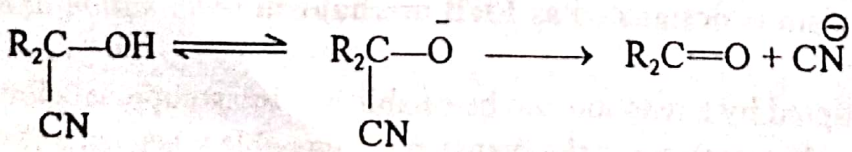
(c) A poor leaving group.

(d) A positively charged substitutent on the α-carbon atom.

Other ElcB reactions are given below.

(*i*) 

(*ii*) Reversal of simple addition to >C=O, *e.g.*, hydrolysis of cyanohydrin to ketone and cyanide ion :



(*iii*) Benzyne formation.

Characteristics of E2 reactions

(*i*) The reaction rate increases with increasing strength of the base, *e.g.*,

$$CH_3COO^- < HO^- < C_2H_5O^- < (CH_3)_3CO^- < NH_2^-$$

(*ii*) The rate increases with the decrease in the dissociation energy of the C—X bond. Thus, the ease of the E2 reaction of alkyl halides is —I > —Br > —Cl > —F because of the following order of the bond dissociation energies.

C—I < C—Br < C—Cl < C—F

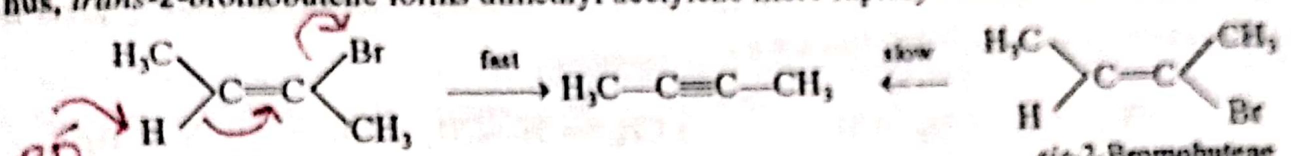
Thus, iodide is the best leaving group of the series and fluroide is the worst.

(*iii*) Among alkyl groups, the order of reactivity is

tertiary > secondary > primary.

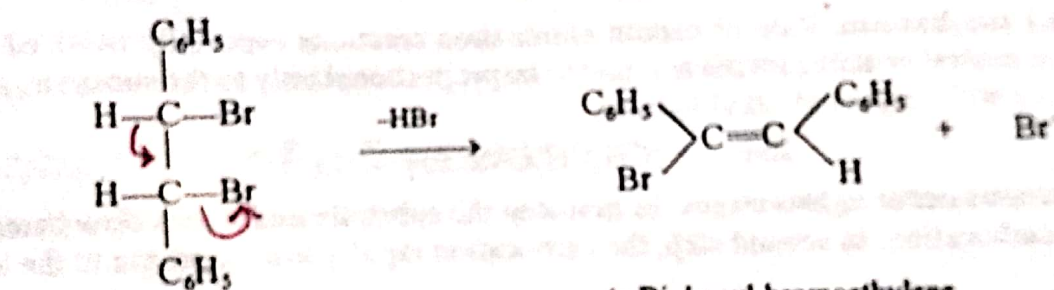
(*iv*) Elimination occurs more readily when the new double bond comes in conjugation with the existing unsaturated bond. Thus, elimination of HBr occurs more readily from $CH_2{=}CH{-}CH_2{-}CH_2Br$ than from $CH_3{-}CH_2{-}CH_2{-}CH_2Br$.

(*v*) The reaction occurs fastest when the two eliminated groups are *trans* to each other rather than *cis*. Thus, *trans*-2-bromobutene forms dimethyl acetylene more rapidly than the *cis* isomer.

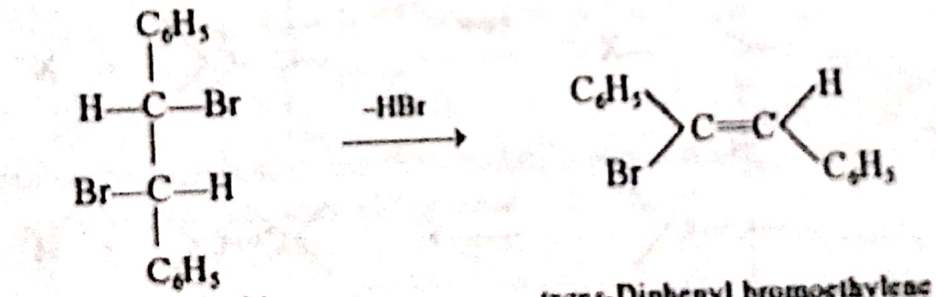


trans-2-Bromobutene *cis*-2-Bromobutene

(*vi*) The nature of products of E_2 reactions of compounds having two chiral carbon atoms depends upon the stereochemistry of the starting isomers. Thus, dehydrobromination of *meso*-stillbene dibromide gives the *cis*-alkene whereas the *trans*-alkene is obtained from the *dl*-isomer.

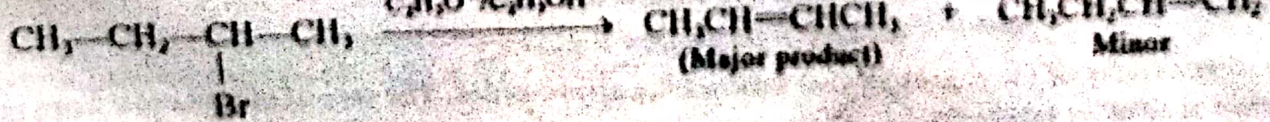


meso-Stilbene dibromide *cis*-Diphenyl bromoethylene



dl-Stilbene dibromide *trans*-Diphenyl bromoethylene

When two different olefins may be formed, the one having the more highly conjugated olefin will be the major product (*Saytzeff rule*). For example,



Exceptions to Saytzeff rule. **(a)** When the proton to be removed is in the sterically more hindered environment, the use of a base having sterically hindered carbon leads mainly the lesser conjugated olefin. For example,

$$(CH_3)_2\underset{\substack{|\\ Br}}{C}{-}CH_2CH_3 \xrightarrow{C_2H_5O^-} \underset{\text{Major}}{(CH_3)_2C{=}CHCH_3} + \underset{\text{Minor}}{CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2CH_3}$$

$$(CH_3)_2\underset{\substack{|\\ Br}}{C}{-}CH_2CH_3 \xrightarrow{Et_3CO^-} \underset{\text{Minor}}{(CH_3)_2C{=}CHCH_3} + \underset{\text{Major}}{CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2CH_3}$$

(b) Elimination from quaternary ammonium ions (Hofmann elimination) usually gives the less highly conjugated olefin (*Hofmann rule*), *e.g.*,

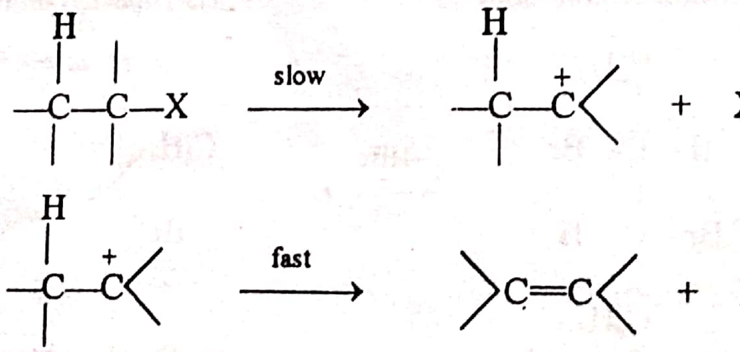
$$CH_3{-}\underset{\substack{|\\ ^+NMe_3}}{CH}{-}CH_2{-}CH_3 \xrightarrow{OH^-} CH_2{=}CH{-}CH_2{-}CH_3 + Me_3N + H_2O$$

(*vii*) The S_N2 reaction always competes with the E2 reaction, the proportion of the product depends upon the nature of the base and the alkyl group.

2. The E1 mechanism. Rate of certain elimination reactions especially those of secondary and tertiary halides in neutral or acidic media is found to be proportional only to the substrate; *i.e.*, they follow first order kinetics with respect to alkyl halides.

$$\text{Rate} = k\,[CH_3CH_2CMe_2Br]$$

These reactions occur in two stages. In first step the substrate undergoes slow heterolysis to form halide ion and a carbocation. In second step, the carbocation rapidly loses a proton to the base and forms the alkene.



Now here in the rate determining step since only one molecule undergoes covalency change, the mechanism is referred to as El (*elimination, unimolecular*). Like E2 reactions, El reactions are often accompanied by substitution as well.

Characteristics of El Reactions :

(*i*) Since stabilities of the carbonium ion follow the order

tertiary > secondary > primary

the order of reactivity of alkyl groups also follows the above order. The rate of elimination from primary alkyl groups is usually negligible.