B.SC PART I PAPER ORGANIC

TOPIC:- Reaction Mechanism Part-2

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MECHANISMS OF ELIMINATION REACTIONS

Elimination reactions are reverse of addition reaction. Here two or four atoms or groups attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a multiple bond. The dehydrohalogenation of alkyl halides with alcoholic alkalis is an example of elimination.

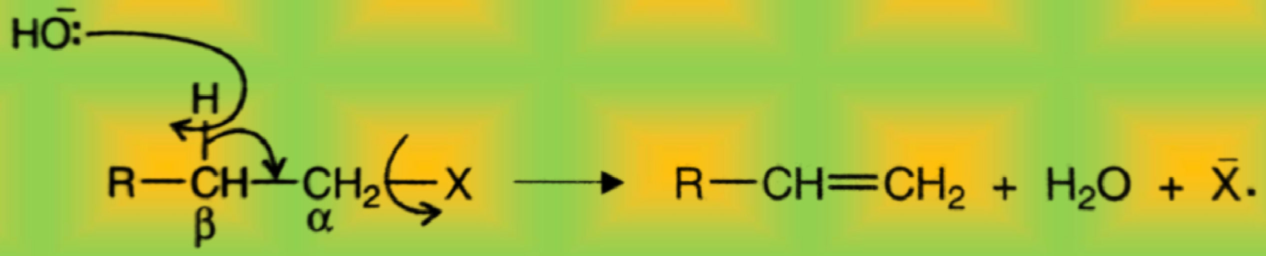
$$R-CH_2-CH_2-X \xrightarrow{\bar{O}H} R-CH=CH_2 + H_2O + \bar{X}$$

These reactions like substitution reactions are also divided into two classes:

(1) E2 Reactions

(2) E1 Reactions

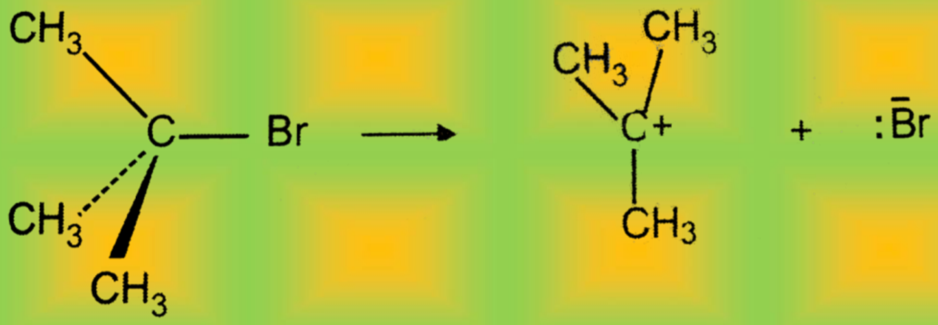
E2 Reaction- E2 stand for biomolecular elimination. When the rate of an elimination reaction depends upon the concentration of a substrate and the nucleophile, the reaction is of second order and is represented as E2. E2 like S_N2 is also a one step process in which the abstraction of the proton from the β-carbon and the expulsion of the halide ion from the α-carbon occurs simultaneously. The mechanism of such a reaction is shown in fig



Elimination by E2 mechanism.

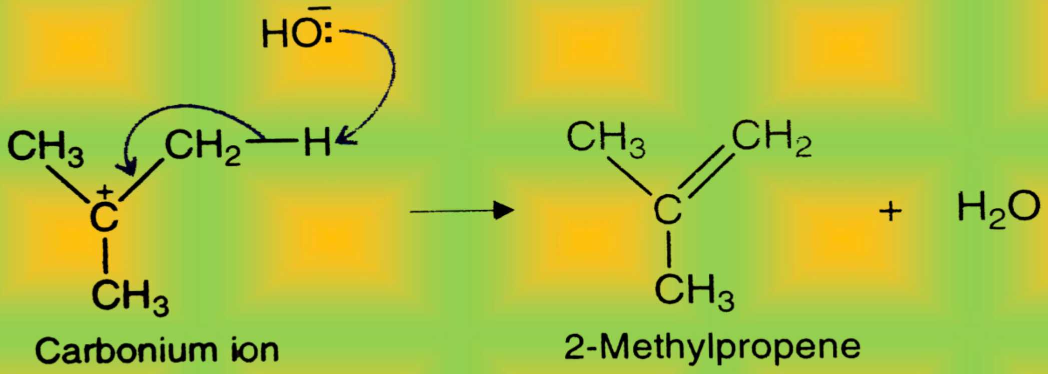
E1 Reaction- E1 stand for unimolecular elimination. When the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 like S_N1 reactions are also two step processes.

Step 1. The alkyl halide ionize to give the carbonium ion.

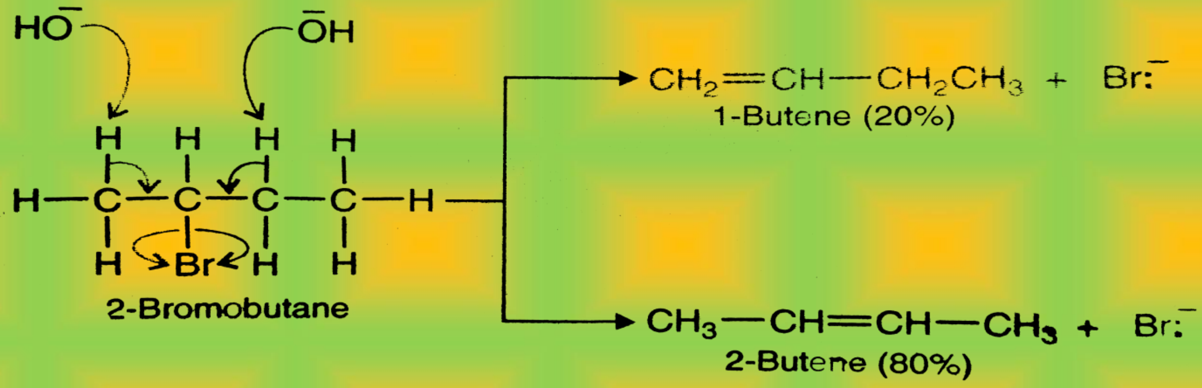


tert-butyl bromide Carbonium ion

Step 2. A proton is abstracted by the base from the adjacent β-carbon atom to give the alkene.



If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according the Saytzeff Rule, the main product is the most highly substituted alkene. For example, two alkenes are possible when 2bromobutane is heated with alcoholic KOH.

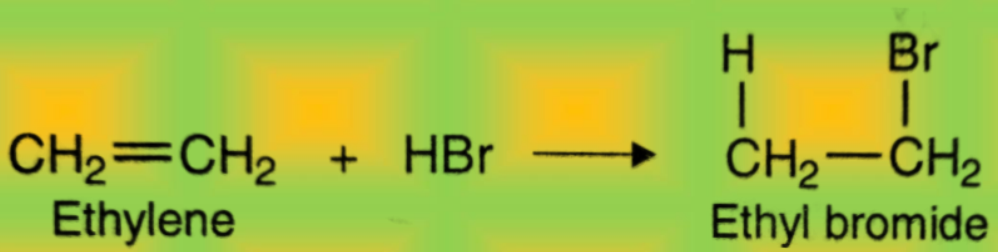


According to the saytzeff Rule, the main product is the disubstituted alkene, 2butene, rather than the monosubstituted, 1-butene.

MECHANISMS OF ADDITION REACTIONS

Addition reactions are those in which atoms or groups of atoms are simply added to a double or triple bond without the elimination of any atom or other molecules. These reactions may be initiated by electrophiles, nucleophiles, or free radicals.

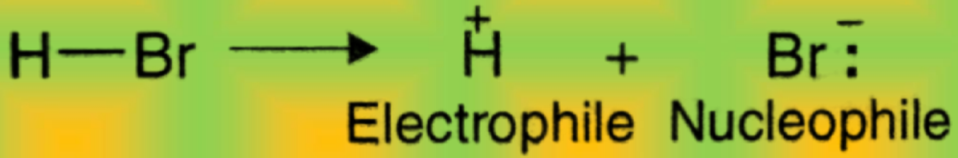
Electrophilic Addition Reactions- When an addition reaction involves the initial attack by an electrophile, the reaction is referred to as electrophilic addition. Compounds containing carbon-carbon double and triple bonds undergo such reactions. The addition of HBr to ethylene is an example of electrophilic addition.



$$CH_2{=}CH_2 + HBr \longrightarrow \underset{}{\overset{H}{\underset{|}{}}CH_2}-\overset{Br}{\underset{|}{}}CH_2$$

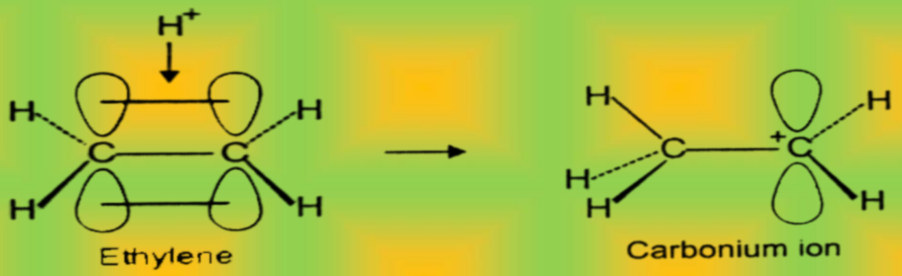
The mechanism of the above reaction involves the following steps:

Step 1. Hydrogen bromide gives a proton(H^+) and bromide ion (Br^-).

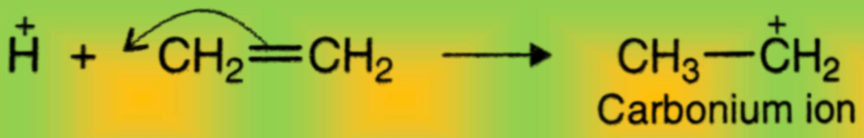


$$H-Br \longrightarrow \overset{+}{H} + \overset{-}{Br:}$$

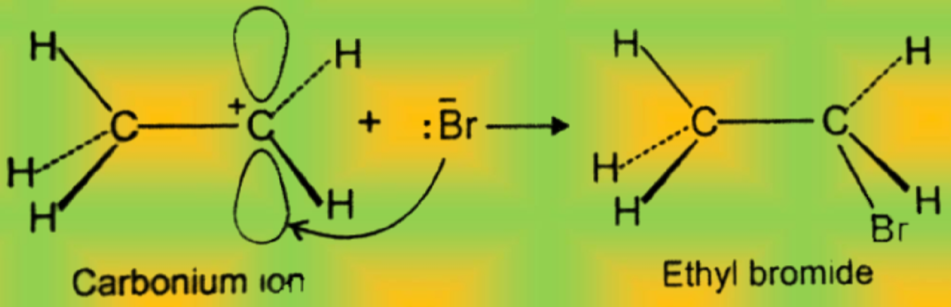
Step 2. The proton (electrphile) attacks the π bond of ethylene to give a carbonium ion.



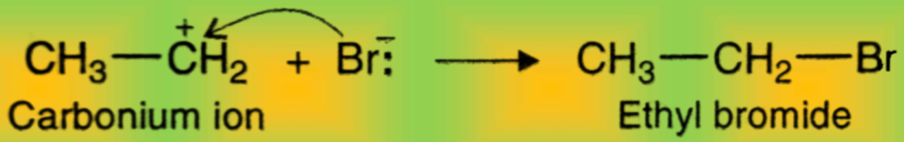
This step can also be written as:



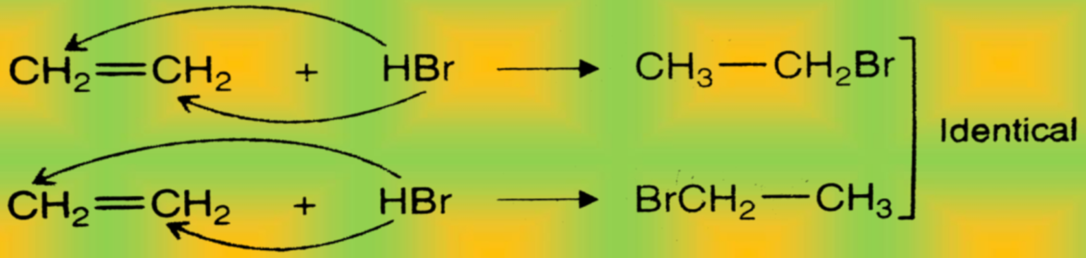
Step 3. The bromide ion (nucleophile) attack the carbonium to give the addition product.



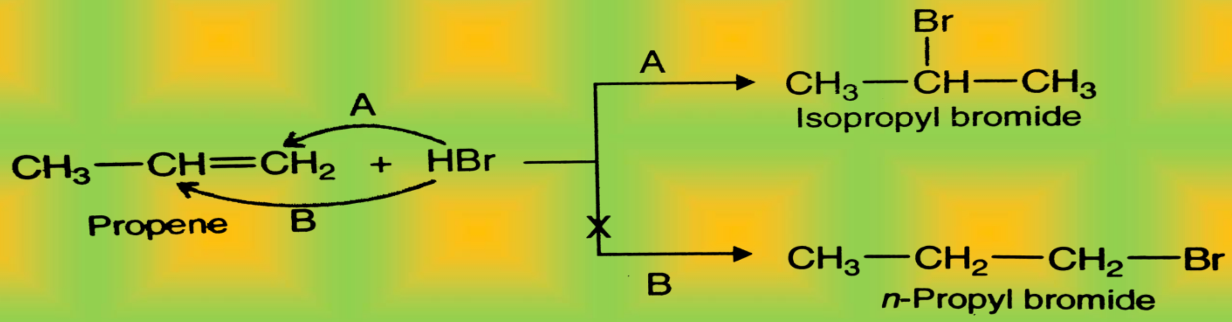
This step can also be written as:



Other reagents like HCL, HOCL, H_2SO_4, H_2O, Br_2, Cl_2,etc., add tp alkenes similarly. When an alkene is symmetrical about the double bond, as ethylene is, the product formed in addition reaction is the same no matter which way the reagent become attached to the alkene.



If however, both the alkene and the adding reagent are unsymmetrical, two alternatives are possible:



$CH_3-CH=CH_2 + HBr$

$CH_3-CH(Br)-CH_3$

$CH_3-CH_2-CH_2-Br$

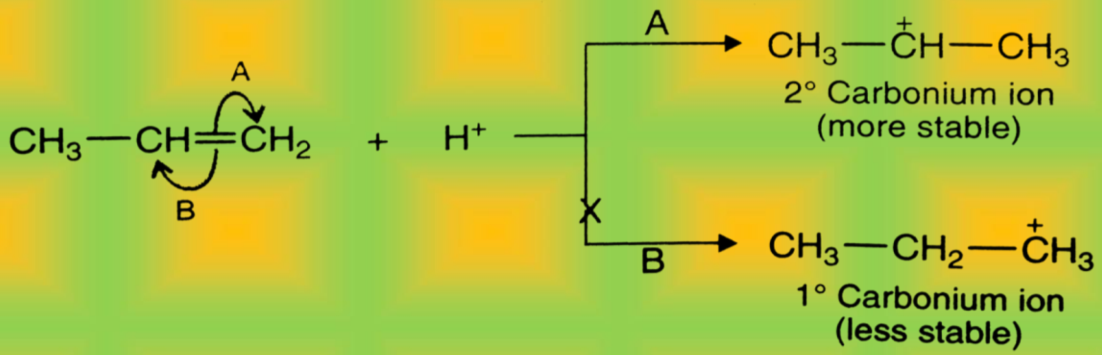
When an unsymmetrical reagent adds to an unsymmetrical double bond, the positive part of the reagent becomes attached to the double-bonded carbon atom which bears the greatest number of hydrogen atoms.

Markovnikov Rule can be rationalized in terms of modern mechanistic theory. Consider the addition of HBr to propene. The mechanism of this reaction involves the following steps:

Step 1. Hydrogen bromide gives a proton (H^+) and a bromide ion ($Br\overset{-}{:}$)

$$H{-}Br \longrightarrow H^{+} + Br\overset{-}{:}$$

Step 2. The proton (electrophile) attacks the π bond of propene to give a more stable carbonium ion.



Remember: The tertiary(3°) carbonium ouns are more stable than secondary (2°) carbonium ions. Secondary (2°) carbonium ions in turn are more stable than primary (1°) carbonium ions.

Step 3. The bromide ion (nucleophile) combines with the more stable secondary carbonium ion to give the major product.

$$CH_3-\overset{+}{C}H-CH_3 + \overset{-}{Br}: \longrightarrow CH_3-\overset{\overset{Br}{|}}{C}H-CH_3$$

2° carbonium ion

Isopropyl bromide

Markovnikov rule may now be restarted**: Addition of an unsymmetrical reagent to an unsymmetrical double bond proceeds in such a way as to involve the most stable carbonium ion.**

Thank You