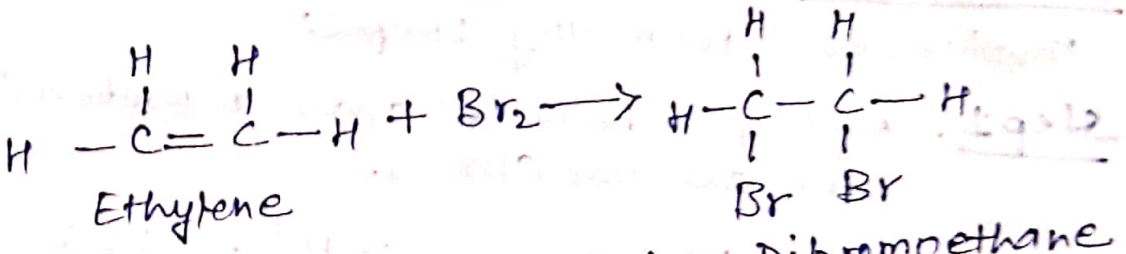
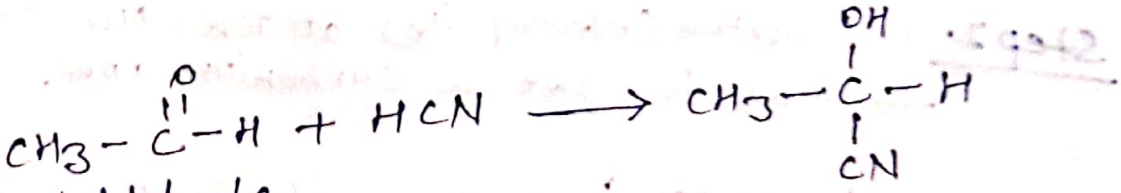
Addition Reactions

Addition reactions are those reactions in which atoms or groups of atoms are simply added to a double bond or triple bond without the elimination of any atom or other molecules. Double bonds become saturated, and triple bonds are converted into double bonds or may become saturated by further addition. In these reactions, at least one π bond is lost while two new σ bonds are formed. For Example -



Ethylene

1, 2-Dibromoethane



Acetaldehyde

Acetaldehyde cyanohydrin

Addition reactions may be initiated by electrophiles, nucleophiles, or free radicals. When these reaction involves the initial attack by an electrophile then these reactions are called electrophilic addition. and when these reaction involves the initial attack by an nucleophile then these reactions are known as nucleophilic addition reactions. when these reactions are carry out by the help of free radicals then these reactions are known as free radical addition reactions.

Electrophilic Addition Reactions

In these reactions, the reactions are carry out by initial attack by an electrophile*. Compounds containing carbon-carbon double and triple bonds undergo such reactions. The addition of HBr to ethylene is an example of Electrophilic addition.

$$CH_2=CH_2 + HBr \longrightarrow \underset{\text{Ethyl bromide}}{\overset{H \quad Br}{|\quad\ |}\ CH_2-CH_2}$$

Ethylene

Mechanism:— The mechanism of the above reaction involves the following steps:

step1. Hydrogen bromide gives a proton (H^+) and bromide ion (Br^-).

$$H-Br \longrightarrow \underset{\text{(Electrophiles)}}{H^+} + \underset{\text{(Nucleophile)}}{Br:}$$

step2. The proton (electrophile) attacks the π bond of ethylene to give a carbonium ion.

$$H^+ + CH_2=CH_2 \longrightarrow \underset{\text{carbonium ion}}{CH_3-\overset{+}{C}H_2}$$

step3. The bromide ion (nucleophile) attacks the carbonium ion to give the addition product.

$$\underset{\text{Carbonium ion}}{CH_3-\overset{+}{C}H_2} + Br^- \longrightarrow \underset{\text{(Addition Product)}}{CH_3-CH_2-Br}$$

Ethyl Bromide

Other reagents like HCl, HOCl, H_2SO_4, H_2O, Br_2, Cl_2 etc., add to alkenes similarly.

★ **Electrophiles**:— A reagent which can accept an electron pair in a reaction is called an electrophile. These are Electron deficient and electron-loving and attacks regions of high electron density (negative centres) in the substrate molecules. They may be positive ions or neutral molecules.

Markovnikov's Rule or Markownikoff's Rule

- This rule is applicable for addition reactions in alkenes.
- According to this rule "when an unsymmetrical reagent adds to an unsymmetrical alkene, the positive part of the reagent becomes attached to the double bonded carbon which bears the greatest number of hydrogen atoms".

For Example – propene react with HBr in two ways.

$$CH_3-CH=CH_2 + H^+Br^- \xrightarrow{(A)\ (More)} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

Propene (Unsymmetrical alkene) — Hydrogen bromide (Unsymmetrical reagent) — Isopropyl Bromide (Major product)

In this reaction H^+ (Positive part) of Unsymmetrical reagent HBr is attached to the double bonded carbon of unsymmetrical alkene which has the more hydrogens. It may be possible that Br^- ion is attached to the double bonded carbon atoms of alkene but it is happened very less and form the minor product.

For Example –

$$CH_3-CH=CH_2 + H^+Br^- \xrightarrow{(B)\ (less)} CH_3-CH_2-CH_2-Br$$

Propene — n-propyl Bromide (Minor Product)

Experimentally it has been found that isopropyl bromide is the major product.

Note :– This rule assigns the orientation* of the electrophilic addition of hydrogen halides to asymmetrical alkenes or alkynes.

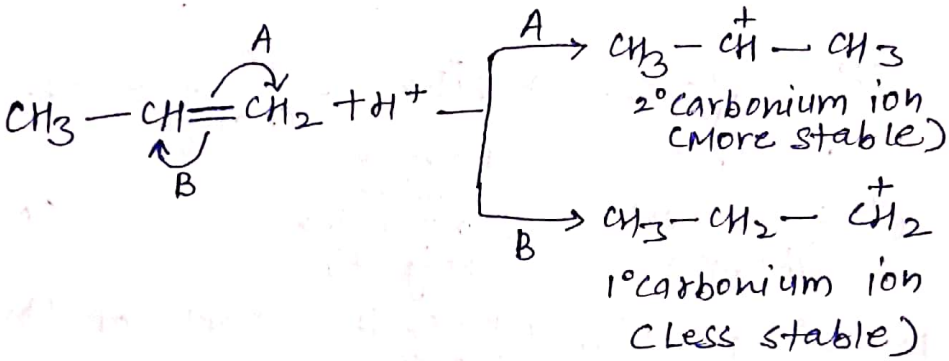
* orientation – guideline.

MECHANISM :- The mechanism of this reaction involves the following steps:

Step 1. HBr ionises to give a proton (electrophile) and a bromide ion (nucleophile)

$$HBr \longrightarrow \underset{\text{Proton}}{H^+} + \underset{\text{Bromide ion}}{:Br^-}$$

Step 2. The proton attacks the double bond to form a more stable carbonium ion.



Step 3. The bromide ion attacks the more stable secondary carbonium ion to give the major product.

$$\underset{\text{2° carbonium ion}}{CH_3-\overset{+}{C}H-CH_3} + :Br^- \longrightarrow \underset{\text{Isopropyl bromide}}{CH_3-\overset{Br}{\overset{|}{C}}H-CH_3}$$

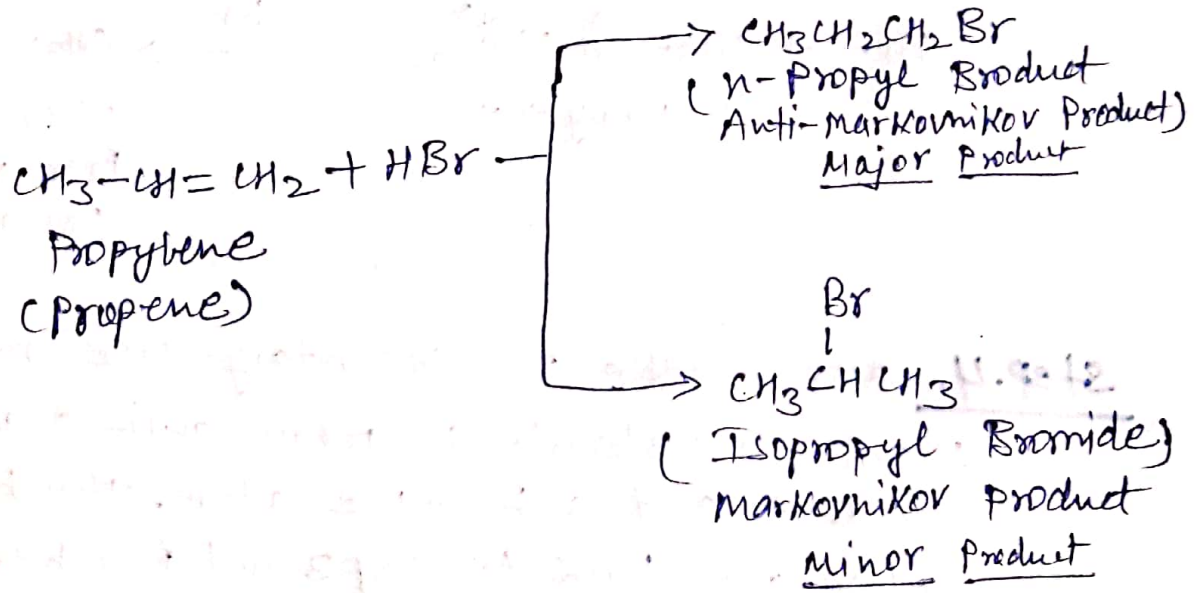
Note :- Tertiary (3°) carbonium ions are more stable than secondary (2°) carbonium ions. Secondary carbonium ions are more stable than primary (1°) carbonium ions.

3° Car. ions > 2° car. ions > 1° Car. ions.

Sequences of stability of carbonium ions.

Anti-Markovnikov's Rule or Anti-Markownikoff's Rule or Peroxide Effect

This rule or phenomenon is opposite of Markovnikov rule. Markovnikov rule is quite general but not ~~this~~ Universal. In 1933 the American chemist M.S. Kharasch discovered that the addition of HBr to unsymmetrical alkenes in the presence of organic peroxides (R–O–O–R) takes a course opposite to that suggested by Markovnikov rule. This phenomenon of anti-Markovnikov addition of HBr caused by the presence of peroxides is known as peroxide effect. For Example–



MECHANISM:– Propylene reacts with HBr in the presence of a peroxide by a Free radical Mechanism. Following steps are involved:

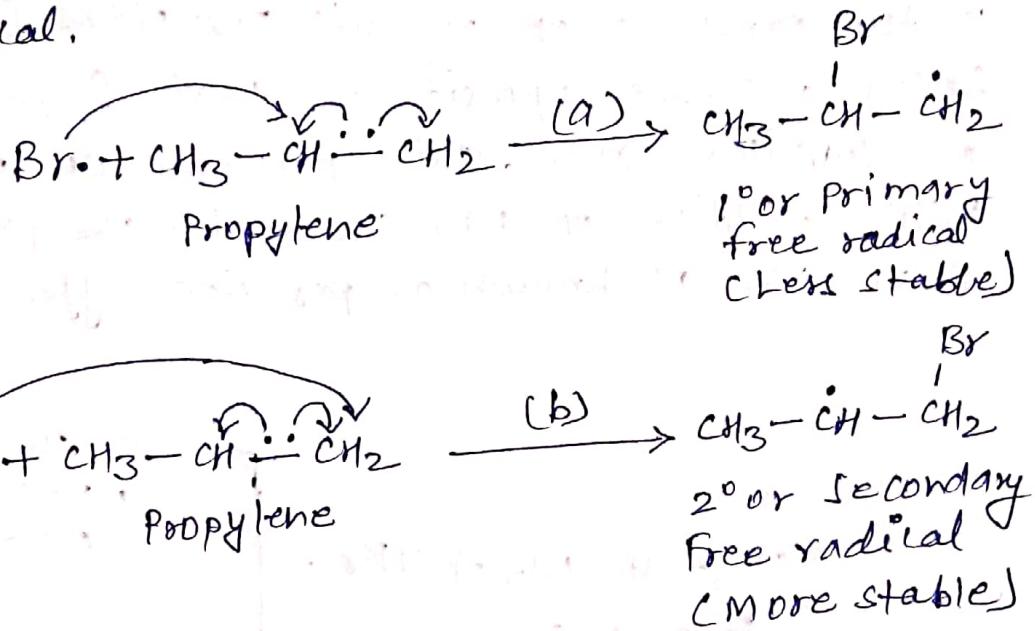
Step 1. Peroxides dissociates to give alkoxy free radicals.

$$R-O-O-R \xrightarrow{\Delta} 2R-O\cdot$$

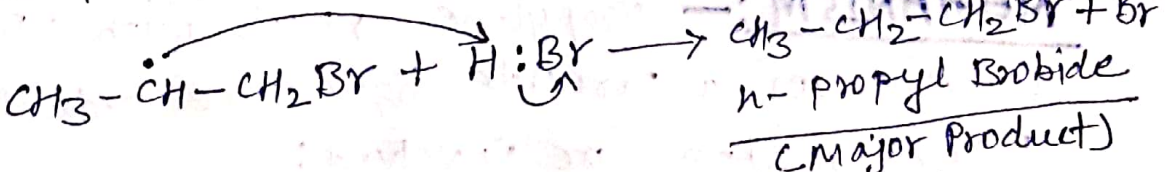
Step 2. Alkoxy free radical attacks HBr to form a bromine atom (a free radical).

$$R-O\cdot + H:Br \longrightarrow R-OH + Br\cdot$$

Step3. Bromine atom can attack propylene to give a primary free radical and a secondary free radical.



Step.4. More stable 2° or secondary free radical attacks the H–Br molecule to form anti-Markovnikov product and a bromine atom. The bromine atom goes back to step3 and further proceed the process.



Note:- The order of stability of free radicals is $3^{\circ} > 2^{\circ} > 1^{\circ}$. Therefore, the more stable 2° free radical is formed predominantly.