BP 202T - PHARMACEUTICAL ORGANIC CHEMISTRY - I

UNIT: 2 ALKANES, ALKENE & CONJUGATED DIENES

CLASS: 6

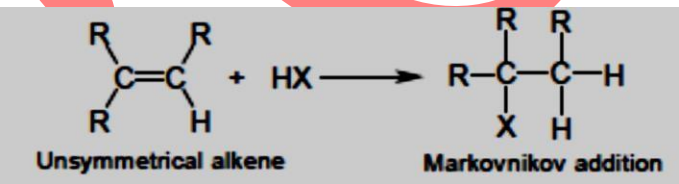
TOPIC: MARKOWNIKOFF'S RULE & FREE RADICAL ADDITION REACTIONS OF ALKENES

ELECTROPHILIC ADDITION TO SYMMETRICAL AND UNSYMMETRICAL πBONDS

- When the same substituents are at each end of the double or triple bond, it is called symmetrical.
- Unsymmetrical means different substituents are at each end of the double or triple bond.
- Electrophilic addition of unsymmetrical reagents (HX, H2O or ROH) to unsymmetrical double or triple bonds follows Markovnikov's rule.

MARKOVNIKOV'SRULE

- In the ionic addition of an acid to the carbon-carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon atom that already holds the greater number of hydrogen. This statement is generally known as **Markovnikov's rule.**

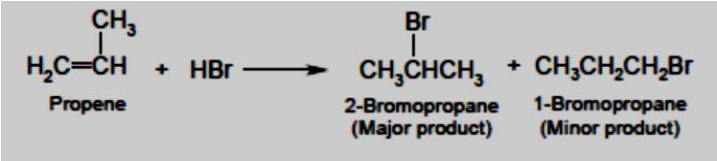


MODERN MARKOVNIKOV RULE

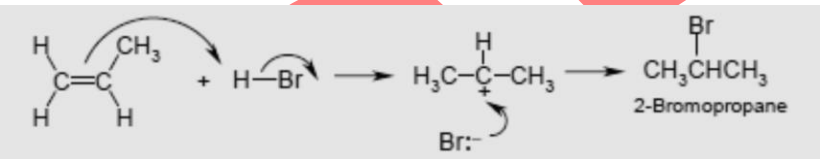
- The modern Markovnikov rule states that, in the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent adds to a carbon atom of the double bond to yield themorestable carbocation as an intermediate.

- For example, Alkenes are converted to alkyl halides by the addition of HX (HCl, HBr or HI). Addition of HX to unsymmetrical alkenes follows Markovnikov's rule.

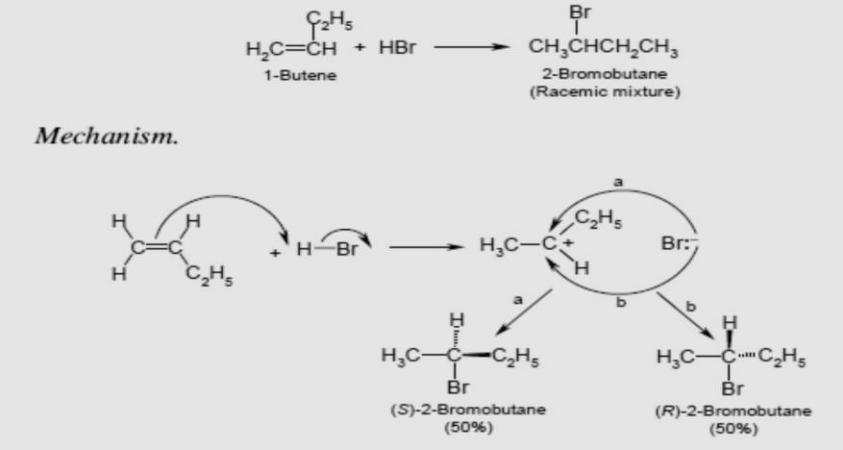
- Addition of hydrogen bromide (HBr) to propene yields 2-bromo propane as the major product.



Mechanism: The double bond *p* electrons attack the electrophile. Protonation of the double bond yields asecondarycarbocationintermediate.Thebrominenucleophileattacksthecarbocationtoform2-bromopropane.



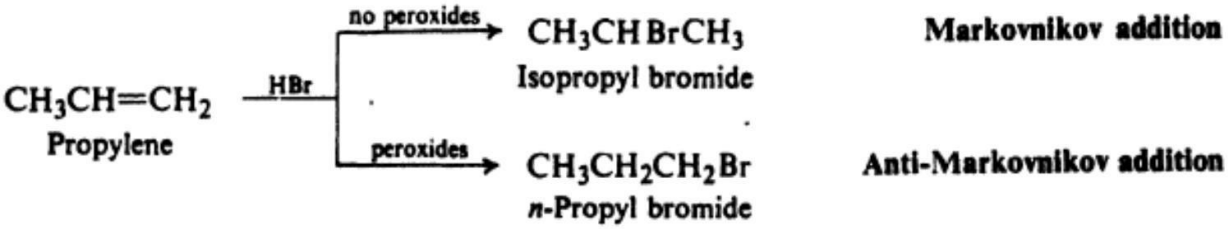
- Addition of HBr to 1-butene yields a chiral molecule. The reaction is region selective and a racemic mixture is formed.



PEROXIDE EFFECT OR KHARASCH EFFECT OR ANTI-MARKOVNIKOV RULE (FREE RADICAL ADDITION REACTION)

- In the absence of peroxides, hydrogen bromide adds to alkenes in agreement with Markovnikov's rule; in the presence of peroxides, the direction of addition is exactly reversed.

- When HBr is added to alkenes in the presence of free radical initiators, e.g: hydrogen peroxide (HOOH) or alkyl peroxide (ROOR).
- For example: 2-methyl propene reacts with HBr in the presence of peroxide (ROOR) to form 1-bromo-2-methyl propane, which is an anti-Markovnikov product.
- Radical additions do not proceed with HCl or HI.

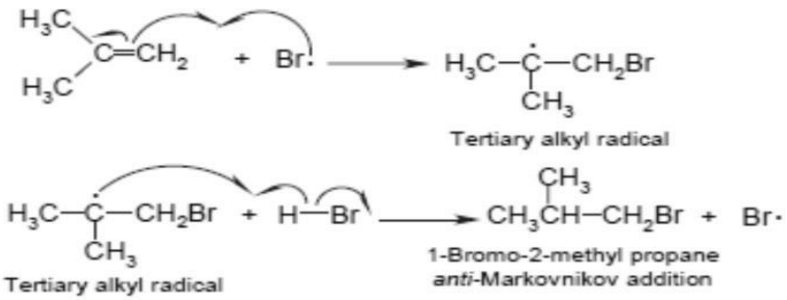


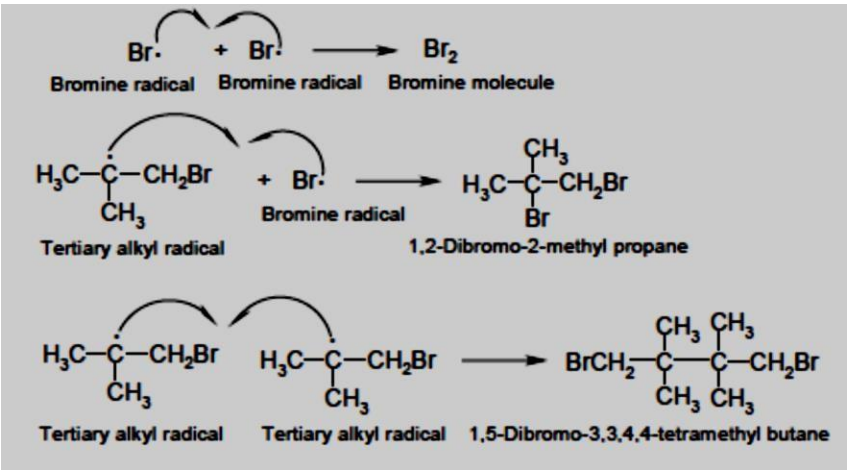
Mechanism: Free radicals reaction occurs in three steps

1. **Initiation:** The oxygen–oxygen bond is weak, and is easily homolytically cleaved to generate two alkoxy radicals, which in turn abstract hydrogen to generate bromine radicals.

2. **Propagation:** The bromine radical is electron deficient and electrophilic.

- The radical adds to the double bond, generating a carbon-centered radical. This radical abstracts hydrogen from HBr, giving the product and bromine radical.
- The orientation of this reaction is **anti - Markovnikov**. The reversal of region chemistry through the use of peroxides is called the **peroxide effect**.





3. **Termination:** Any two radicals present in there action mixture can combine in a termination step and end the radical chain reaction. Thus, radical reactions produce a mixture of products

2MARKS QUESTIONS

1. Define Markonikoff's rule
2. Define peroxide effect
3. What is modern markonikoff's rule?

5 MARKS QUESTIONS

1. Explain Anti-Markonikoff's rule with mechanism
2. Explain peroxide effect with mechanism