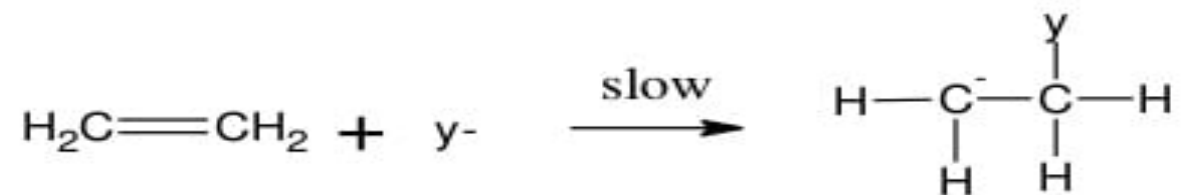


Addition Reactions

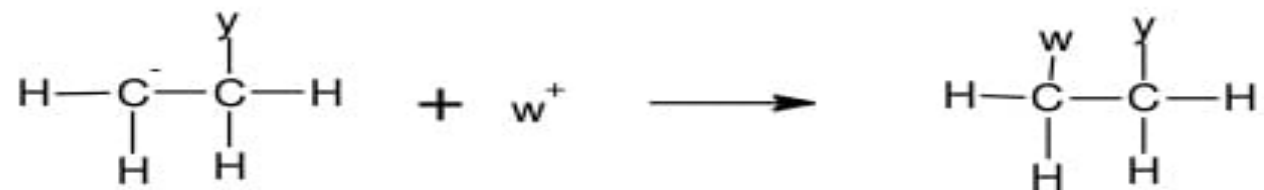
Dt. 03/01/2022

NUCLEOPHILIC ADDITION

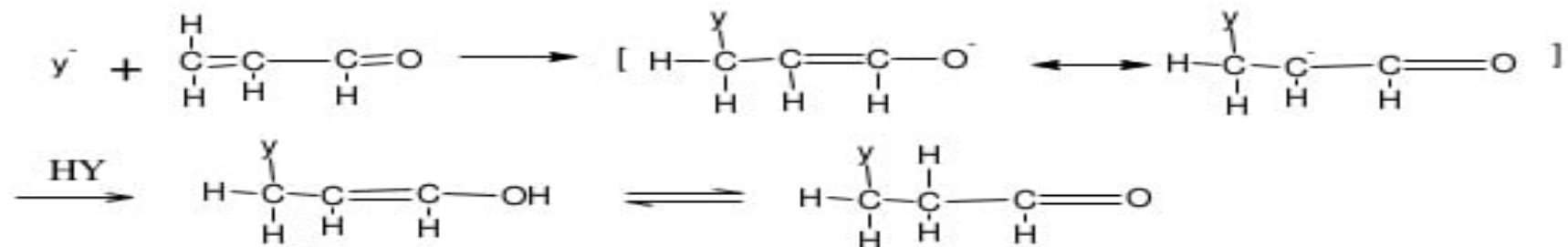
step 1



step 2



Addition of HY to a substrate of the form $-\text{C}=\text{C}-\text{Z}$, where $\text{Z} = \text{CHO}, \text{COR}, \text{COOR}, \text{CONH}_2, \text{SOR}, \text{SO}_2\text{R}$ etc.



Protonation occur at oxygen

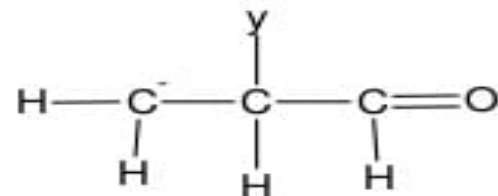
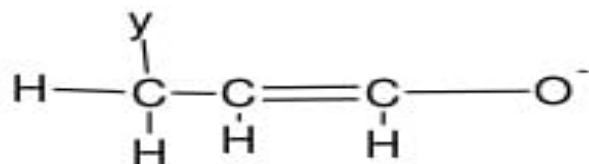
The mechanism is 1,4 nucleophilic addition.

When $Z = \text{CN}$ or CO

Y^- attack to the carbon, similar to the above

Mechanism may be 1,2 or 1,4 addition .

Y^- never attack at 3 position



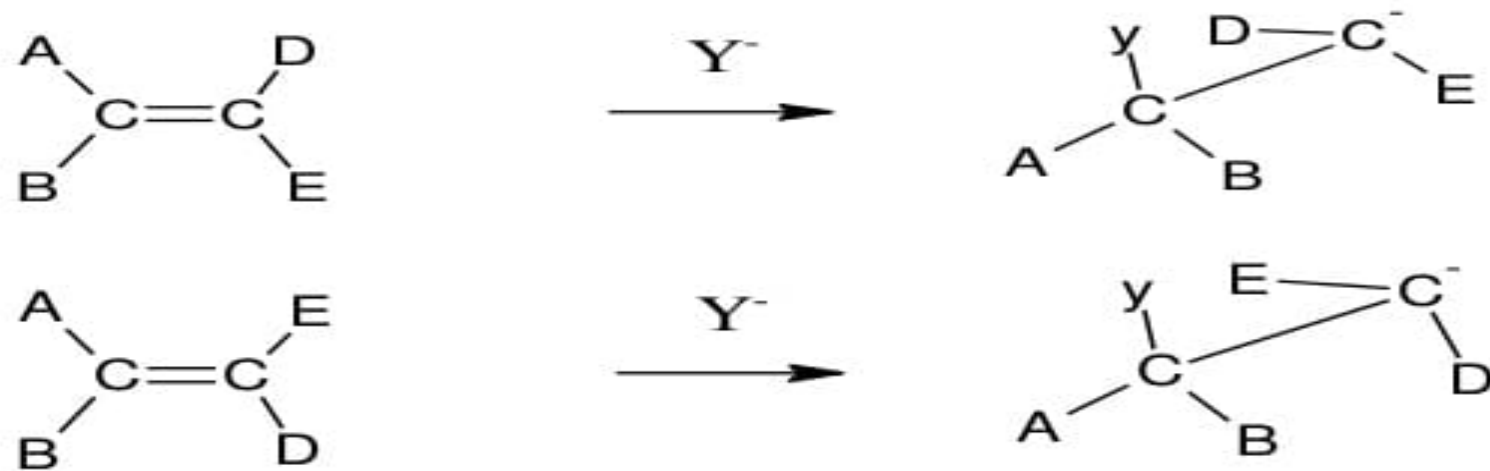
An important substrate of this type is acrylonitrile and 1,4 addition to is called cyanoethylation, because the Y is cyanoethylated



STEREO CHEMISTRY

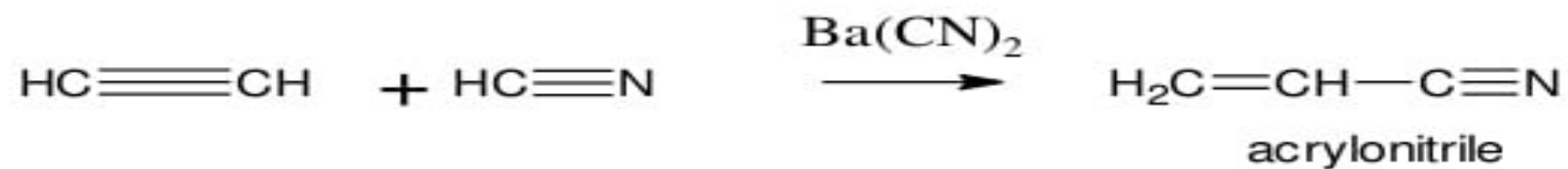
- Nucleophilic addition is carbanion mechanism
- Addition should be nonstereospic and stereoselective.

Eg ; E and Z from of an olefin ABC=CDE

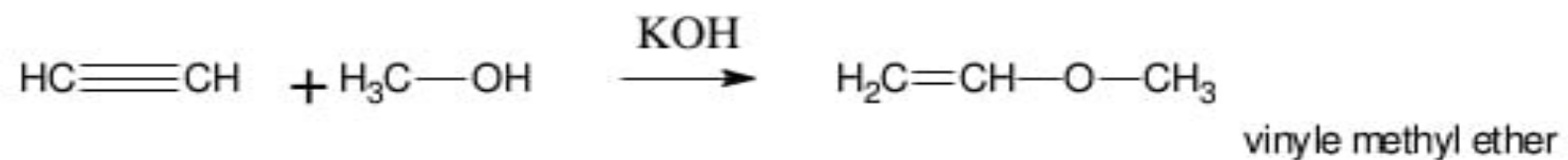


Eg ; addition of HCN, addition of alcohols

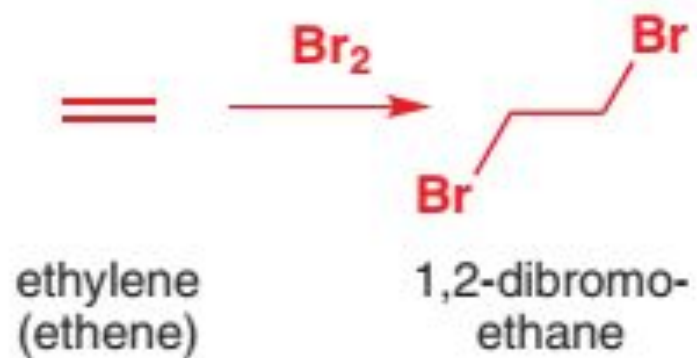
Addition of HCN



Addition of alcohols



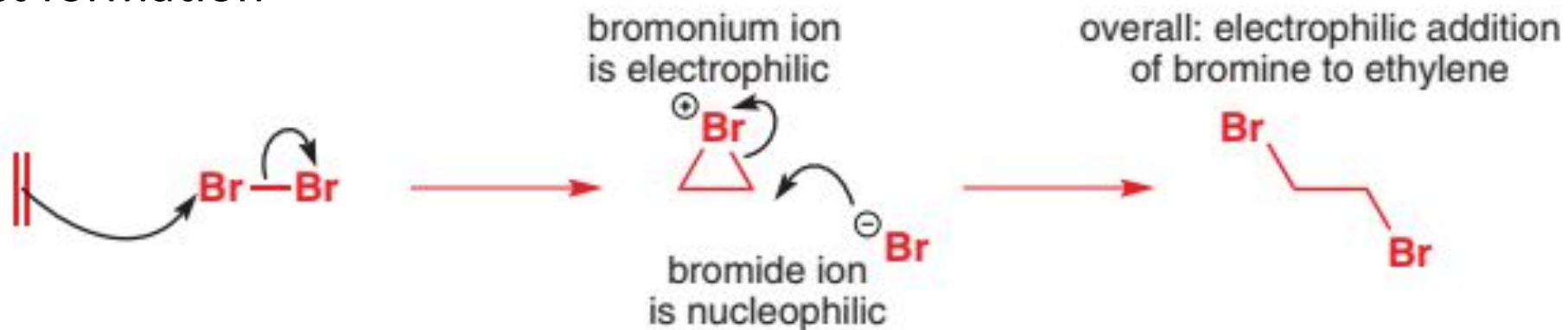
- Simple, unconjugated alkenes are nucleophilic and react with electrophiles.



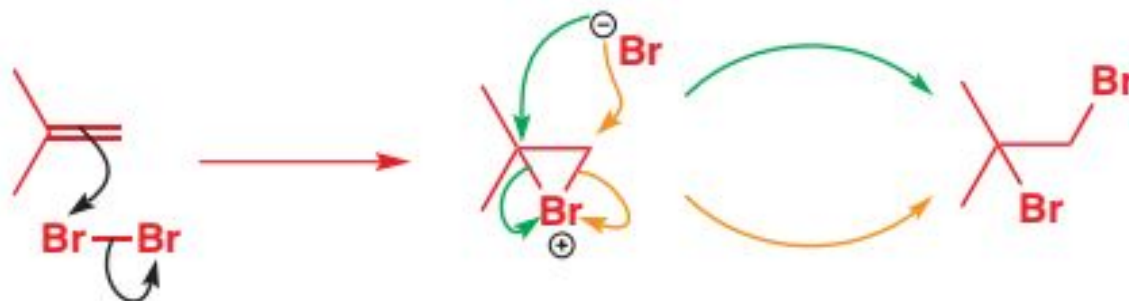
- Representation



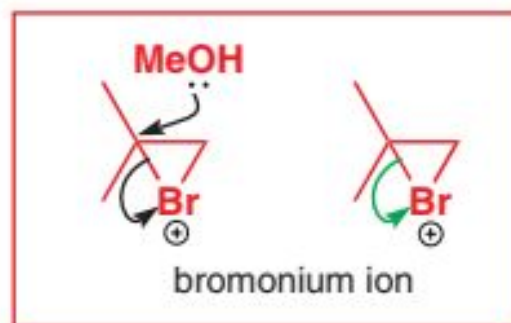
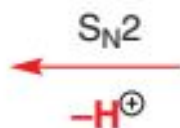
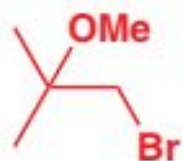
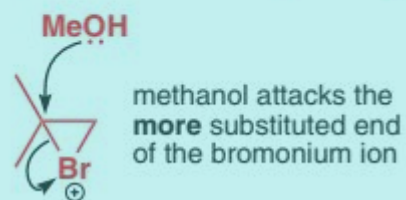
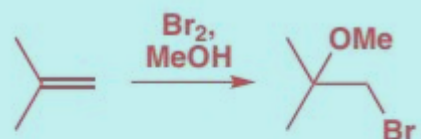
- Product formation



Unsymmetrical bromonium ions open regioselectively

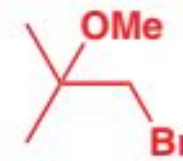
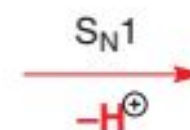
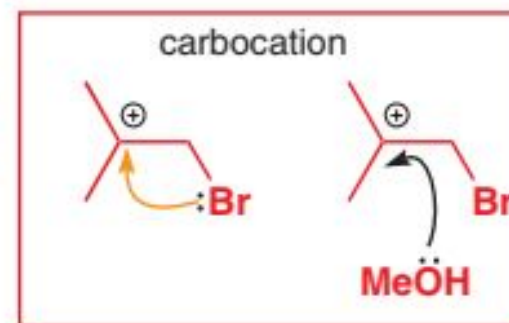


same product whichever end is attacked

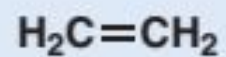
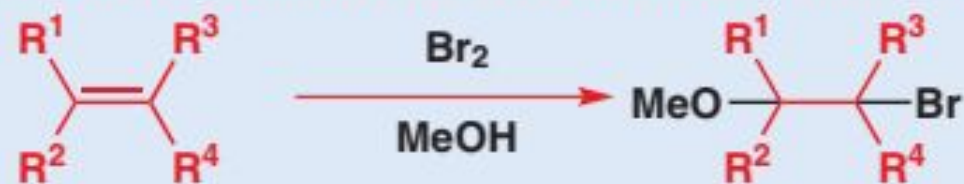


departure of leaving group

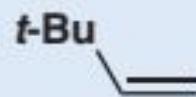
stabilization of cation



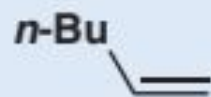
relative rates of reaction of alkenes with bromine in methanol



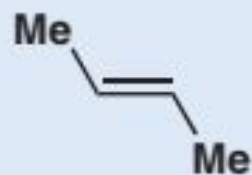
1



27



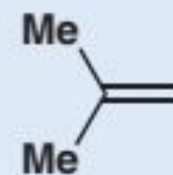
100



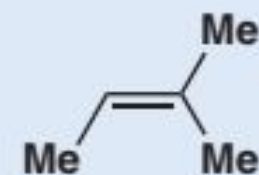
1750



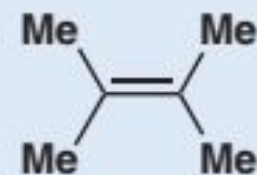
2700



5700



13000

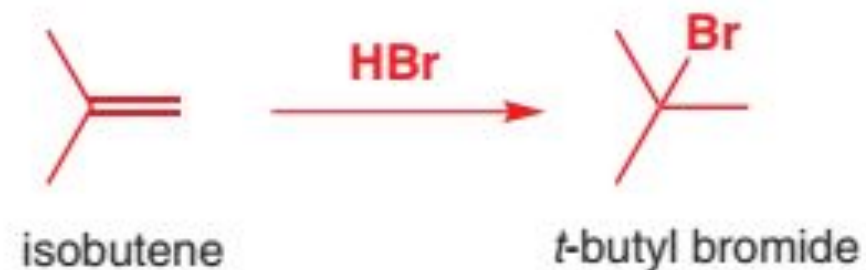
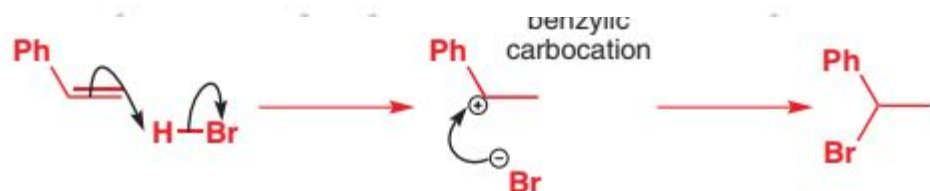
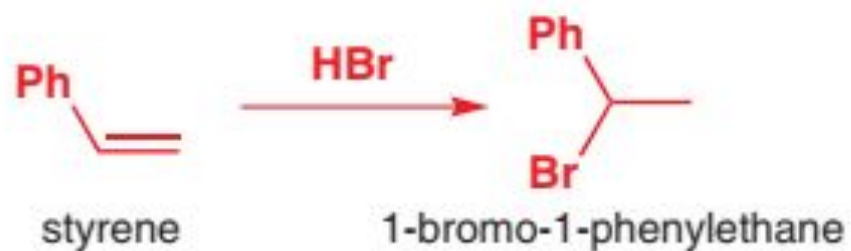
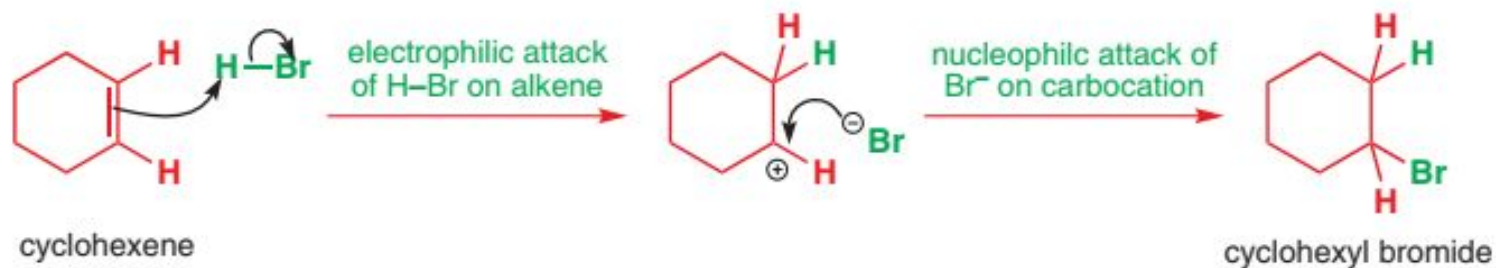


1900000

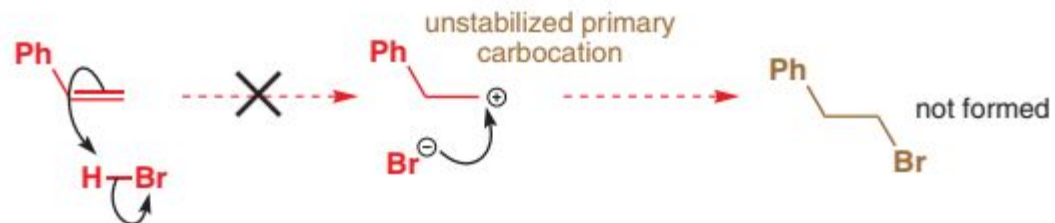
slowest

fastest

Electrophilic addition to unsymmetrical alkenes is regioselective



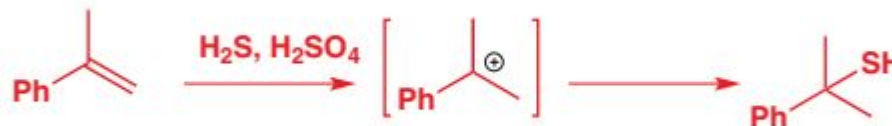
Protonation at the other end would give a highly unstable primary cation, and therefore does not take place.

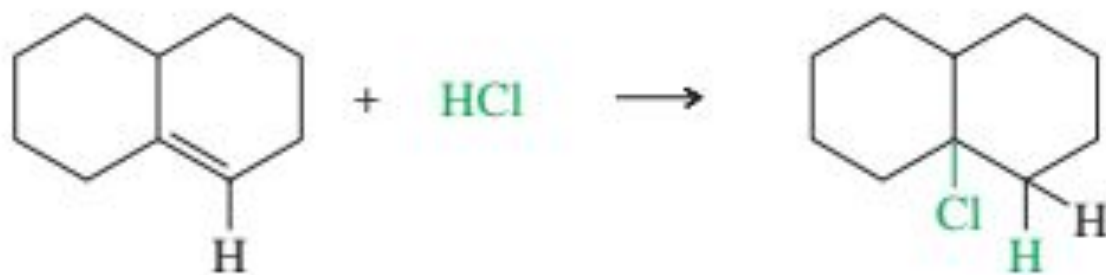
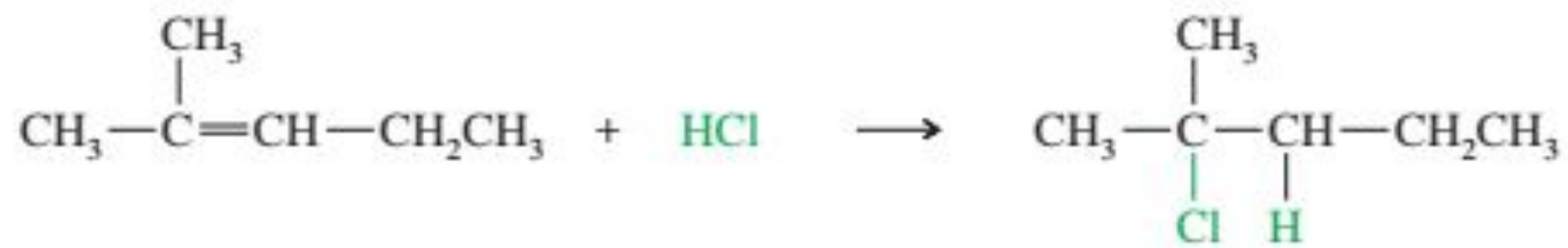


Markovnikov's rule

There is a traditional guideline called Markovnikov's rule for electrophilic additions of H–X to alkenes, which can be stated as: 'The hydrogen ends up attached to the carbon of the double bond that had more hydrogens to start with.'

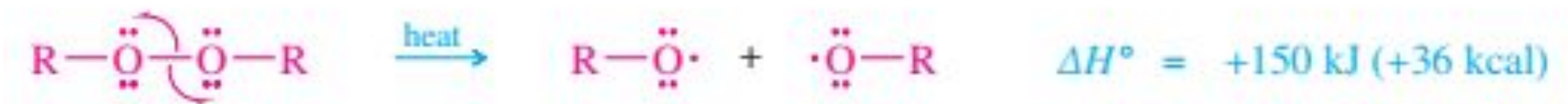
As with all 'rules' it is much more important to understand the reason behind it. For example, you can now predict the product of the reaction below.





In 1933, M. S. Kharasch and F. W. Mayo found that some additions of HBr (but not HCl or HI) to alkenes gave products that were opposite to those expected from Markovnikov's rule. These **anti-Markovnikov** reactions were most likely when the reagents or solvents came from old supplies that had accumulated peroxides from exposure to the air.

Peroxides give rise to free radicals that initiate the addition, causing it to occur by a radical mechanism. The oxygen–oxygen bond in peroxides is rather weak, so it can break to give two alkoxy radicals.



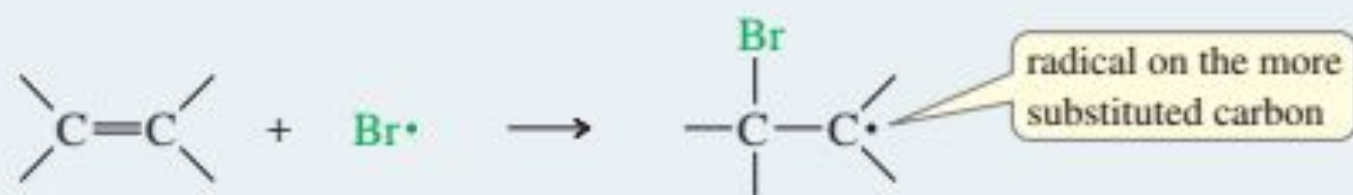
MECHANISM 8-3 Free-Radical Addition of HBr to Alkenes

Initiation: Formation of radicals.



Propagation: A radical reacts to generate another radical.

Step 1: A bromine radical adds to the double bond to generate an alkyl radical on the more substituted carbon atom.



Step 2: The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.



The bromine radical generated in Step 2 goes on to react with another molecule of alkene in Step 1, continuing the chain.

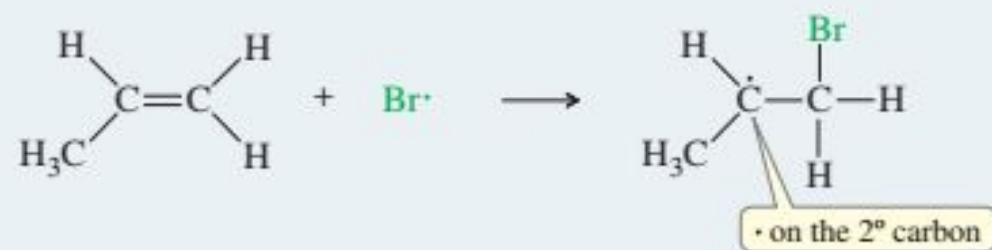
EXAMPLE: Free-radical addition of HBr to propene.

Initiation: Radicals are formed.



Propagation: A radical reacts to generate another radical.

Step 1: A bromine radical adds to the double bond to generate an alkyl radical on the secondary carbon atom.

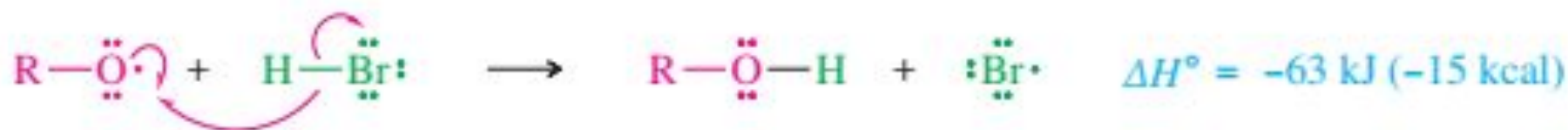


Step 2: The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.

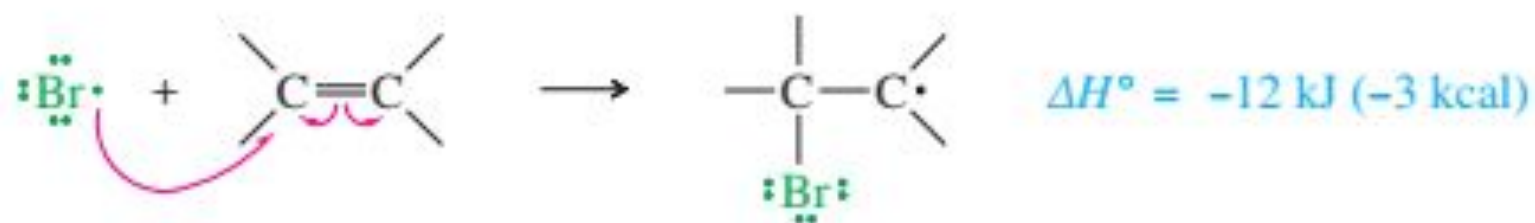


The bromine radical generated in Step 2 goes on to react in Step 1, continuing the chain.

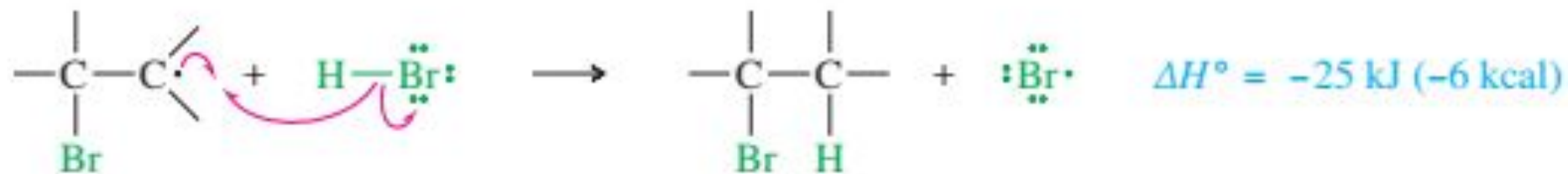
Let's consider the individual steps. In the initiation step, free radicals generated from the peroxide react with HBr to form bromine radicals.



The bromine radical lacks an octet of electrons in its valence shell, making it electron-deficient and electrophilic. It adds to a double bond, forming a new free radical with the odd electron on a carbon atom.



This free radical reacts with an HBr molecule to form a C—H bond and generate another bromine radical.



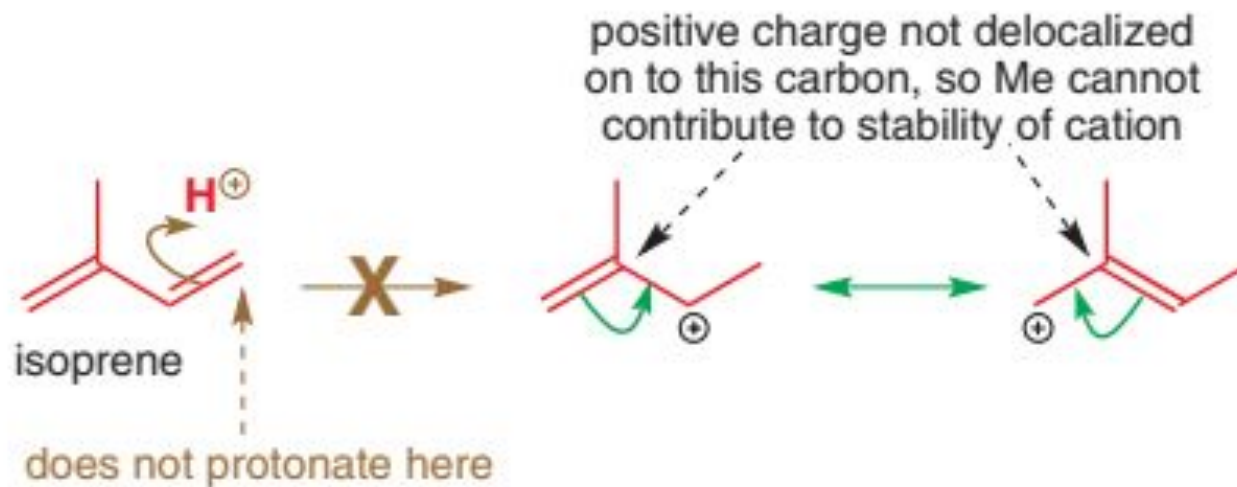
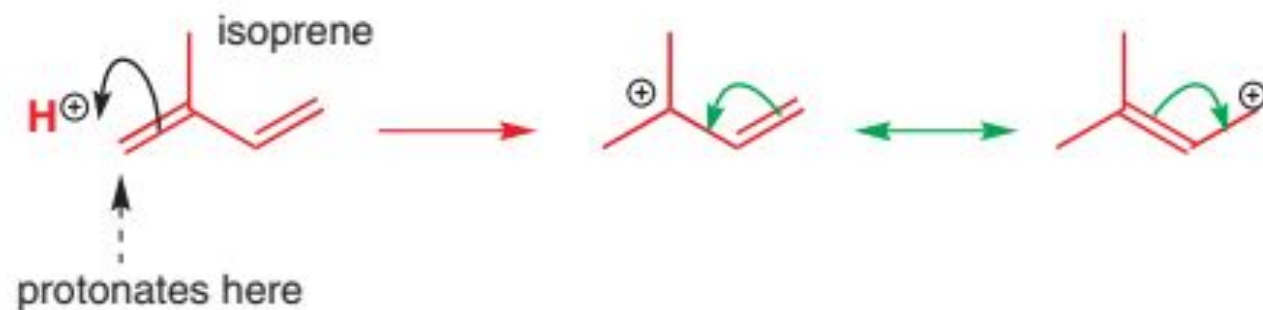
Problem-solving Hint

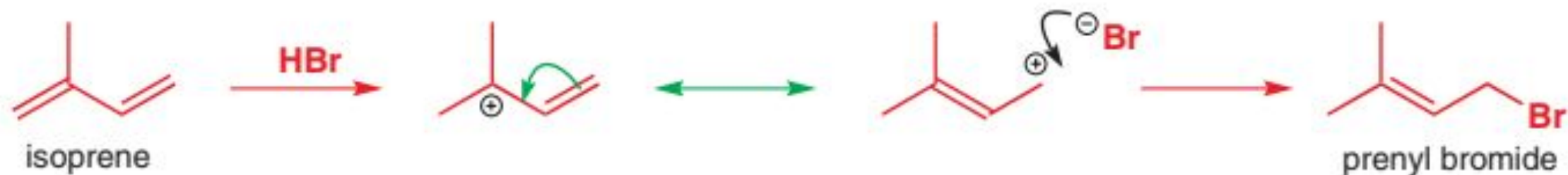
Stability of radicals:



A radical adds to a double bond to give the most stable radical in the intermediate.

Electrophilic addition to dienes

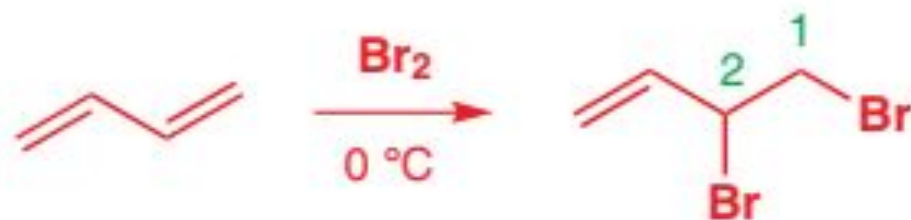




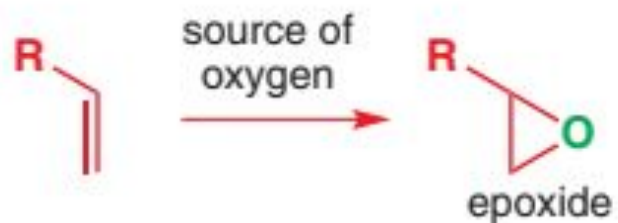
Overall, the atoms H and Br are added to the ends of the diene system. The same appears to be the case when dienes are brominated with Br₂.



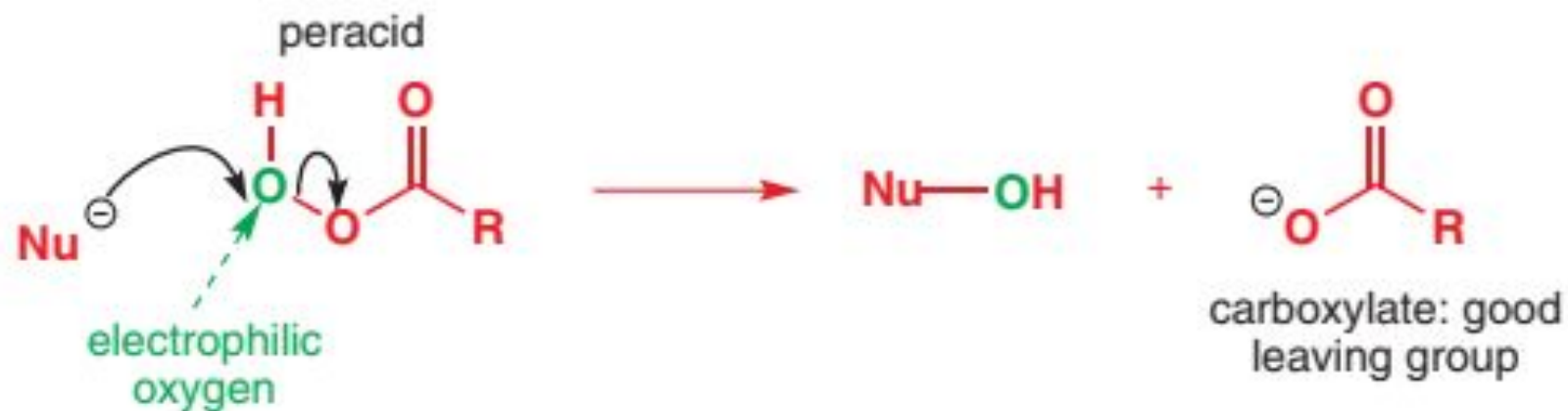
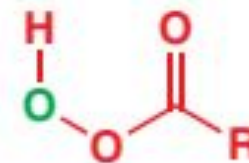
Changing the conditions slightly gives a different outcome. If the reaction is done at lower temperatures, the bromine just adds across one of the double bonds to give a 1,2-dibromide.



Oxidation of alkenes to form epoxides

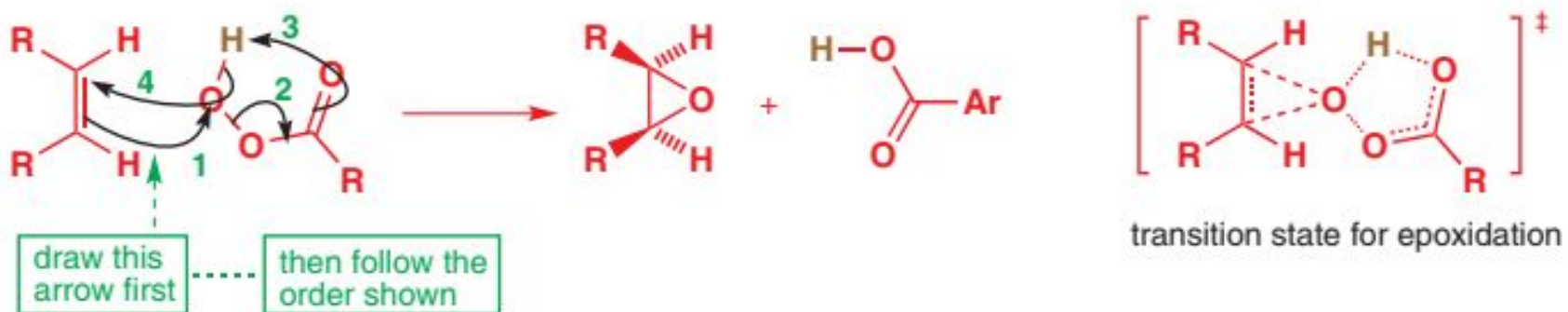


commonest oxidants in this reaction are peroxy-carboxylic acids:





- Representation



Epoxidation is stereospecific

