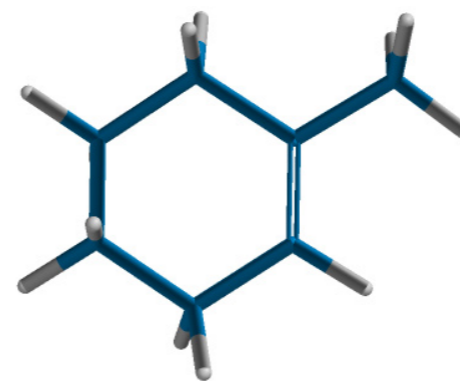


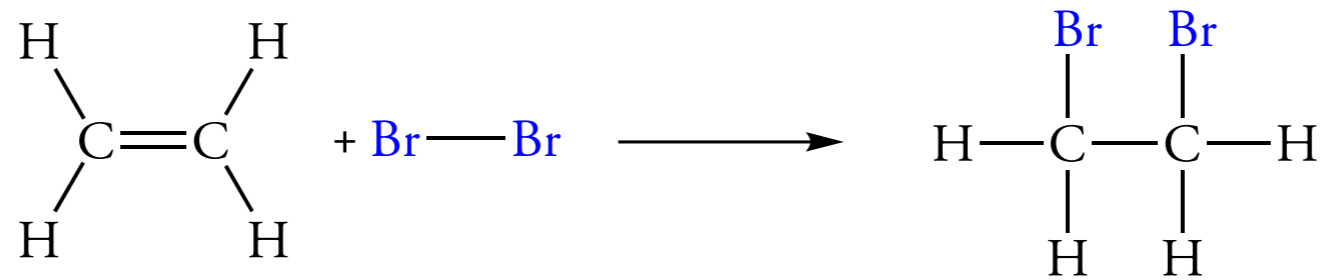
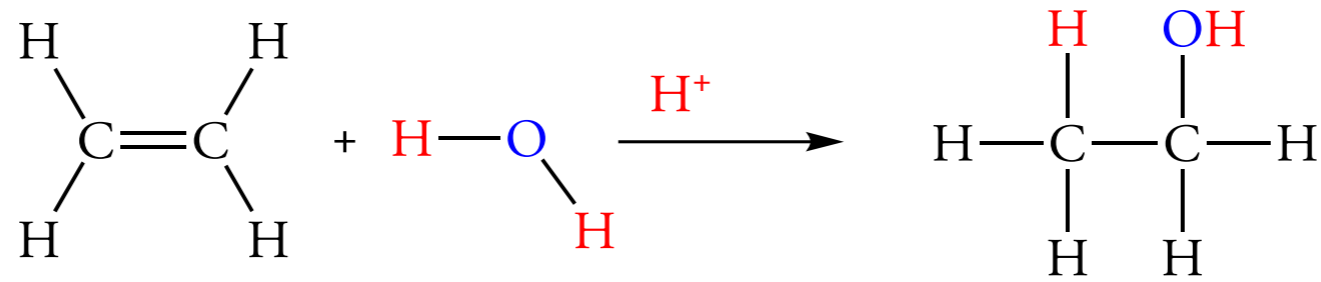
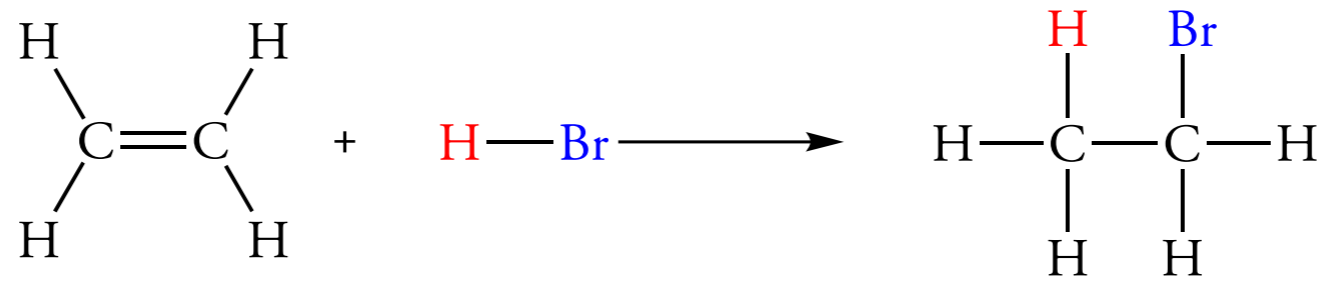
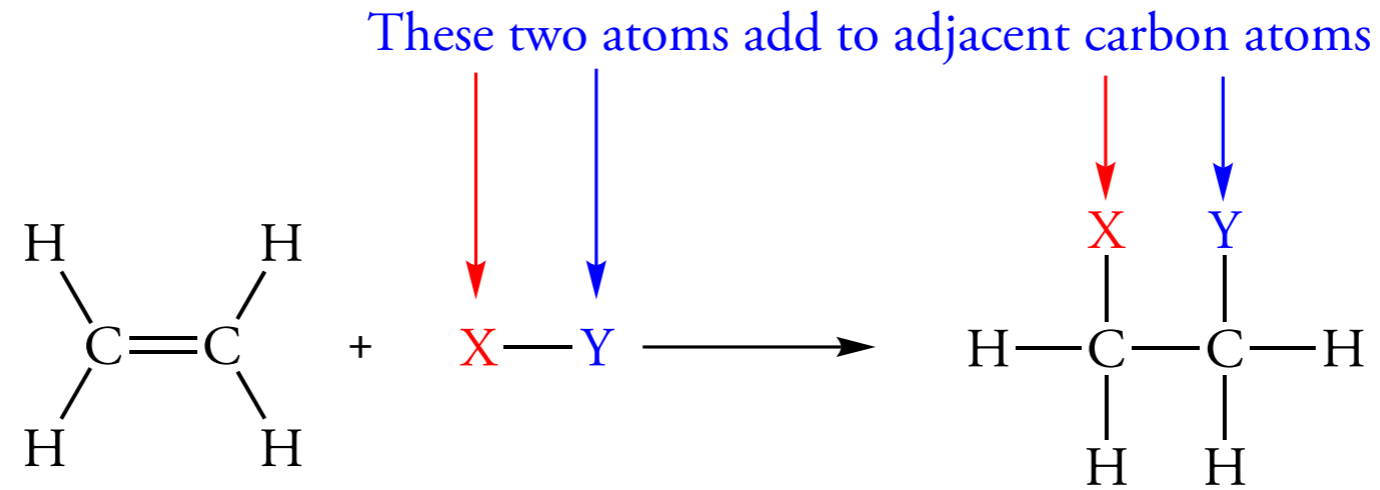
6

# ALKENES

## ADDITION REACTIONS



## 6.1 CHARACTERISTICS OF ADDITION REACTIONS

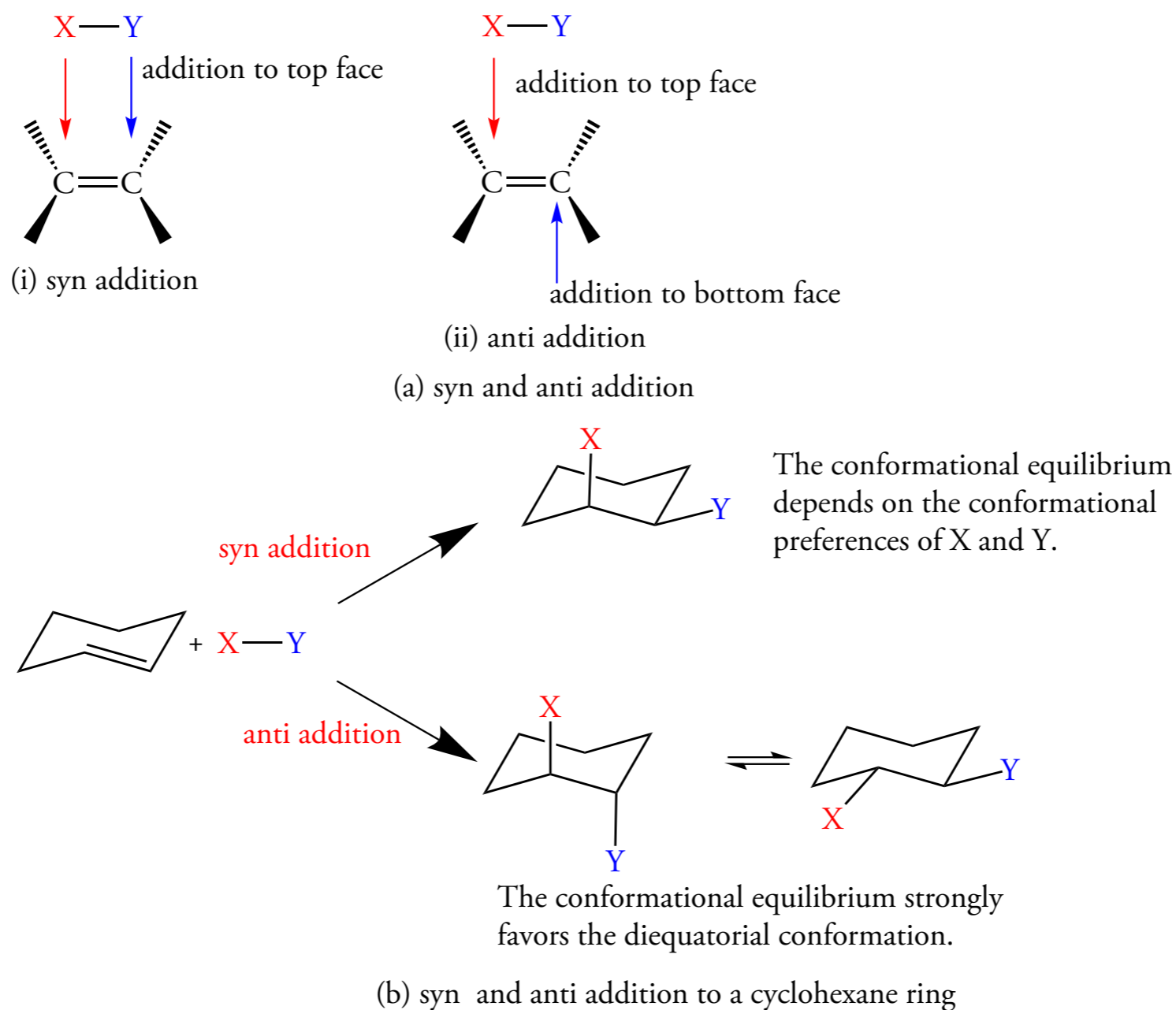


## 6.1 CHARACTERISTICS OF ADDITION REACTIONS

### Stereochemistry of Addition Reactions

#### Figure 6.1 Syn and Anti Addition to Alkenes

The two possible modes of addition of a reagent X—Y to an alkene are shown in (a). In syn addition, both groups add to the same side or face of the molecule. In anti addition, the groups add to the opposite faces of the molecule. The consequences of syn and anti additions are shown in (b). Geometric isomers can result from the addition of a reagent X—Y to the double bond of a cycloalkene. Syn addition produces a *cis* product, whereas anti addition produces a *trans* product.

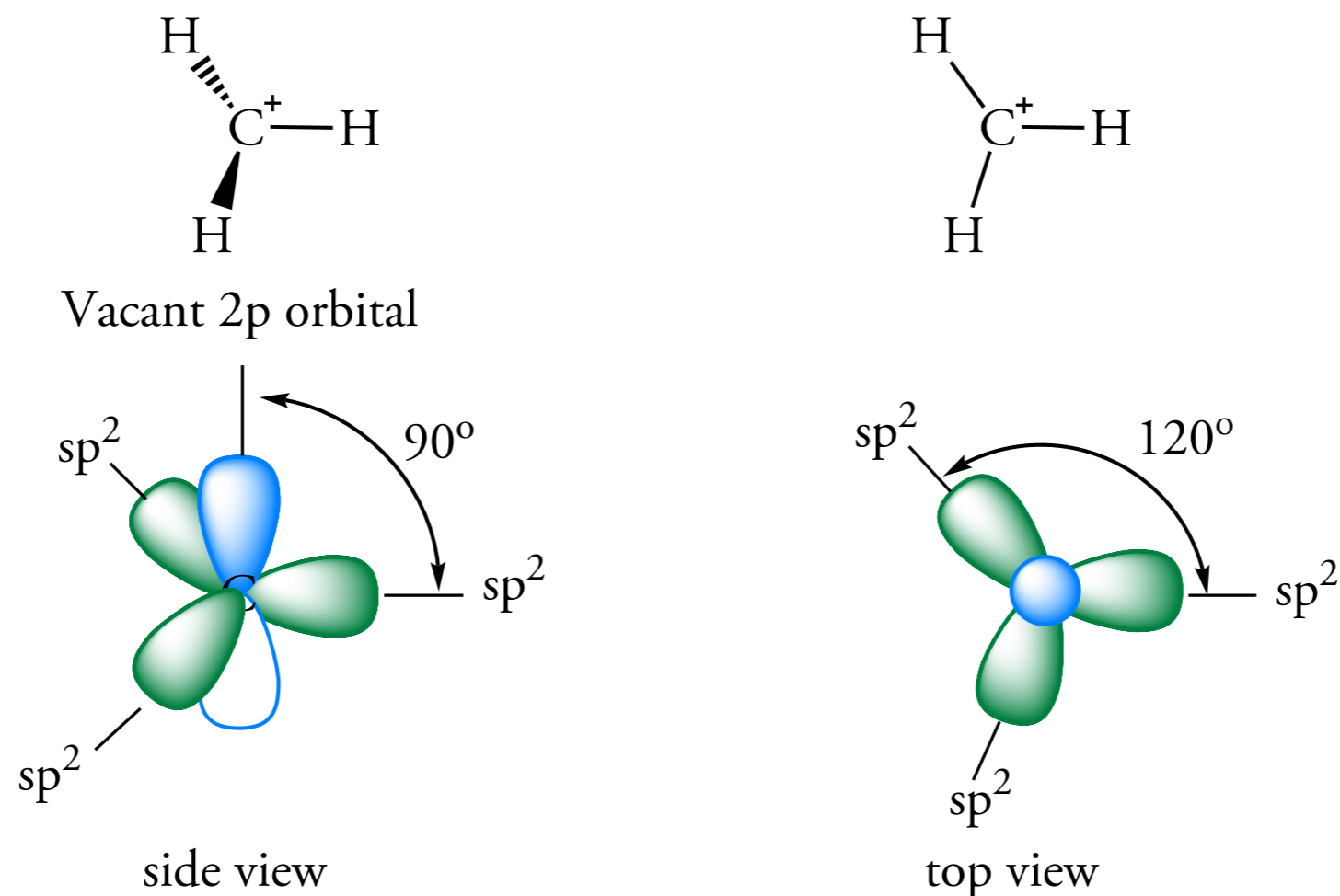


## 6.1 CHARACTERISTICS OF ADDITION REACTIONS

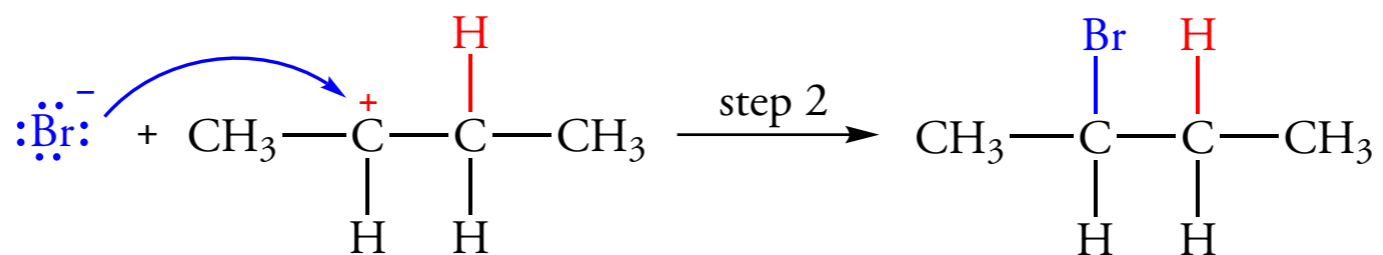
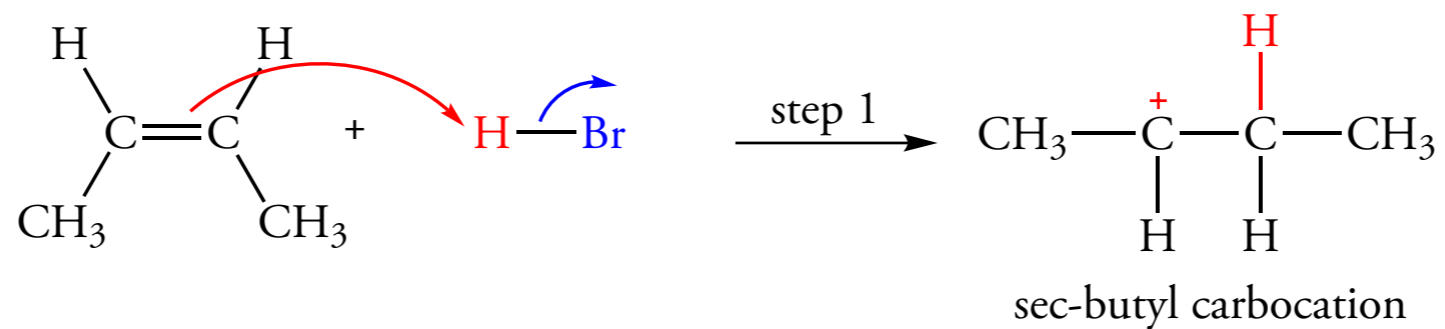
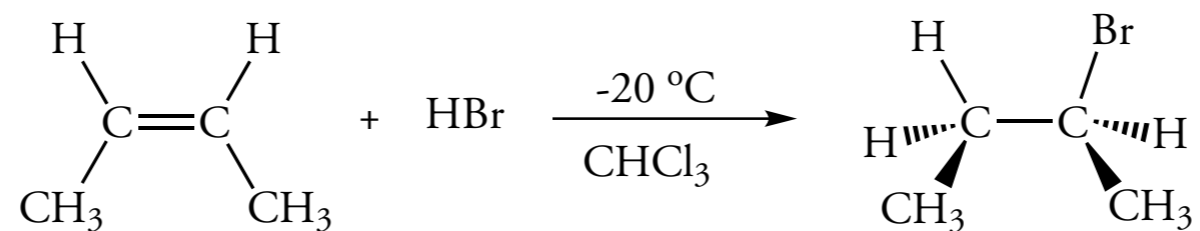
### Carbocations in Addition Reactions

#### Figure 6.2 Structure and Hybridization of the Methyl Carbocation

The methyl carbocation has an  $sp^2$  hybridized carbon. The H—C—H bond angles are  $120^\circ$ , and the carbon atom has a vacant  $2p$  orbital that is perpendicular to the plane of the four atoms.

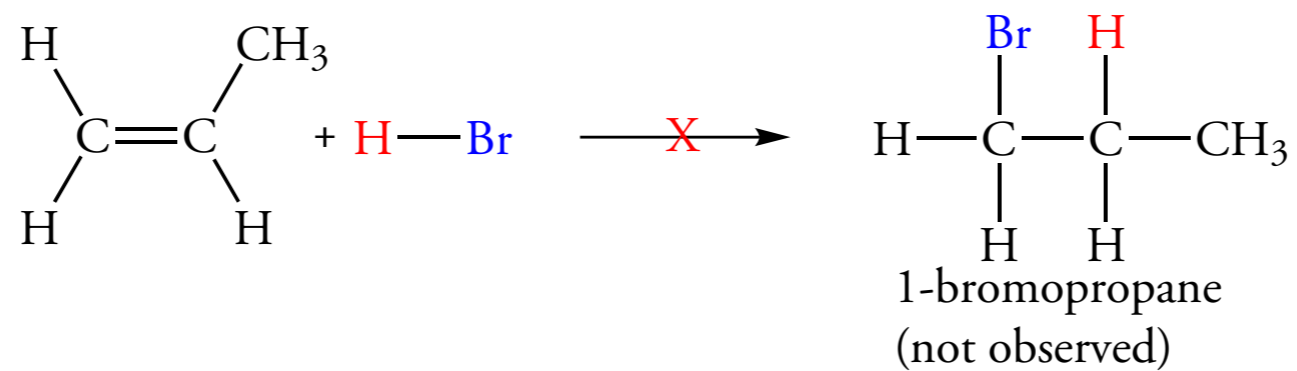
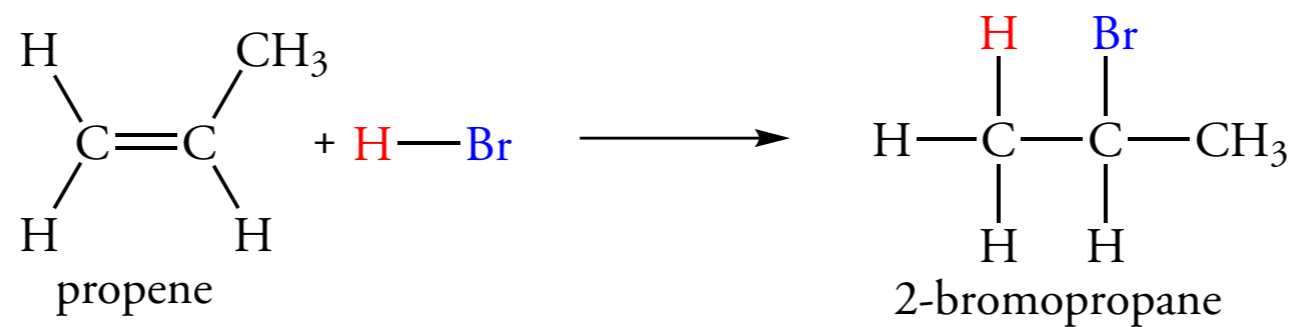


## 6.2 ADDITION OF HYDROGEN HALIDES TO ALKENES



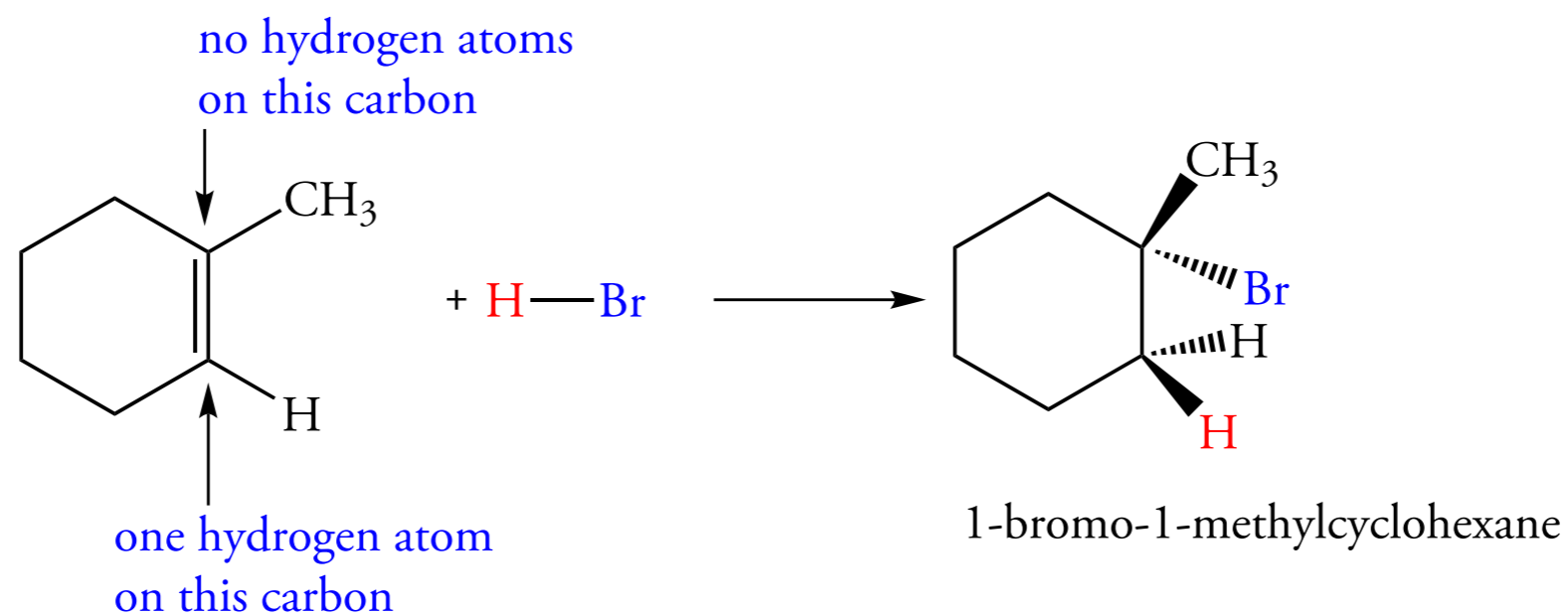
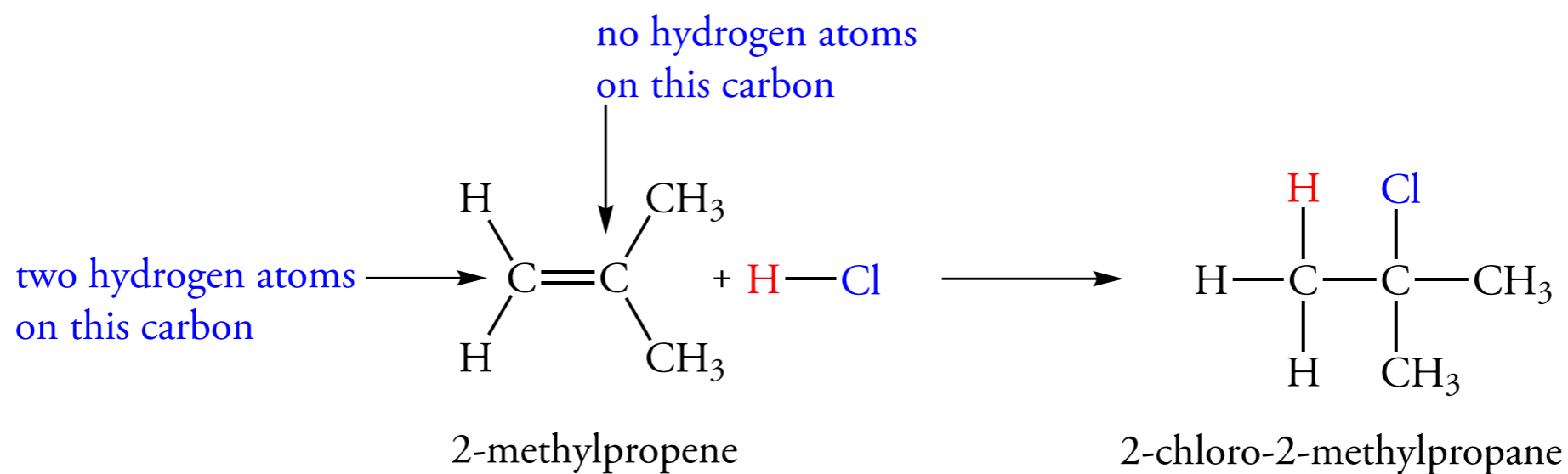
## 6.2 ADDITION OF HYDROGEN HALIDES TO ALKENES

### Regiospecificity of Hydrogen Halide Addition

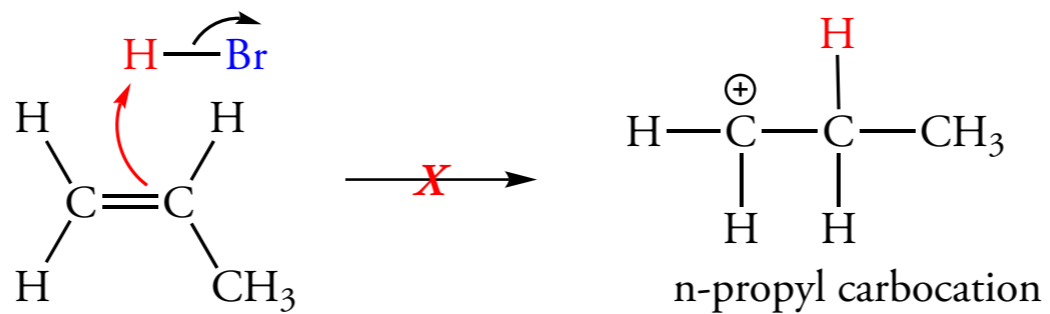
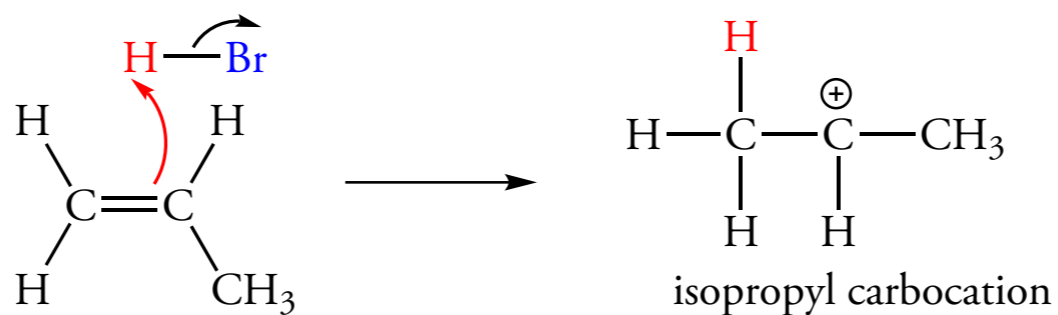
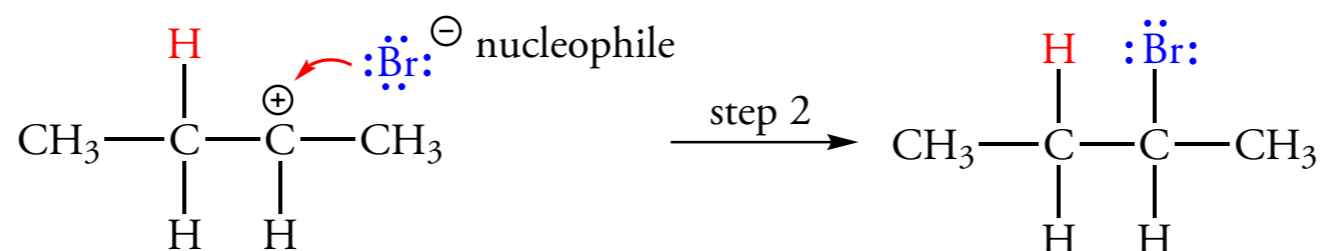
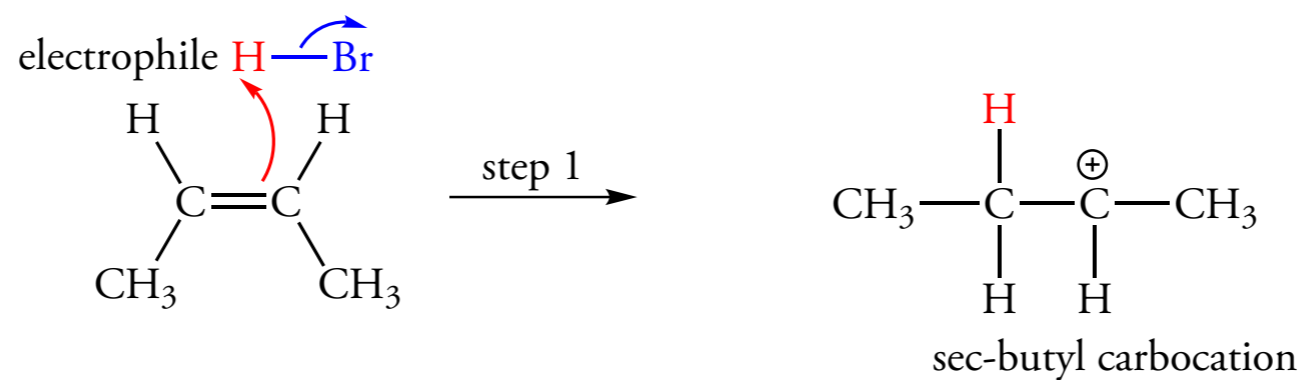


## 6.2 ADDITION OF HYDROGEN HALIDES TO ALKENES

### Markovnikov's Rule



## 6.3 THE MECHANISTIC BASIS OF MARKOVNIKOV'S RULE



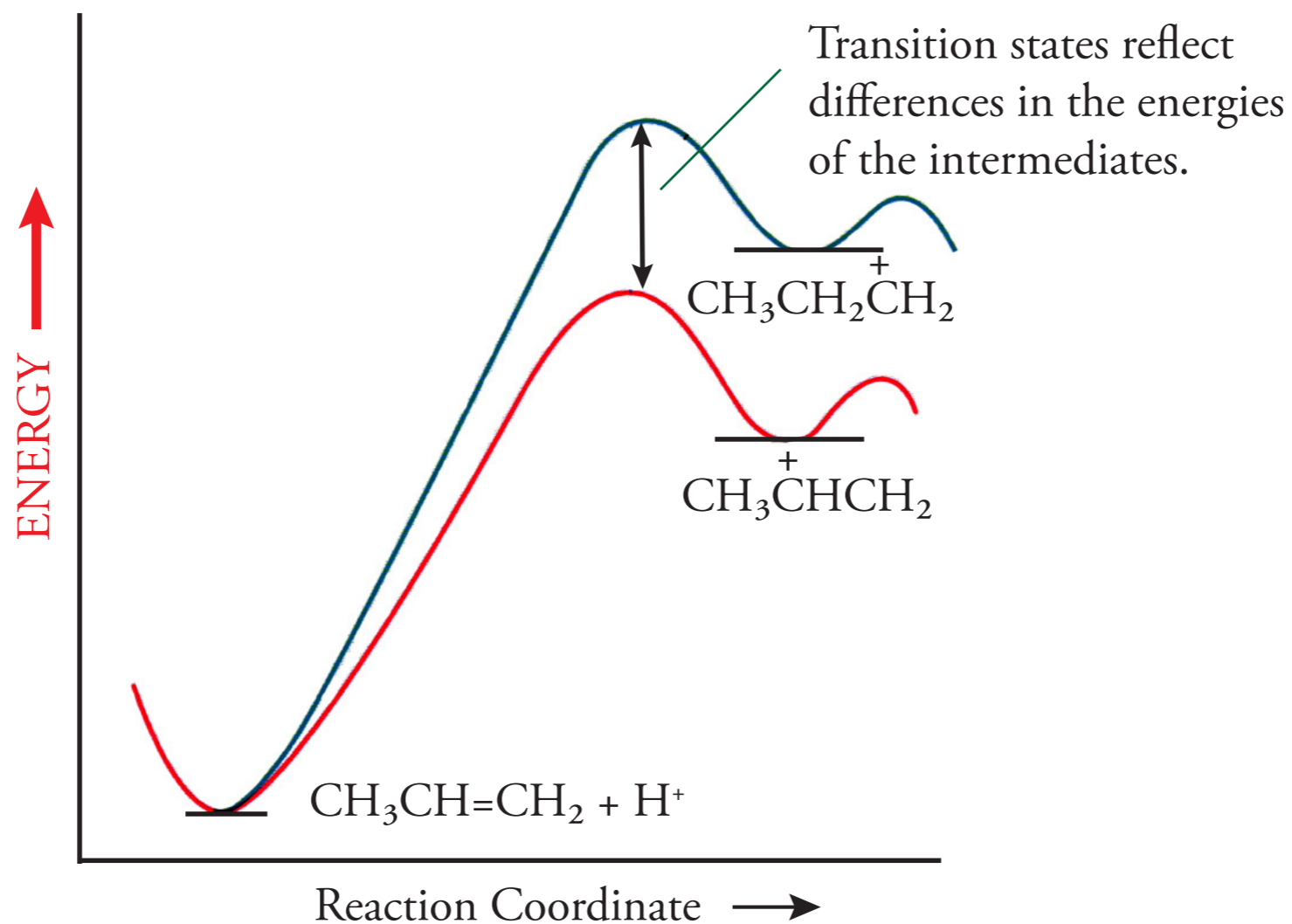


## 6.3 THE MECHANISTIC BASIS OF MARKOVNIKOV'S RULE

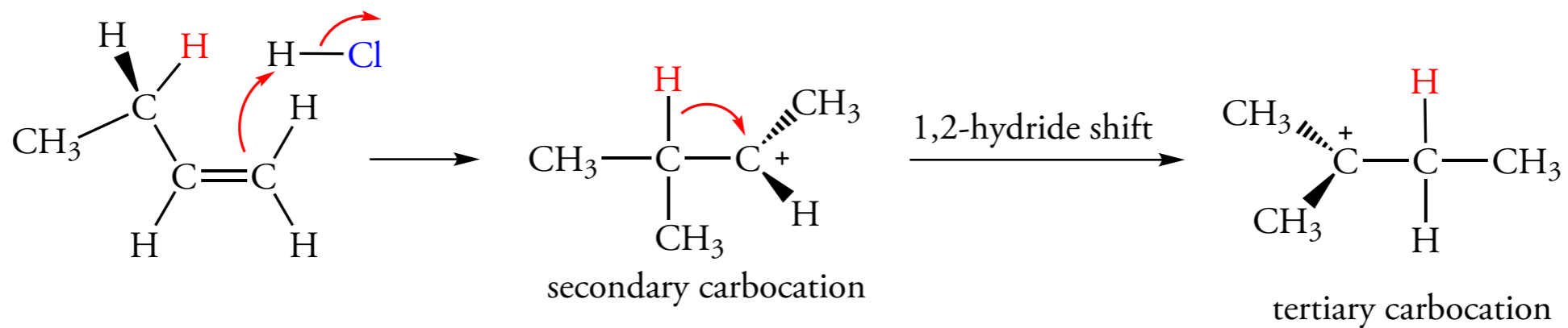
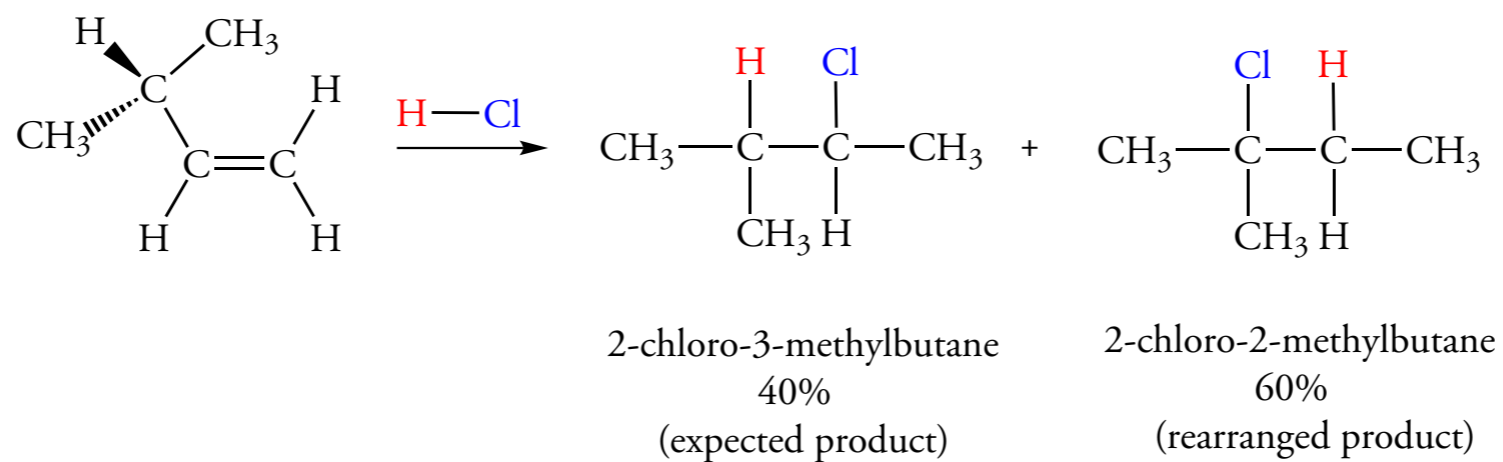
### Hammond Postulate and Electrophilic Addition

#### Figure 6.3 Reaction Coordinate Diagrams for Electrophilic Addition Reactions

The transition state that leads to the less stable primary carbocation is of higher energy than the transition state that leads to the more stable secondary carbocation. Subsequent reaction of either carbocation with a nucleophile occurs rapidly.



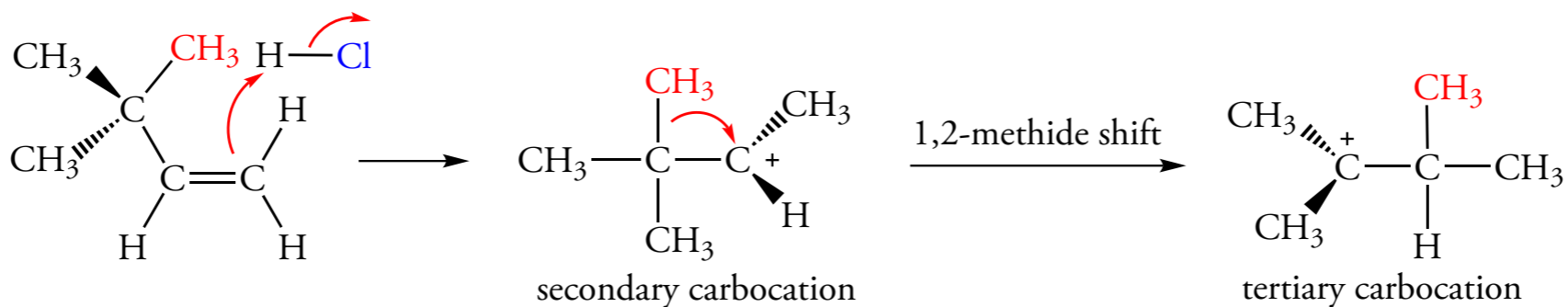
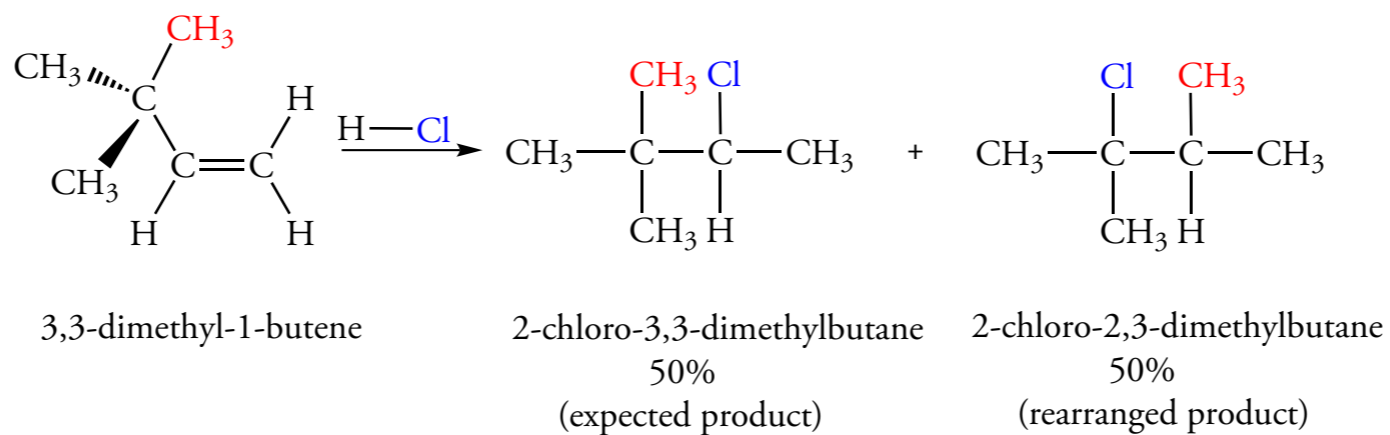
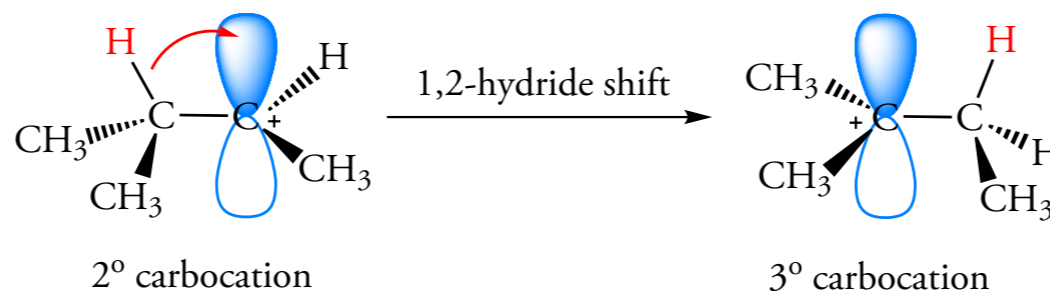
## 6.4 CARBOCATION REARRANGEMENT REACTIONS



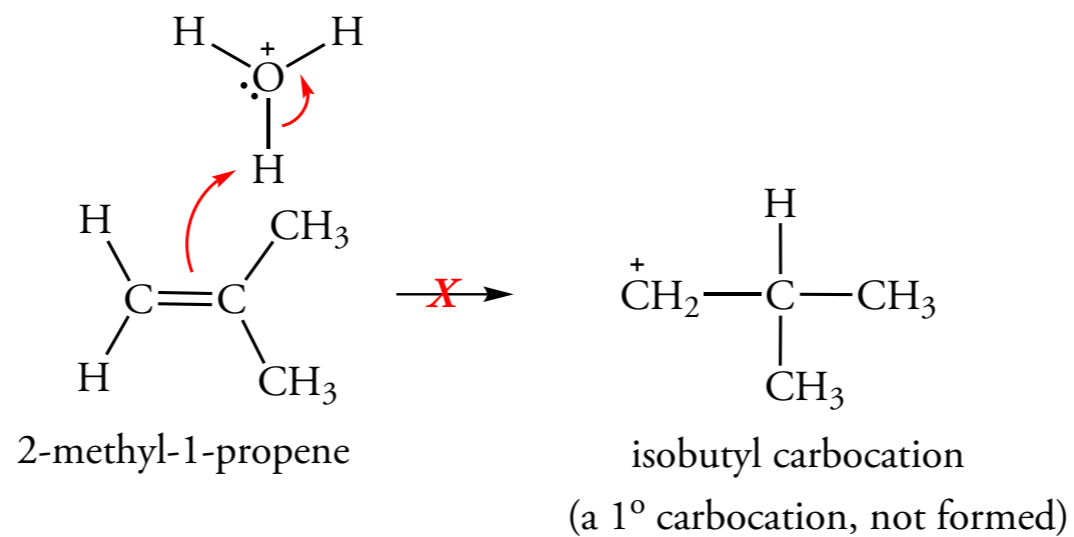
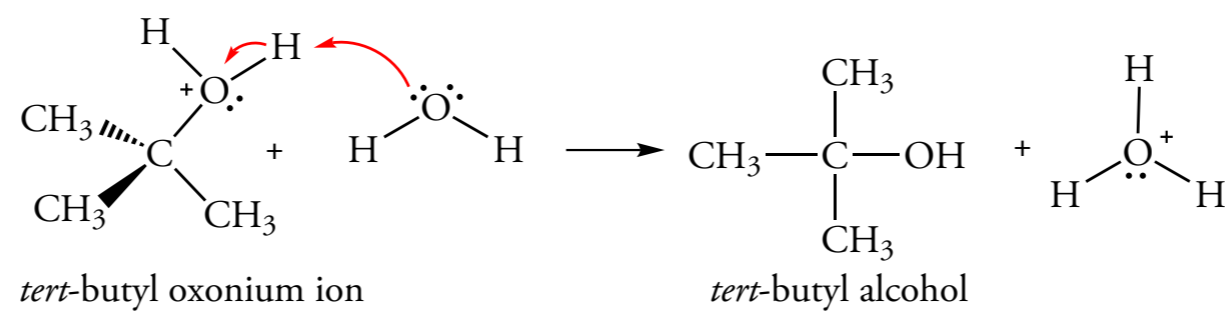
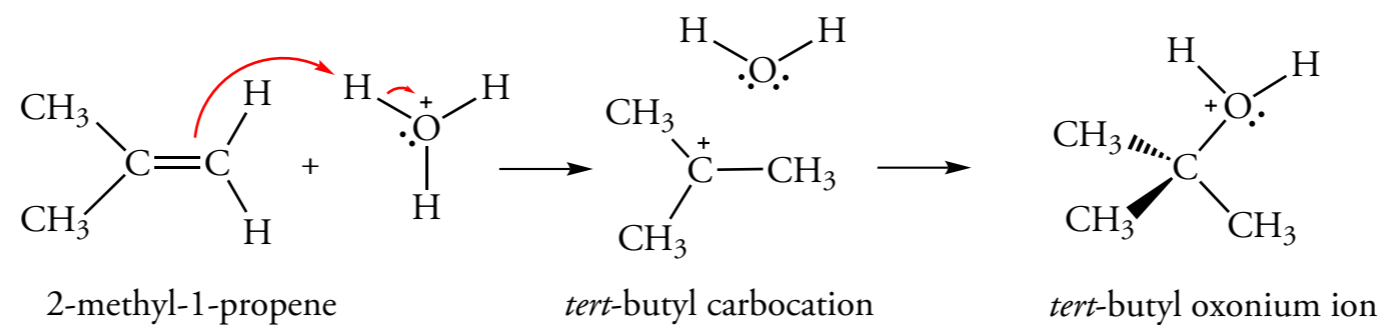
## 6.4 CARBOCATION REARRANGEMENT REACTIONS

### Figure 6.4 Rearrangement of a Carbocation by a 1,2-Hydride Shift

The bonding pair of electrons of the migrating group, a hydride anion, must be coplanar with the vacant 2p orbital of the carbocation for migration to occur.

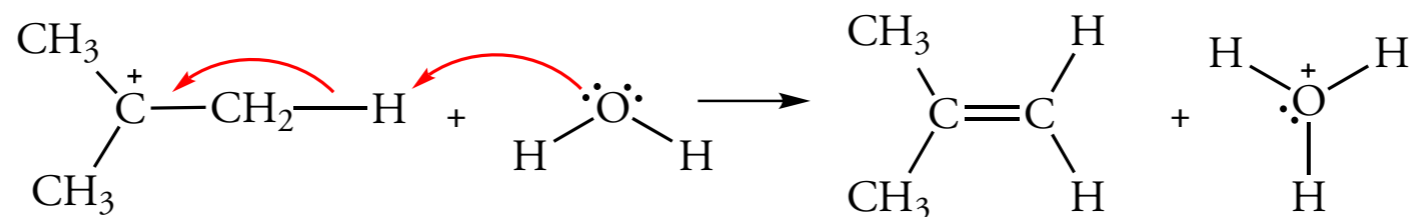
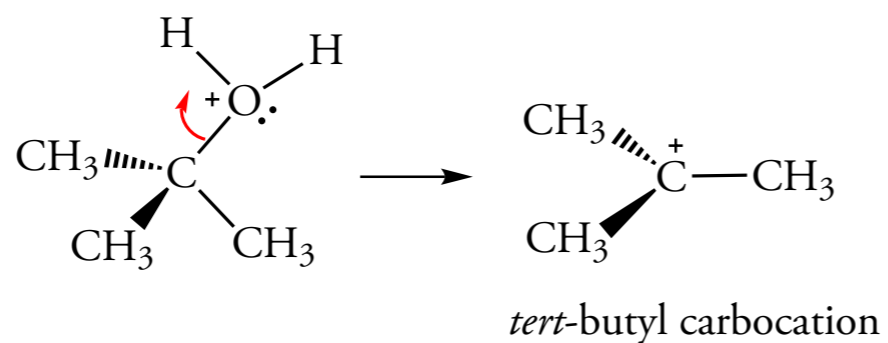
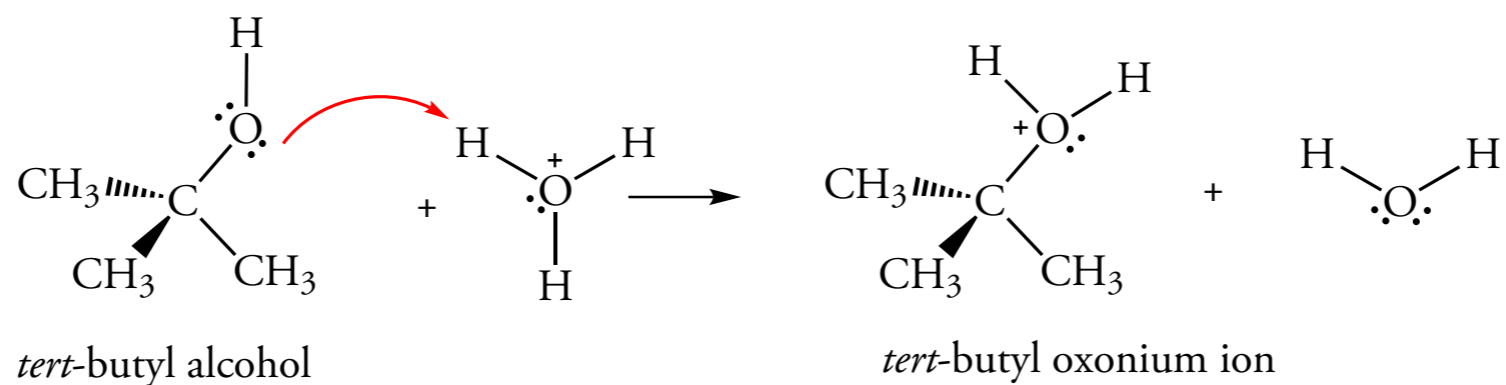
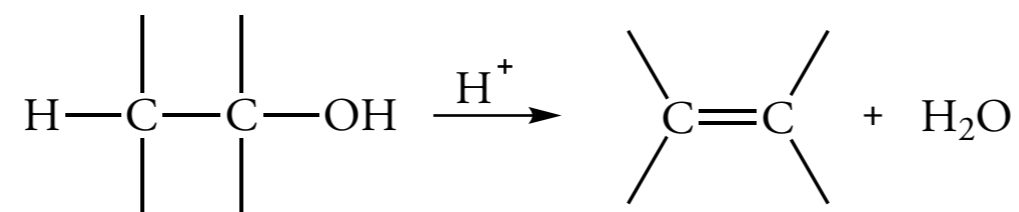


## 6.5 HYDRATION OF ALKENES

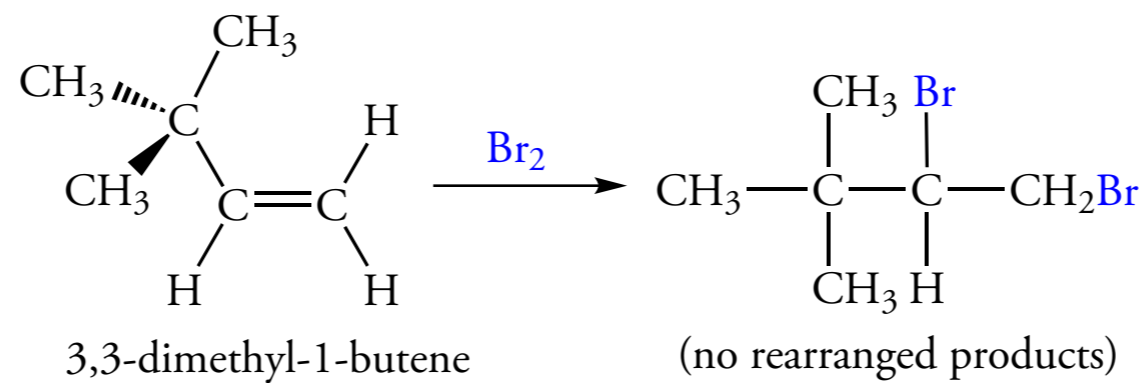
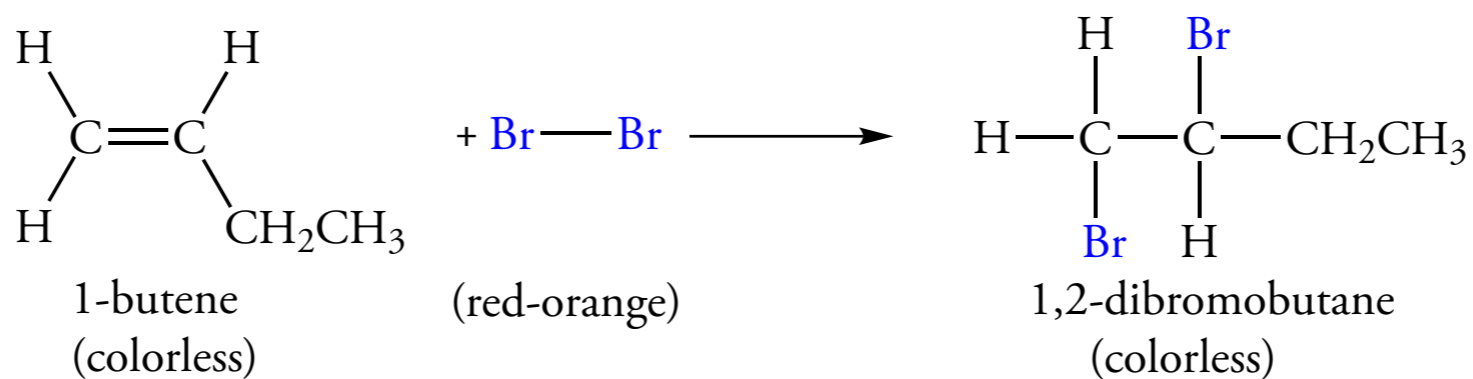
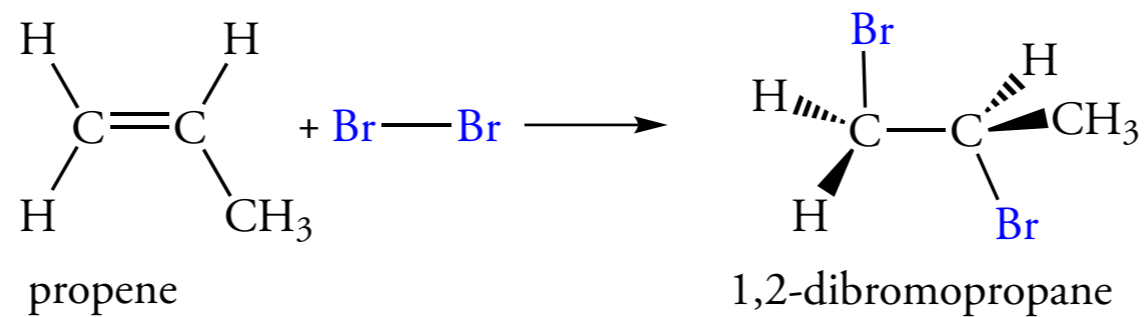


## 6.5 HYDRATION OF ALKENES

### Reversibility of Hydration

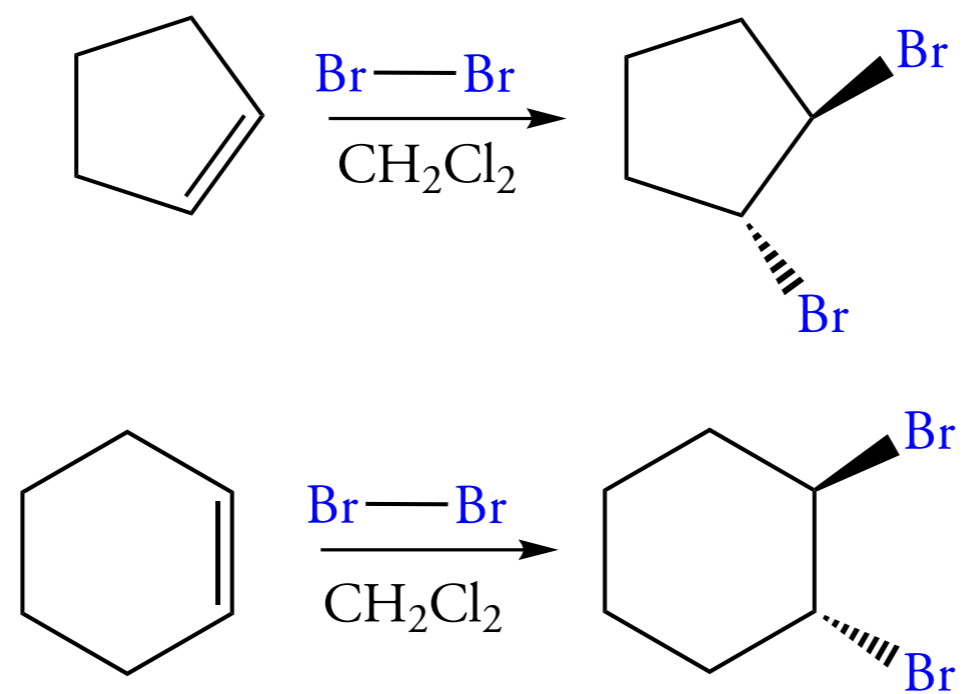


## 6.6 ADDITION OF HALOGENS



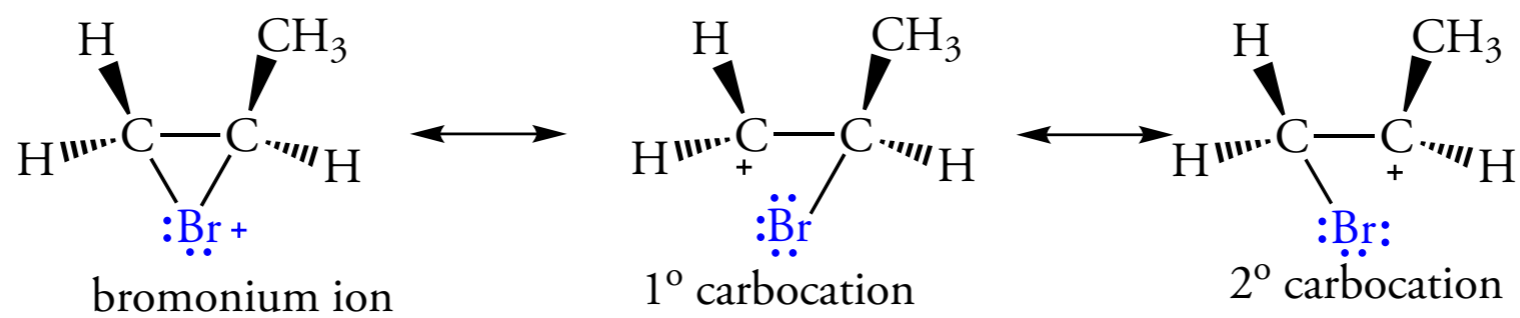
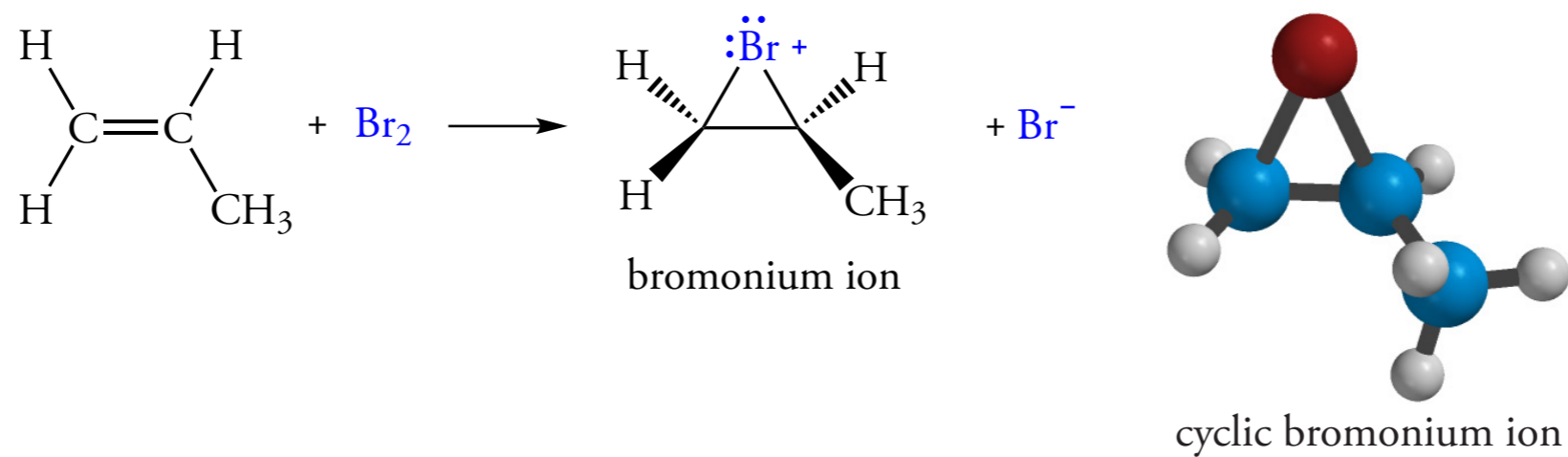
## 6.6 ADDITION OF HALOGENS

### Stereochemistry of Halogen Addition



## 6.6 ADDITION OF HALOGENS

### Mechanism of Halogen Addition

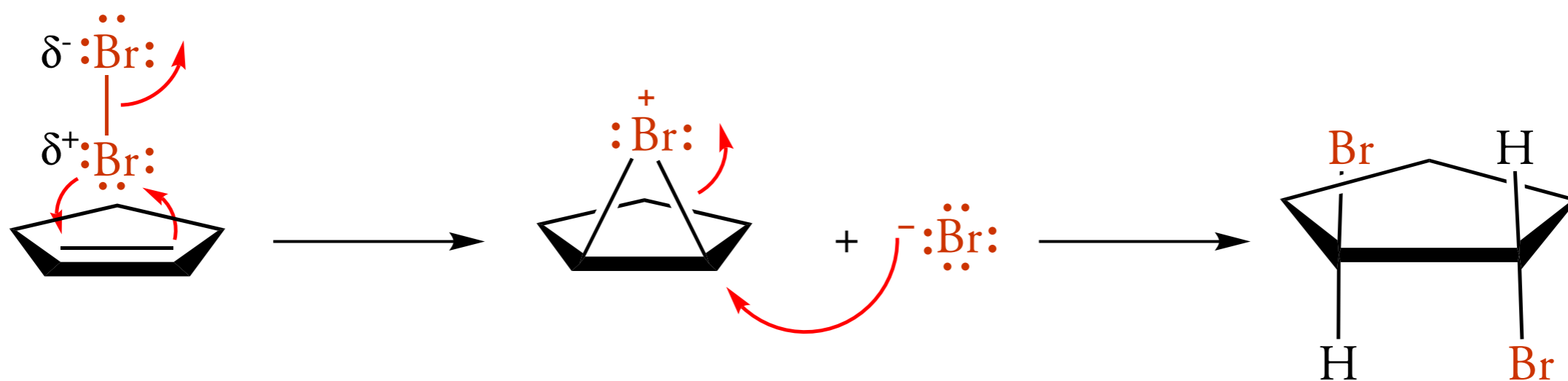




## 6.6 ADDITION OF HALOGENS

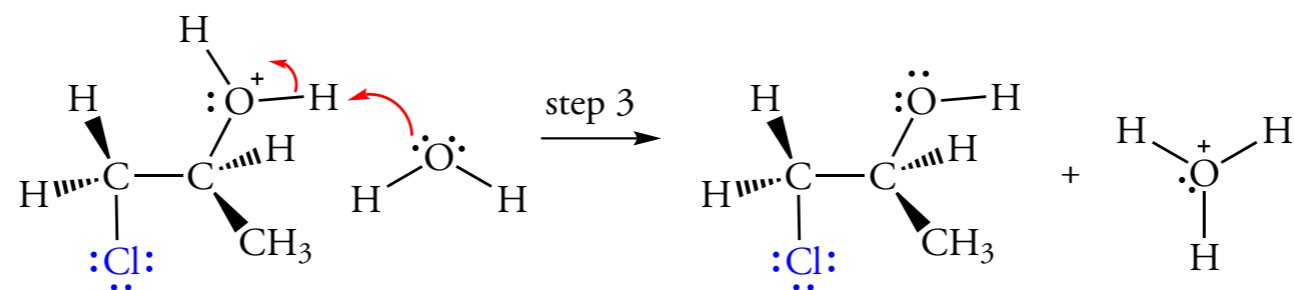
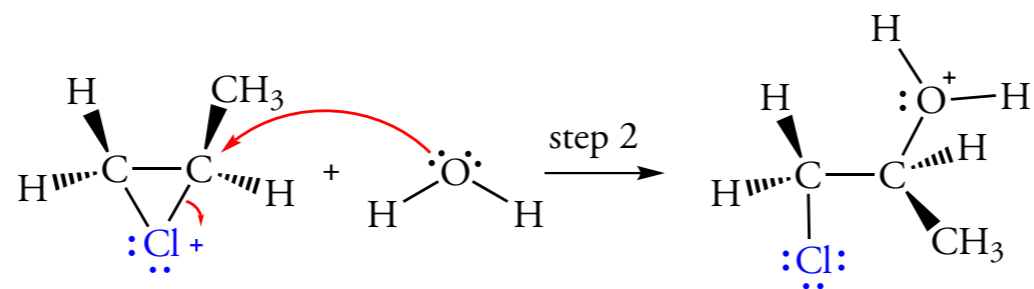
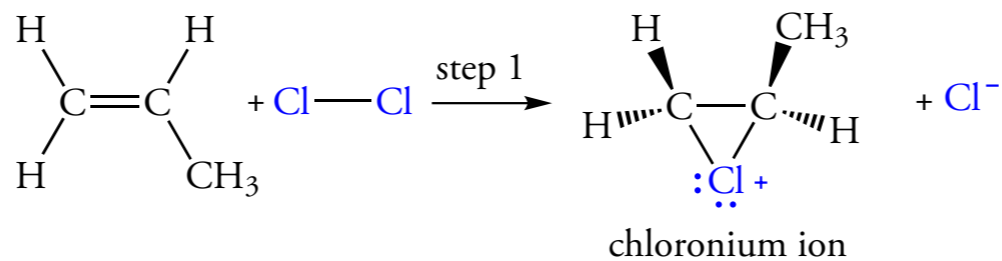
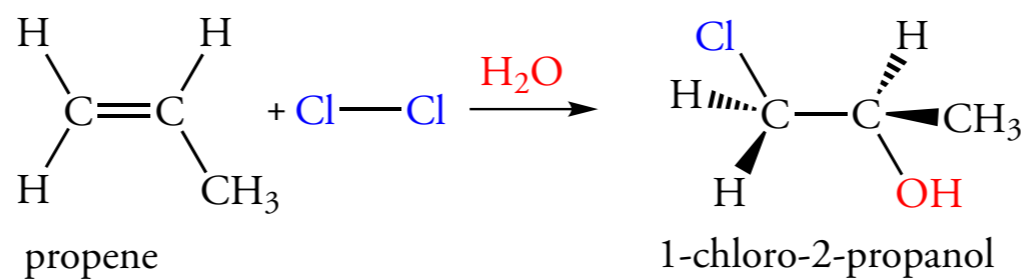
### Figure 6.5 Mechanism of Bromine Addition

The  $\pi$  electrons of the alkene act as a nucleophile to displace bromide ion from bromine. The resulting cyclic bromonium ion can be viewed as the addition of  $\text{Br}^+$  to the double bond. Bromine has two covalent bonds and a formal 1+ charge in this intermediate. Attack of the nucleophilic bromide ion occurs from the opposite face because the bromine atom that is already there blocks approach from the same face.



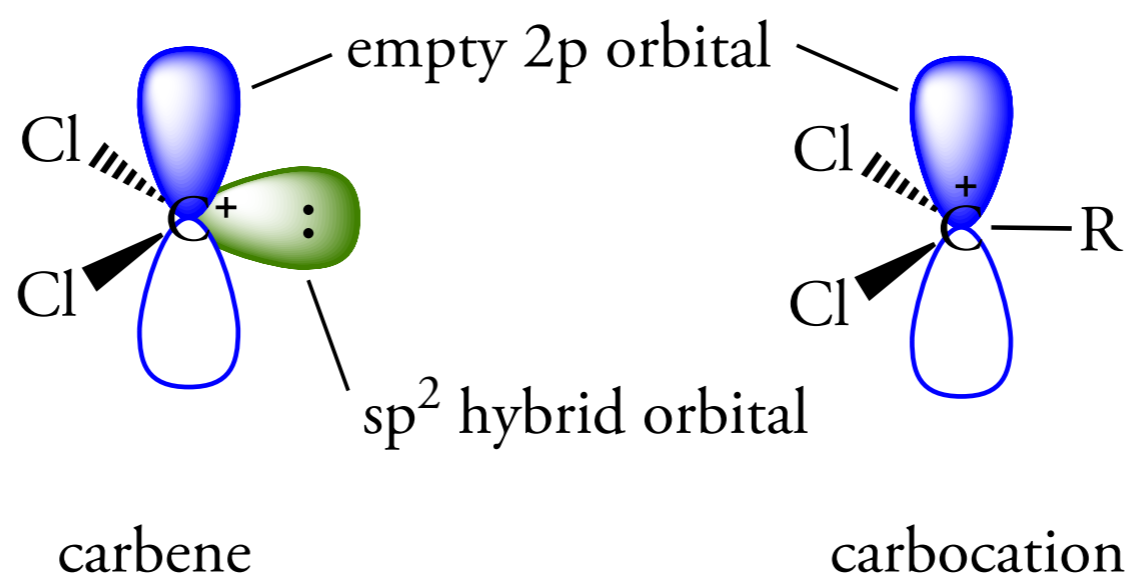
## 6.6 ADDITION OF HALOGENS

### Formation of Halohydrins



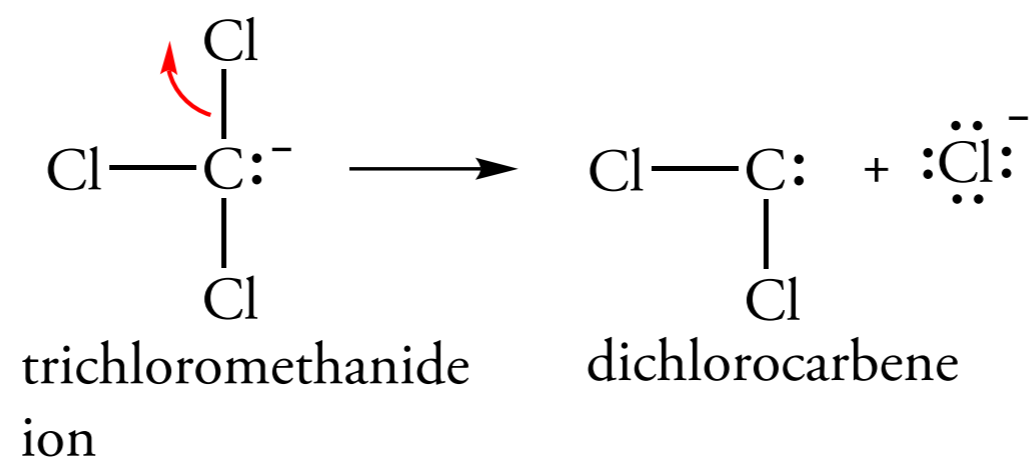
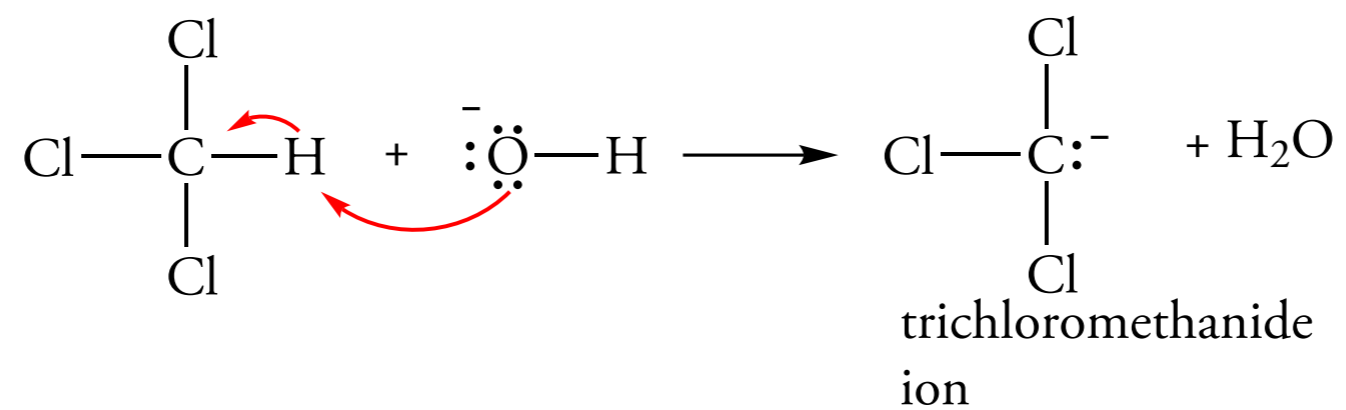
## 6.7 ADDITION OF CARBENES

Figure 6.6 Structure of a Carbene Compared to a Carbocation



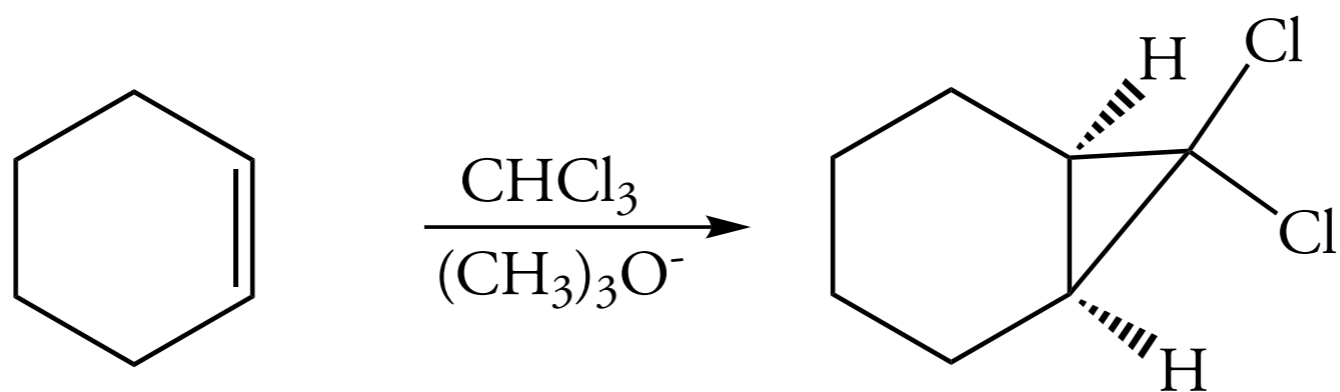
## 6.7 ADDITION OF CARBENES

### Formation of Dichlorocarbene



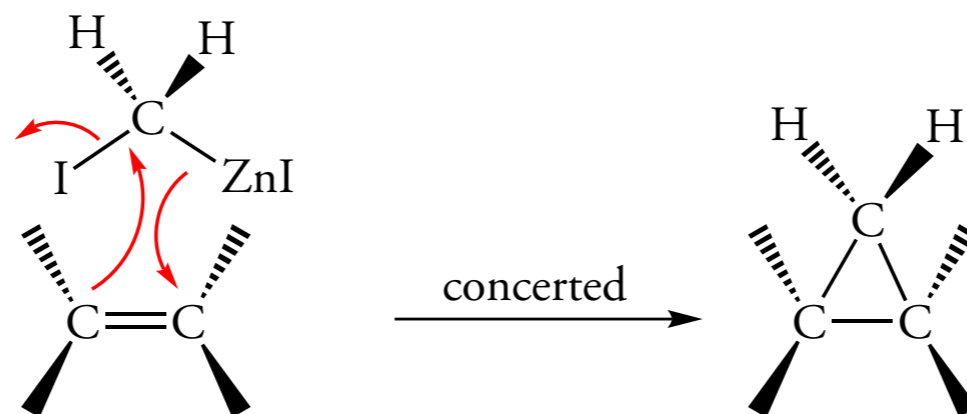
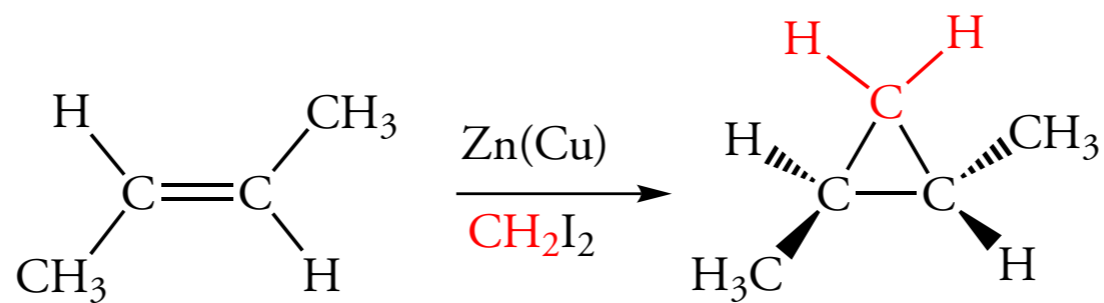
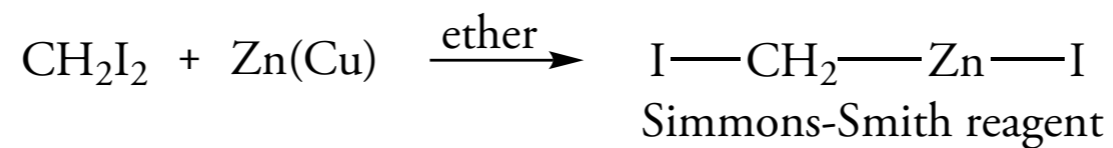
## 6.7 ADDITION OF CARBENES

### Stereospecificity of Carbene Addition Reaction

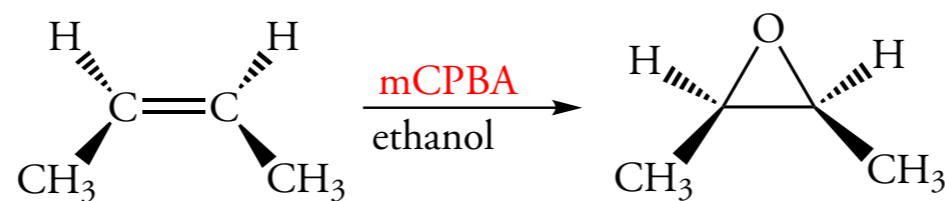
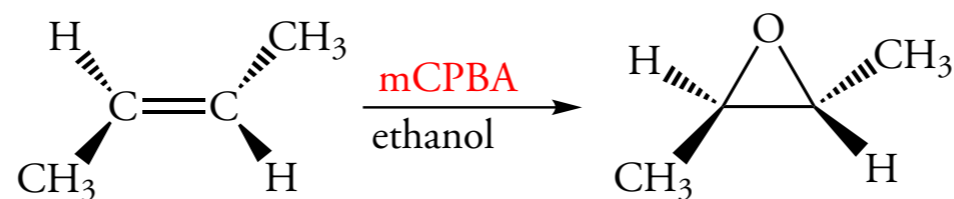
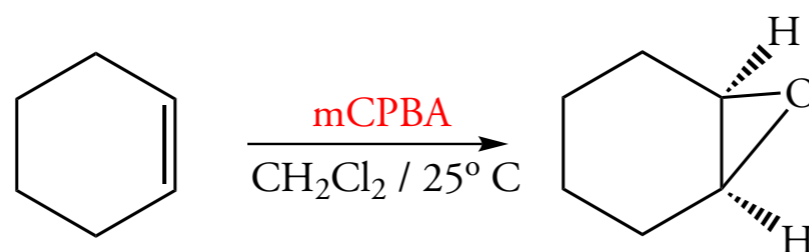
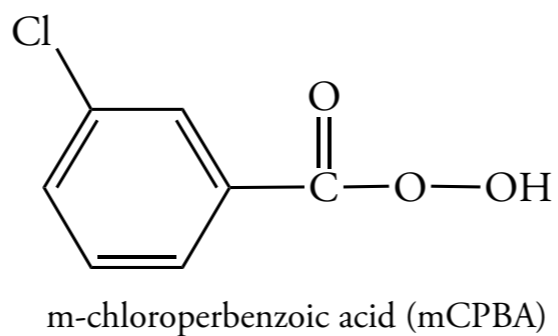
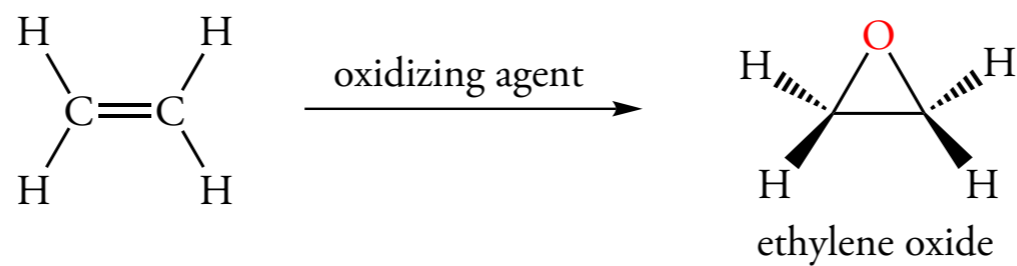


## 6.7 ADDITION OF CARBENES

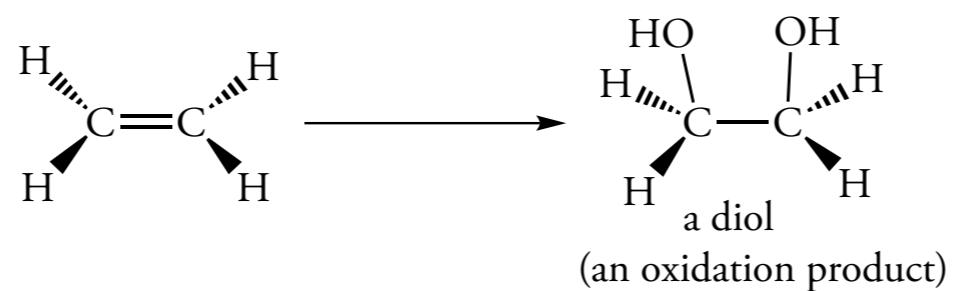
### Carbenoid Species



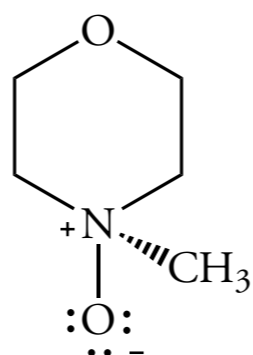
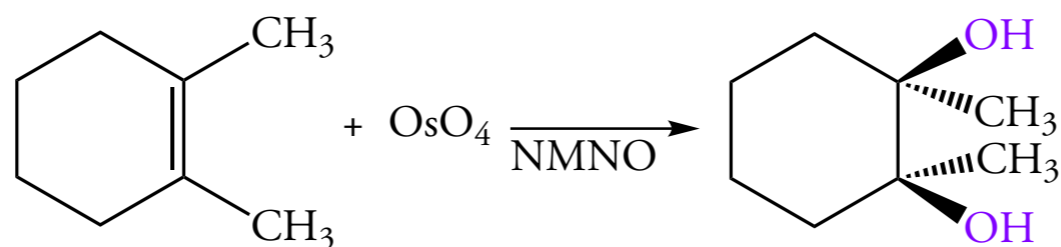
## 6.8 EPOXIDATION OF ALKENES



## 6.9 DIHYDROXYLATION OF ALKENES



### Dihydroxylation with Osmium Tetraoxide

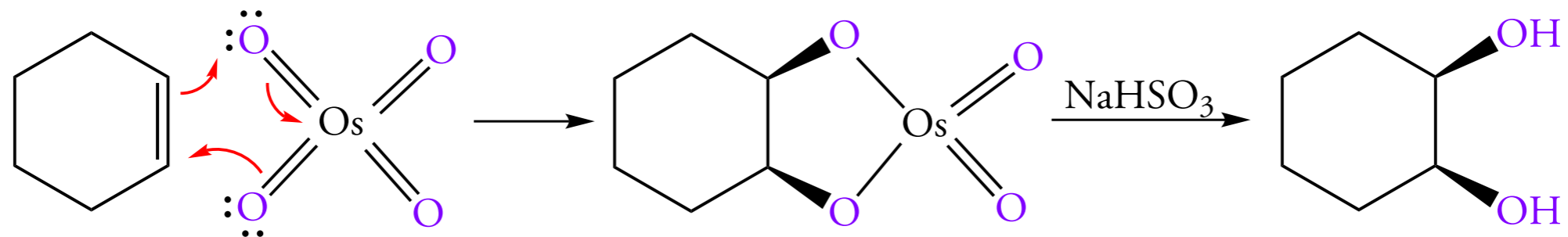


N-methylmorpholine-N-oxide (NMNO)  
(regenerates OsO<sub>4</sub>)

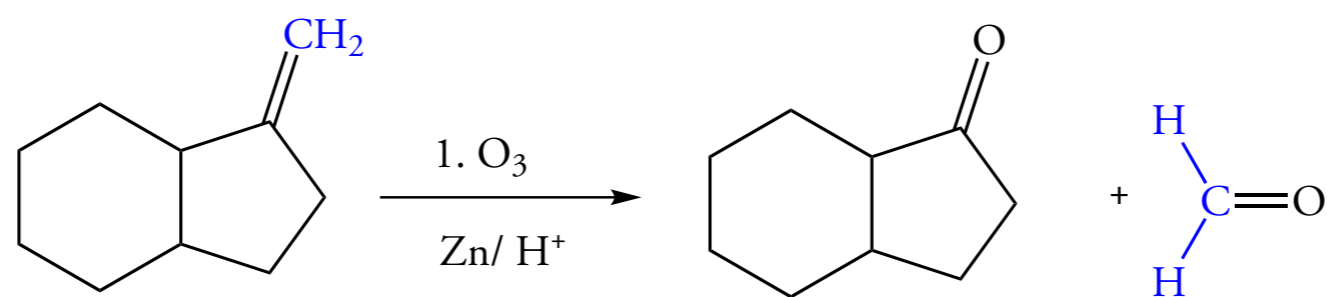


## 6.9 DIHYDROXYLATION OF ALKENES

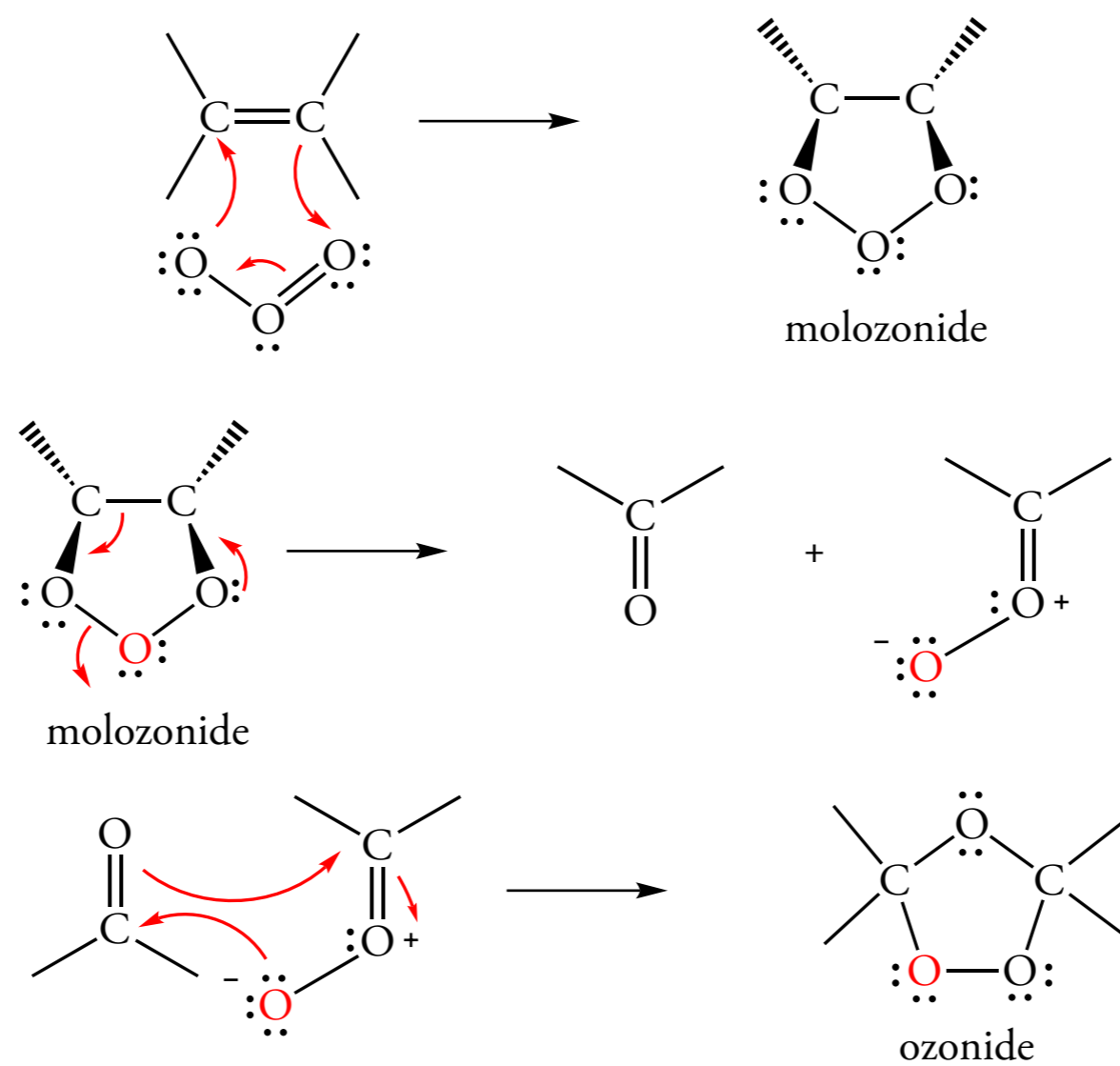
### Mechanism of Syn Dihydroxylation



## 6.10 OZONOLYSIS OF ALKENES



### Mechanism of Ozonolysis



## 6.10 OZONOLYSIS OF ALKENES

### Reductive and Oxidative Workup

