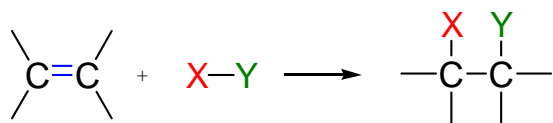
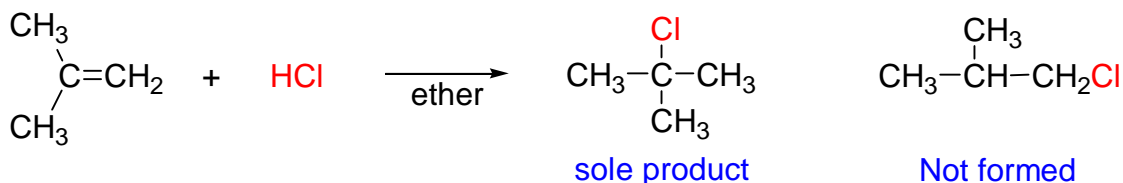


## 4. Reactions of Alkenes and Alkynes

Addition reaction of X-Y to the C=C and C≡C multiple bonds



### 4.1 Addition of HX to Alkenes: Hydrohalogenation



The reaction is **regiospecific** – only one of the two possible directions of addition occurs.

#### Markovnikov's Rule

In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents, and the X attaches to the carbon with more alkyl substituents

**The more highly substituted carbocation intermediate is formed.**



[chapter 04 01 Markov.ppt](#) (Markovnikov vs Anti-Markovnikov addition)

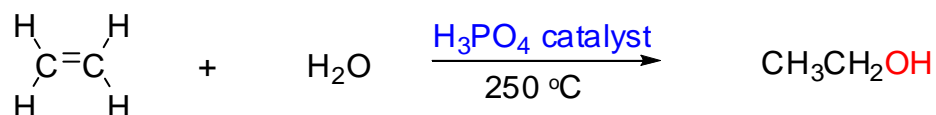
#### Carbocation Stability

Carbocation stability increases with increasing alkyl substitution: more highly substituted carbocations are more stable than less substituted ones because alkyl groups tend to donate electrons to the positively charged carbon atom.

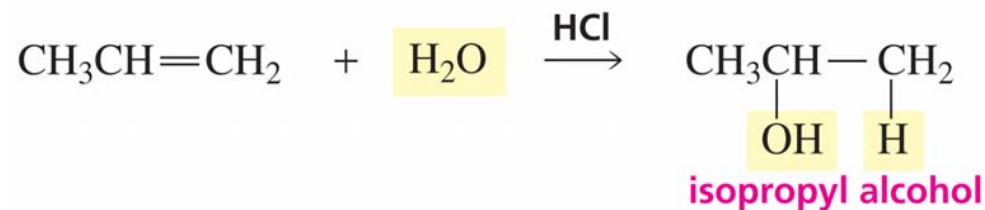
[chapter 04 02 carbocation.ppt](#)

### 4.2 Addition of H<sub>2</sub>O to Alkenes: Hydration

Water adds to alkenes to yield alcohols, ROH, a process called **hydration**.

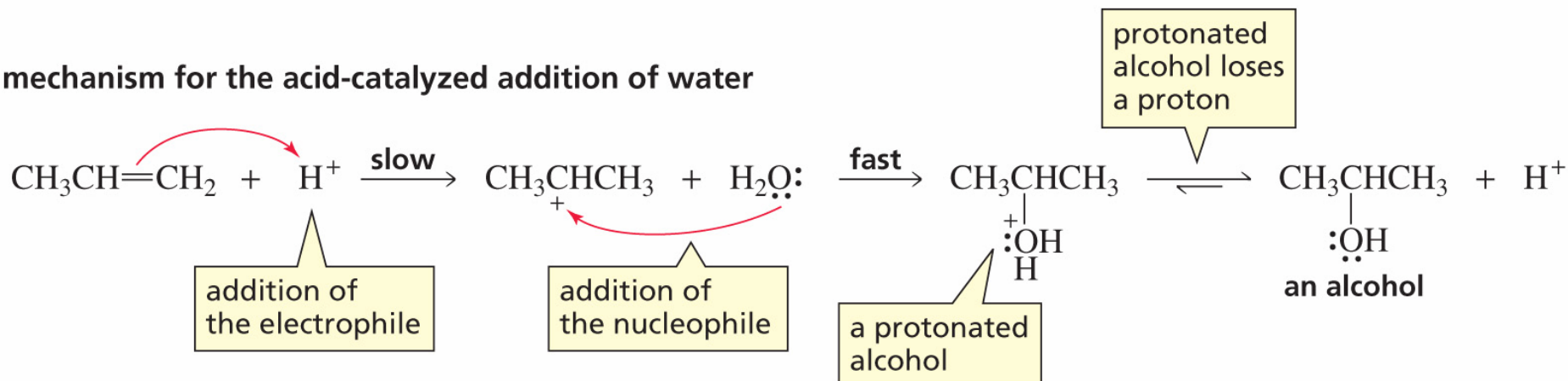


The addition of water to an unsymmetrical alkene follows **Markovnikov's rule**, giving the more highly substituted alcohol as product.



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### mechanism for the acid-catalyzed addition of water



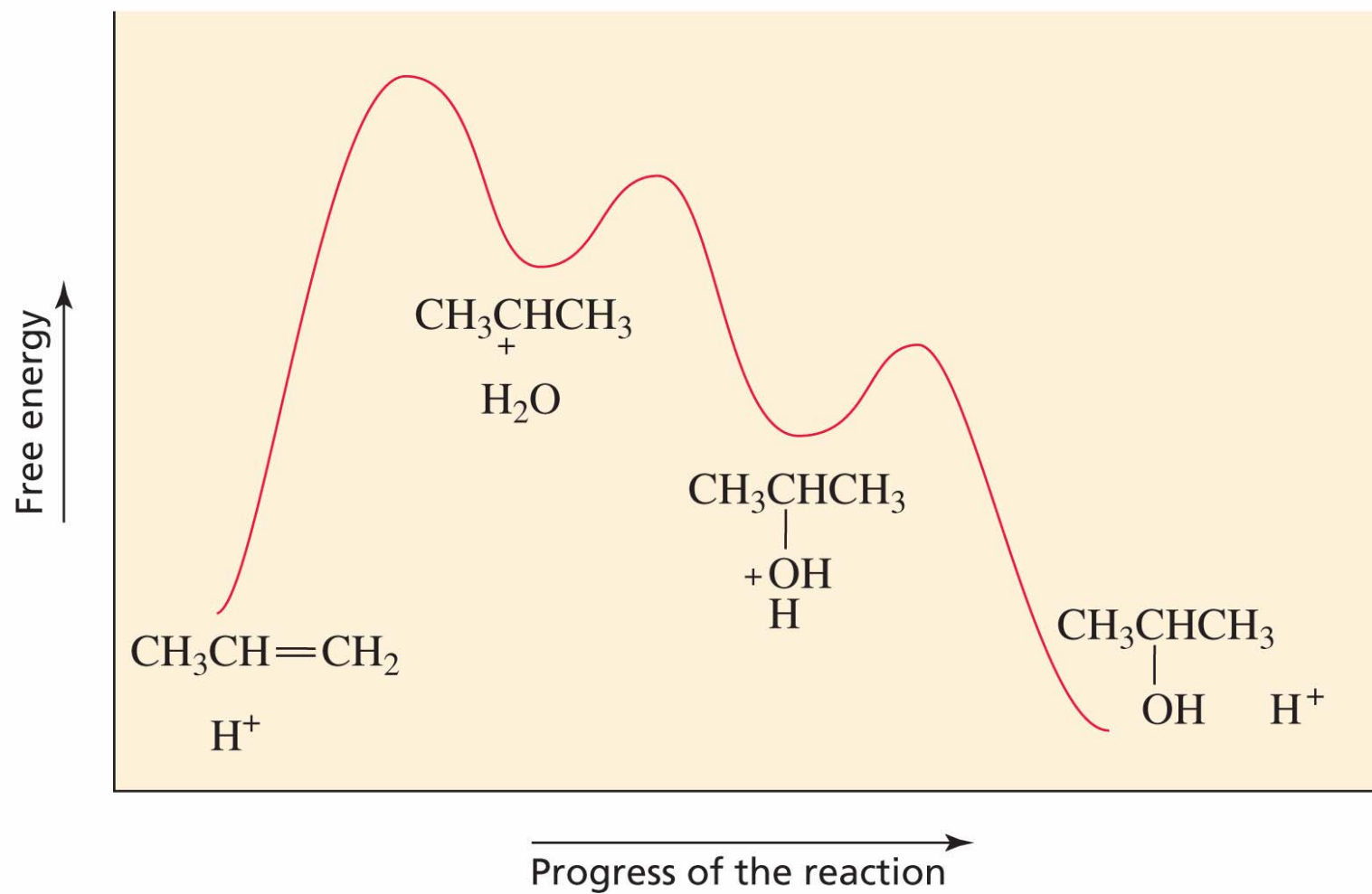
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**Step 1.** The alkene double bond reacts with  $\text{H}^+$  to yield **a carbocation intermediate**.

**Step 2.** Water acts as a nucleophile to donate a pair of electrons to form a carbon-oxygen bond and produce **a protonated alcohol intermediate**.

**Step 3.** Loss of  $\text{H}^+$  from the protonated alcohol intermediate then gives the neutral alcohol product and **regenerates the acid catalyst**.

## Reaction energy diagram

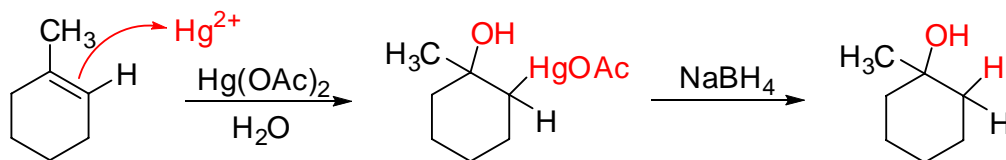


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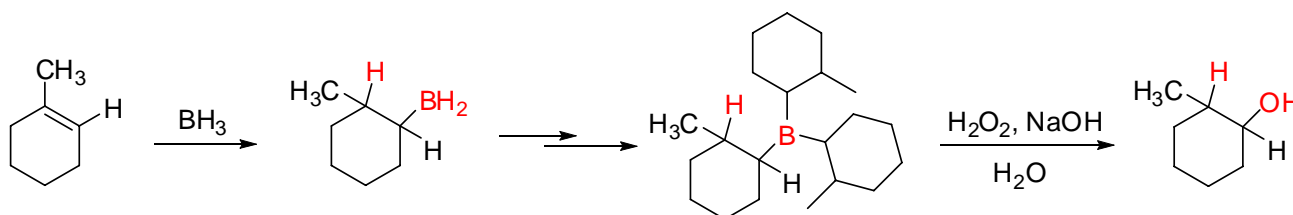
The reaction conditions are so severe that molecules are sometimes destroyed by the high temperatures and strongly acidic conditions.

### Some mild procedures for hydration.

(a) Oxymercuration-demercuration (**Markovnikov** addition)



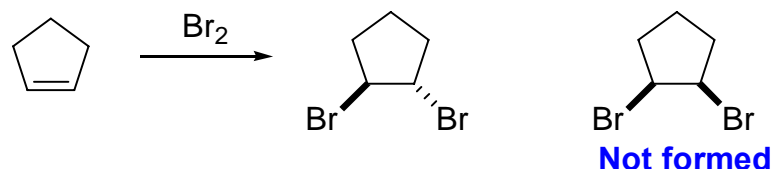
(b) Hydroboration-oxidation (**Anti-Markovnikov** addition)



[chapter\\_04\\_03\\_Hydration.ppt](#)

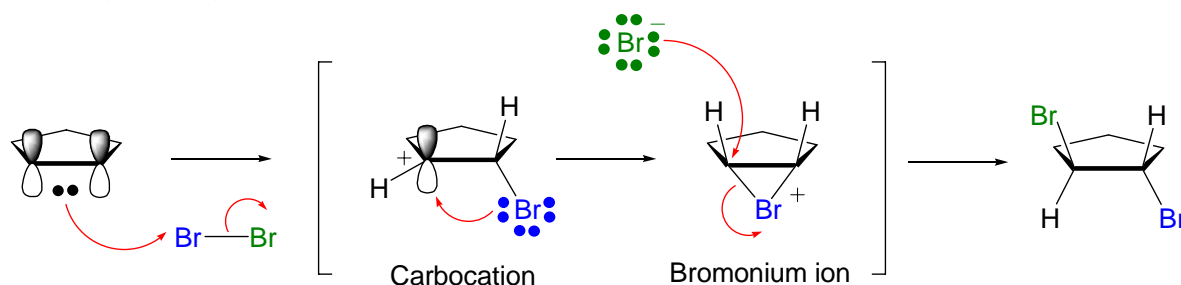
### 4.3 Addition of X<sub>2</sub> to Alkenes: **Halogenation**

Addition of Br<sub>2</sub> acts as a simple and rapid laboratory test for unsaturation.



**Anti-stereospecific** addition reaction – the two Br atoms add to opposite face of the cyclopentene double bond.

The reaction intermediate is not a true carbocation but is instead **a bromonium ion**, R-Br<sup>+</sup>-R, formed by overlap of bromine lone-pair electrons with the vacant p orbital of the neighboring carbon.



The bromine atom effectively “shield” one side of the molecule, reaction with Br<sup>-</sup> ion in the second step occurs from the opposite side to give the anti product.

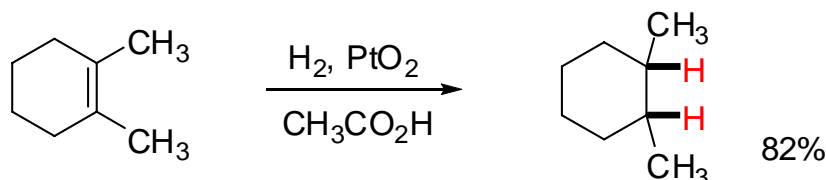
[chapter\\_04\\_04\\_halogenation.ppt](#)

#### 4.4 Addition of H<sub>2</sub> to Alkenes: **Hydrogenation**

Addition of H<sub>2</sub> to the C=C bond in the presence of a catalyst (Pd, PtO<sub>2</sub>).

**Heterogeneous** process – the hydrogenation reaction occurs on the surface of solid catalyst particles rather than in solution.

**Syn stereochemistry** – both hydrogens add to the double bond from the same side.

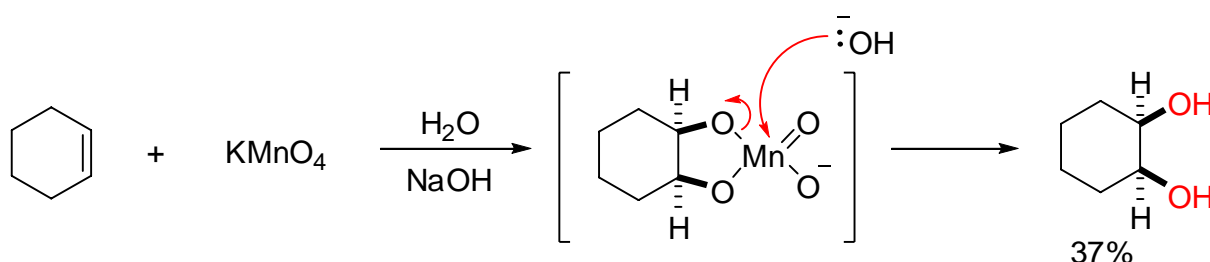


[chapter 04\\_05 hydrogenation.ppt](#)

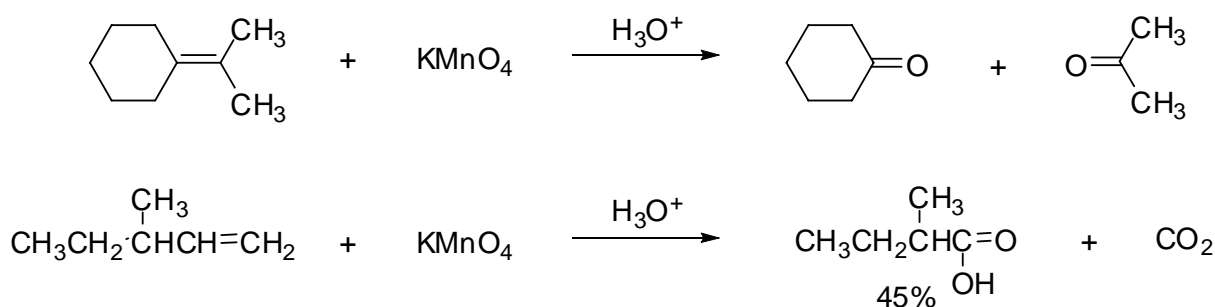
#### 4.5 Oxidation of Alkenes: **Hydroxylation and Cleavage**

**Hydroxylation** of an alkene – the addition of an –OH group to each of the alkene carbons producing 1,2-diol (glycol) can be carried out by the reaction with potassium permanganate, KMnO<sub>4</sub>, in basic solution.

**Syn stereochemistry**



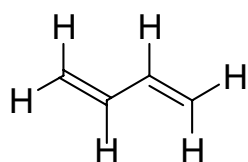
When oxidation of the alkene is carried out with KMnO<sub>4</sub> in **acidic solution, cleavage** of the double bond occurs



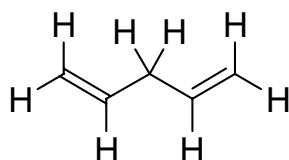
#### 4.6 Conjugated Dienes

Multiple bonds that alternate with single bonds are said to be **conjugated**.

There is an **electronic interaction** between the two double bonds of a conjugated diene: **p orbital overlap across the central single bond – extra stabilization**.



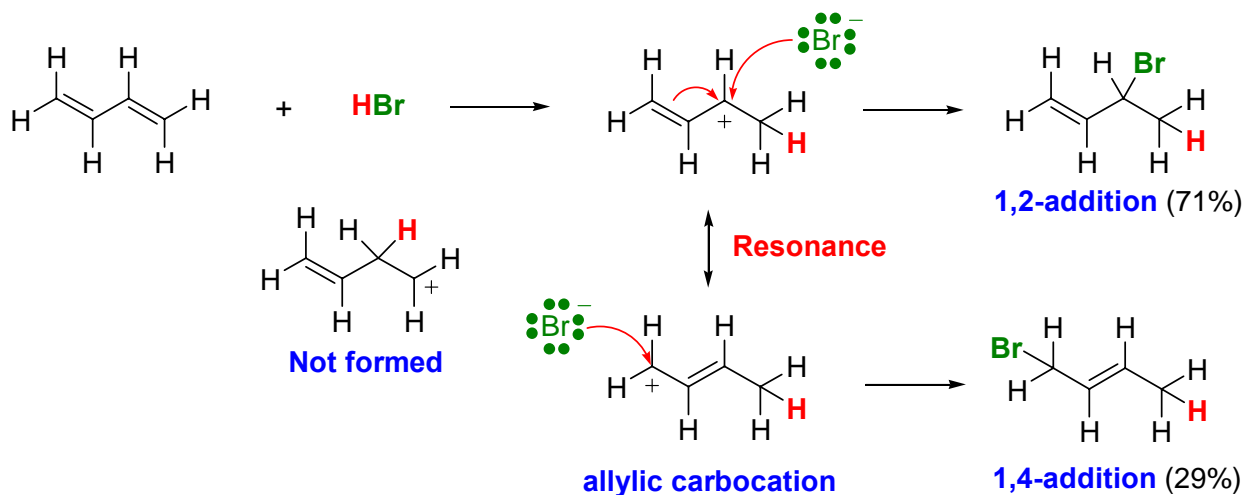
conjugated diene



isolated diene

[chapter 04\\_06 Conjugation.ppt](#)

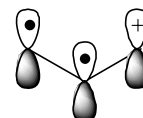
### Addition reaction with electrophiles (1,2- vs 1,4-addition)



Allylic means “next to a double bond.”

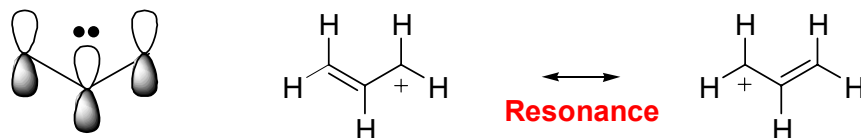
### Stability of Allylic Carbocations: Resonance

The positively charged carbon atom has a vacant  $p$  orbital that can overlap the  $p$  orbitals of the neighboring double bond.



An allylic carbocation is **symmetrical**.

All three carbon atoms are  $sp^2$ -hybridized, and each has a  $p$  orbital. The  $p$  orbital on the central carbon can overlap equally well with  $p$  orbitals on either of the two neighboring carbons, and the two electrons are free to move over the entire three-orbital array.



symmetrical

Neither of the resonance structure is correct by itself; the true structure of the allylic carbocation is somewhere between the two (two C-C bonds are equivalent).

An allylic carbocation has a single, unchanging structure called **a resonance hybrid**.



