

## **SECTION 6 – REACTIONS AND SYNTHESIS OF ALKENES**

### **6-1 -- Addition of Halogens ( $X_2$ )**

- Stereochemistry (Anti-Addition Observed)
- Bromonium Ion Intermediate
- Nucleophilic Solvent ( $H_2O$ ) vs. Inert Solvent ( $CCl_4$ )

### **6-2 -- Halohydrin Formation**

- Use of Hypobromous Acid ( $HO-Br$ )
- Anti-Addition of  $-Br$  and  $-OH$

### **6-3 -- Hydration Reactions**

- Conversion of Alkenes to Alcohols
- Markovnikov Regiochemistry
- Acid-Catalyzation of Hydration Reactions
- The Principle of Microscopic Reversibility

### **6-5 -- Oxymercuration Reaction**

- Markovnikov Addition of  $-H$  and  $-OH$
- Use of  $NaBH_4$  as a Source of Hydride ( $:H^-$ )
- No Carbocation Rearrangements Observed
- Hydride Shift

### **6-6 -- Hydroboration Reaction**

- Borane,  $BH_3$
- Replacing Borane's  $-H$ 's with Alkyl Groups (Substitution)
- Mechanism for Hydroboration is "Concerted"
- Reaction of  $BH_3$  with the Solvent Tetrahydrofuran (THF)
- Steric Effects Control the Regiochemistry of the Observed Products
- Syn-Addition ("Cis"-like)

### **6-9 -- Non-Markovnikov Addition of $HBr$**

- Does Not Work with the Reagents  $HCl$  or  $HI$
- Free-Radical Chain Mechanism
- Initiation and Propagation Steps of the Mechanism
- $3^\circ$  Radical vs.  $1^\circ$  Radical Intermediates (Stability)
- Radical Stabilities
- Polymer Production (Teflon, Polystyrene, Polyvinylchloride [PVC], and Plexiglass)

### **6-11 -- Catalytic Hydrogenation Reaction**

- Syn-Addition of  $H_2$  Across a Double Bond

### **6-11 -- Hydroxylation Reaction**

- Conversion of an Alkene to a Diol

### **6-12 -- Oxidative Cleavage Reactions**

- The Ozonolysis Reaction

- Permanganate Reactions ( $\text{MnO}_4^-$ )

#### **6-12 -- Carbene Additions Across a Double Bond**

- Their Use in Producing 3-Membered Rings
- How Carbenes are Generated

#### **6-13 -- The Simmons-Smith Reaction**

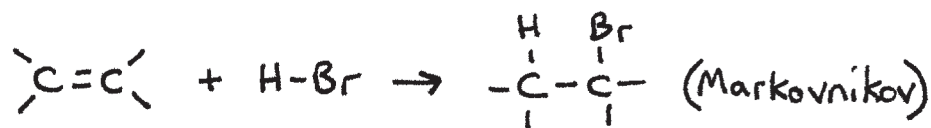
- Carbenoids
- $\text{Zn}(\text{Cu}) = \text{“Zn-Cu”}$  Couple

#### **6-14 -- Periodic Acid Cleavage**

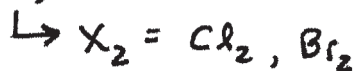
- Cleavage of Diols to Produce 2 Carbonyl Compounds

## Section 6 = Reactions and Synthesis of Alkenes. 6-1

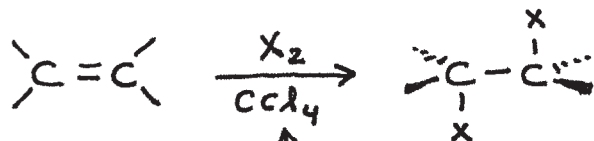
- we'll be studying 13 reactions.
- we already studied the following reaction in section 5:



### ① Addition of Halogens ( $\text{X}_2$ ).



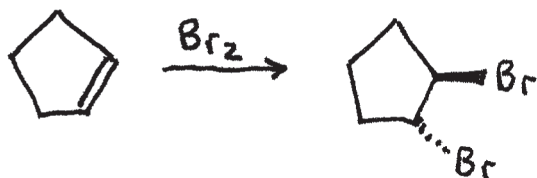
general form:



inert solvent (non-participating)

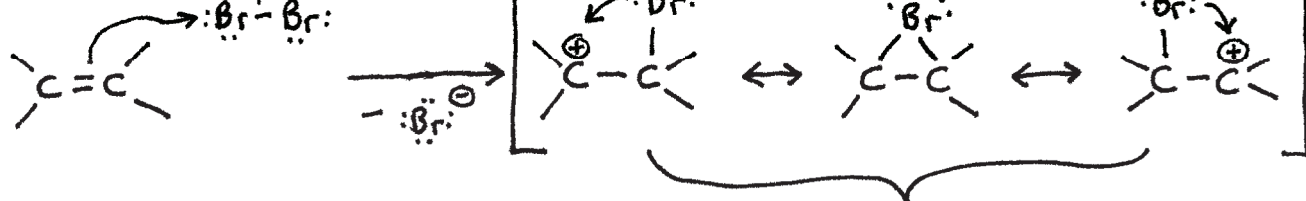
- stereochemistry  $\Rightarrow$  halogens are added to opposite faces of the double-bond (d.b.)

anti-addition

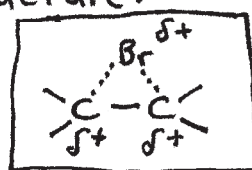


- no carbocation rearrangements are observed.

mechanism:  $\delta^+ \quad \delta^-$



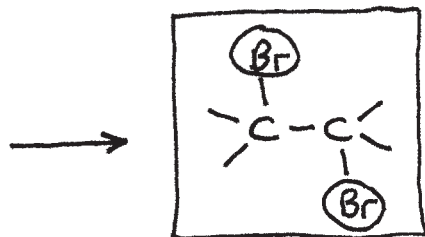
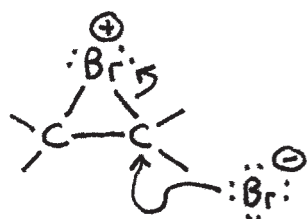
3 resonance structures are averaged to get actual structure:



bromonium ion  
(reactive intermediate)

\* 2<sup>nd</sup> step of the mechanism on the next page...

2nd step:



anti-addition

↳  $:\ddot{\text{Br}}:^{\ominus}$  approaches from opposite side.

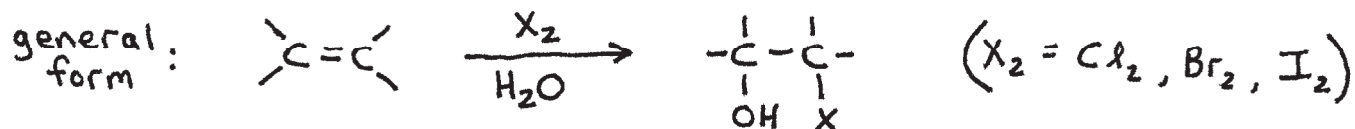
6-2

Q: What if  $\text{H}_2\text{O}$  (a nucleophilic solvent) is used as the solvent instead of the inert solvent,  $\text{CCl}_4$ ?

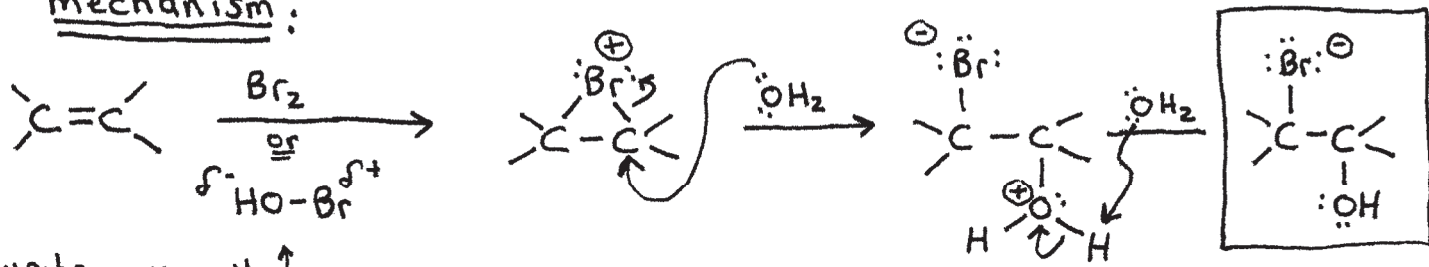
↳ A: Then we get a totally different reaction with different products.

⇐

## ② Halohydrin Formation.

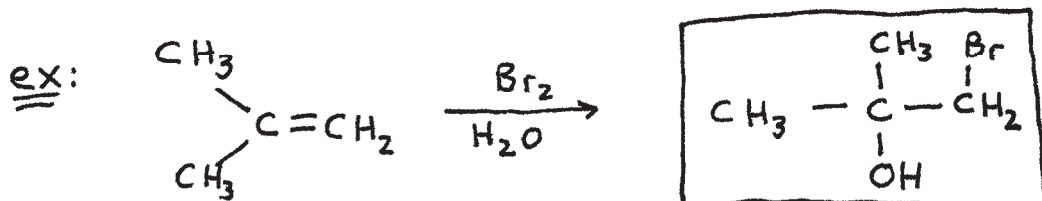


mechanism:



hypobromous acid ↑  
present in solutions  
of  $\text{Br}_2$  and  $\text{H}_2\text{O}$

\* anti-addition of  $-\text{Br}$  and  $-\text{OH}$

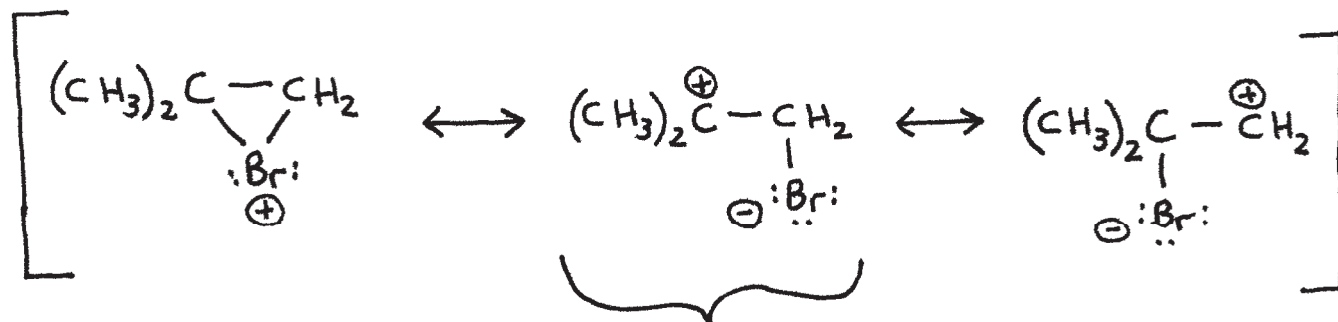


↳ Q: Why does  $-\text{OH}$  go on the more substituted carbon?

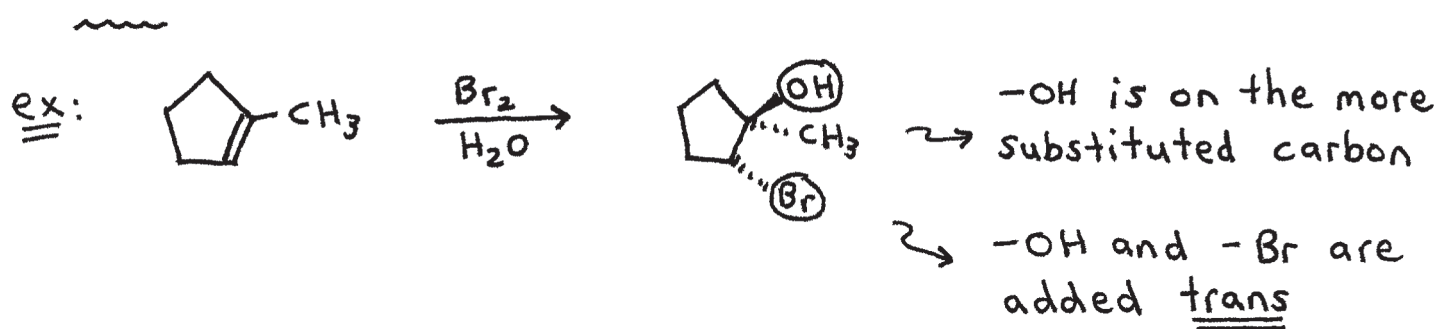
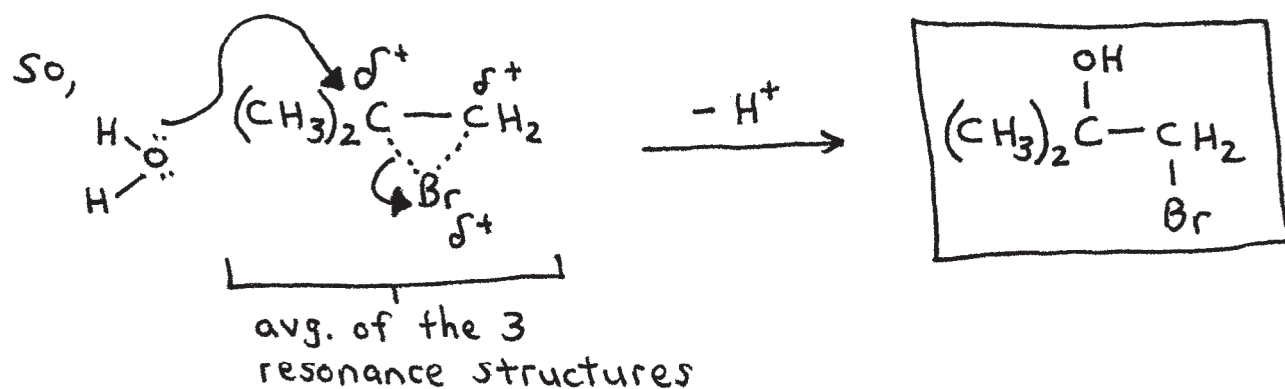
↳ A: examine the reaction intermediate to see why...

... 3 resonance structures:

6-3

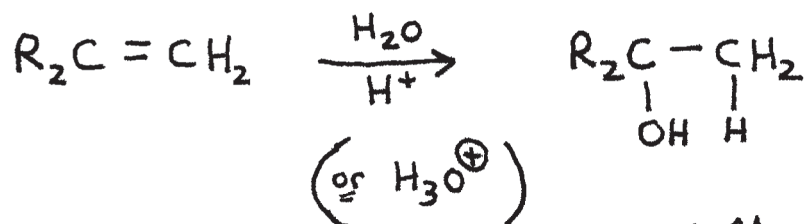


\* more important because  $\oplus$  charge on the 3° carbon.



③ Hydration Reactions = addition of  $\text{H}-\text{OH}$  ( $\text{H}_2\text{O}$ ) across a d.b.

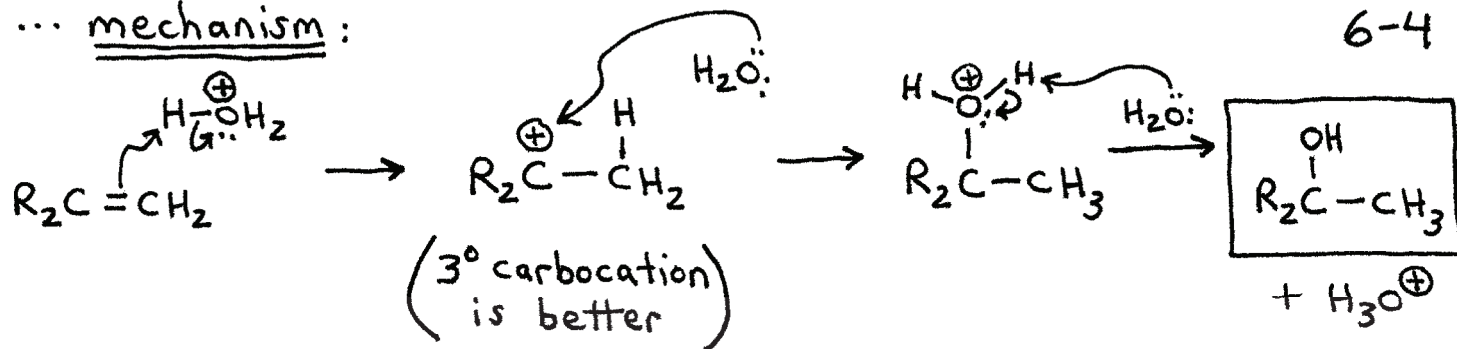
↳ converts alkenes to alcohols.



\* Markovnikov regiochemistry is observed.

- mechanism = next page...

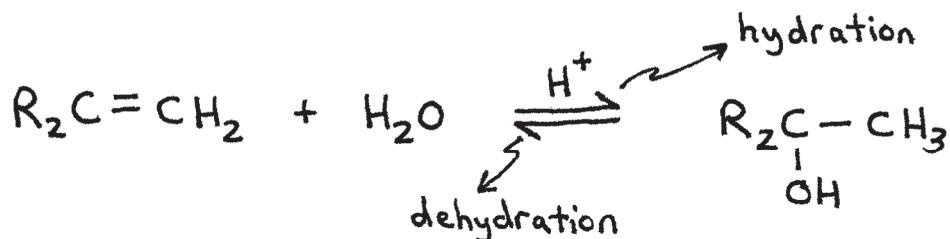
... mechanism:



- hydration is acid-catalyzed

↳  $H^+$  ( $H_3O^+$ ) is used but later regenerated.

- hydration of alkenes is reversible.



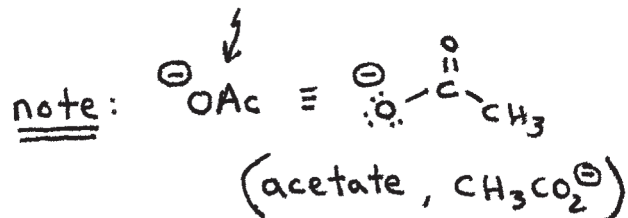
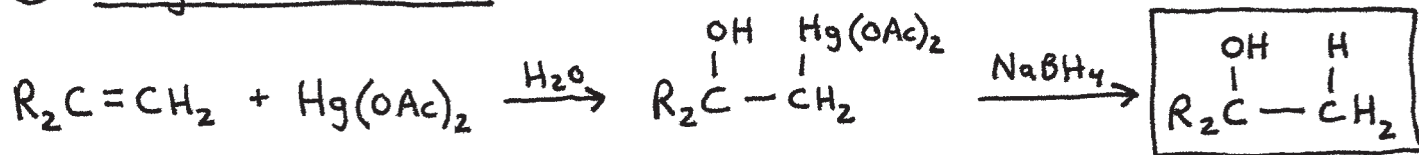
Le Châtelier's  
Principle:

→ excess  $H_2O$  drives equilibrium to the right.

→ removal of  $H_2O$  or adding concentrated  $H_2SO_4$  or  $H_3PO_4$  drives equilibrium to the left.

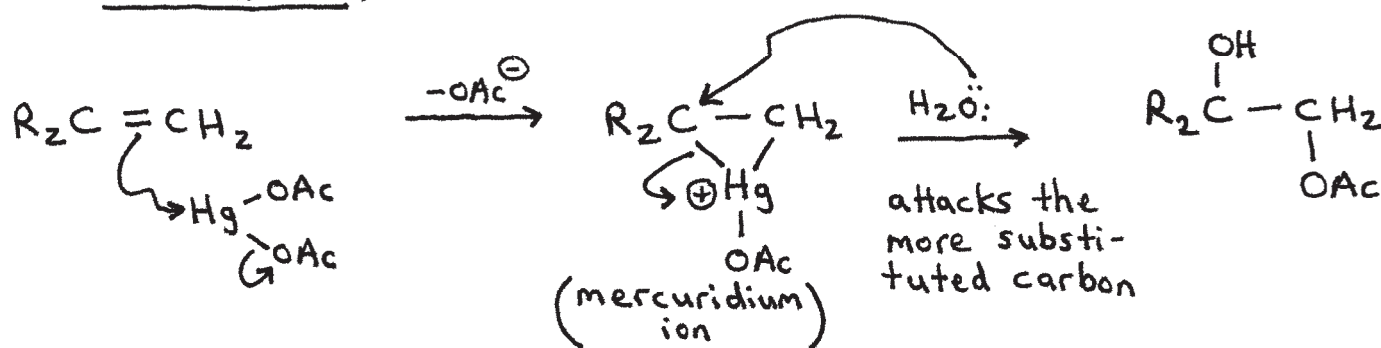
- Principle of Microscopic Reversibility = forward and reverse reactions go via the same mechanism, same intermediate, and the same transition state.

↳ there's only one lowest-energy pathway.

④ Oxymercuration.

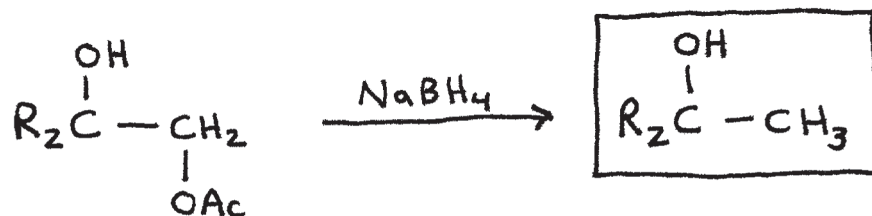
Markovnikov  
addition of  
-H and -OH

- mechanism:



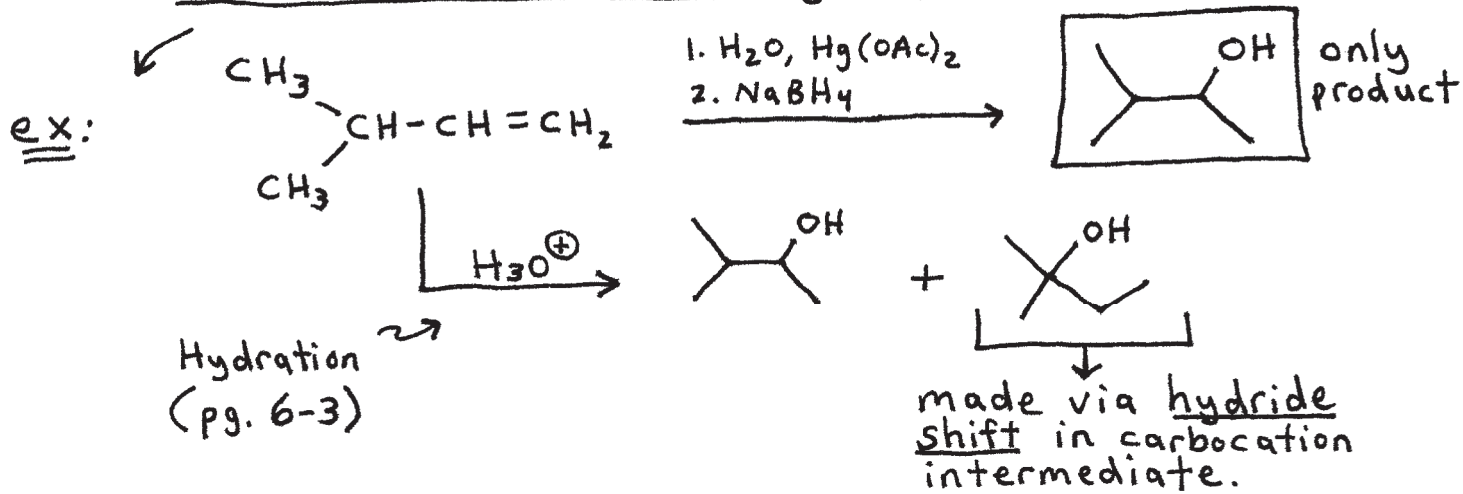
2nd step:

mech. is  
unimportant



\*  $NaBH_4$  is a source of hydride ( $":H^-"$ );  
It kicks out and replaces  $-HgOAc$

\* net result  $\Rightarrow$  Markovnikov addition of -H and -OH, but no carbocations involved, so no carbocation rearrangements.



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