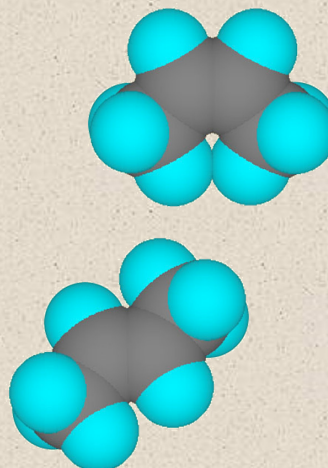


# Reactions of Alkenes

Chapter 6



1

## Reactions Mechanisms

- A reaction mechanism describes how a reaction occurs and explains the following.
  - Which bonds are broken and which new ones are formed.
  - The order and relative rates of the various bond-breaking and bond-forming steps.
  - If in solution, the role of the solvent.
  - If there is a catalyst, the role of a catalyst.
  - The position of all atoms and energy of the entire system during the reaction.

2

## Gibbs Free Energy

- Gibbs free energy change,  $\Delta G^0$ :
  - A thermodynamic function relating enthalpy, entropy, and temperature.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

- **Exergonic reaction**: A reaction in which the Gibbs free energy of the products is lower than that of the reactants; **the position of equilibrium for an exergonic reaction favors products.**
- **Endergonic reaction**: A reaction in which the Gibbs free energy of the products is higher than that of the reactants; **the position of equilibrium for an endergonic reaction favors starting materials.**

3

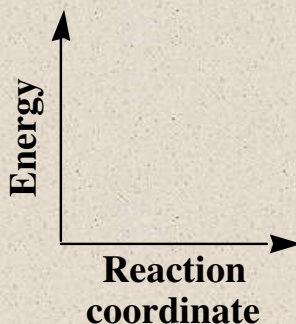
## Energy Diagrams

- **Enthalpy change,  $\Delta H^0$** : The difference in total bond energy between reactants and products.
  - a measure of bond making (exothermic) and bond breaking (endothermic).
- **Heat of reaction,  $\Delta H^0$** : The difference in enthalpy between reactants and products.
  - **Exothermic reaction**: A reaction in which the enthalpy of the products is lower than that of the reactants; a reaction in which heat is released.
  - **Endothermic reaction**: A reaction in which the enthalpy of the products is higher than that of the reactants; a reaction in which heat is absorbed.

4

## Energy Diagrams

- **Energy diagram:** A graph showing the changes in energy that occur during a chemical reaction.
- **Reaction coordinate:** A measure in the change in positions of atoms during a reaction.



5

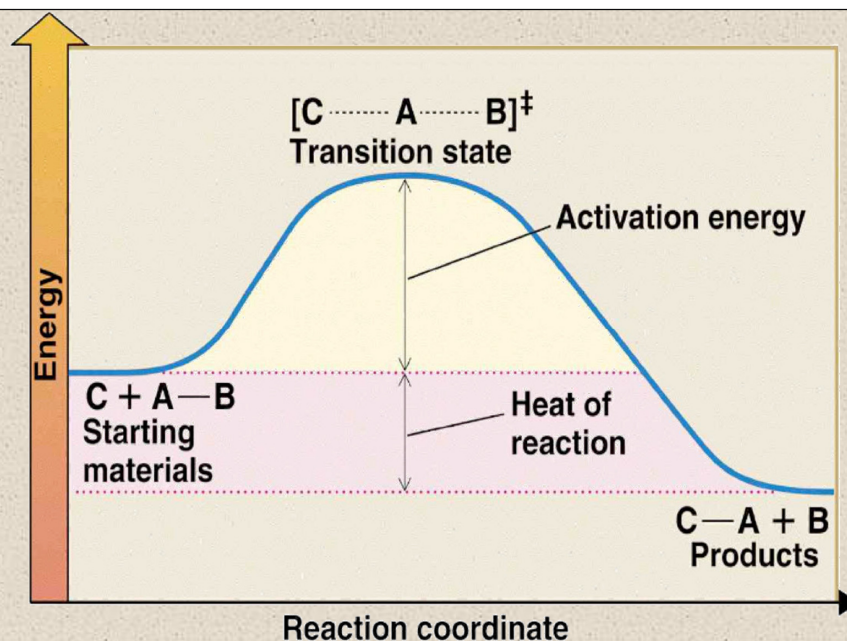
## Activation Energy

- **Transition state  $\ddagger$ :**
  - An unstable species of maximum energy formed during the course of a reaction.
  - A maximum on an energy diagram.
- **Activation Energy,  $\Delta G^\ddagger$ :** The difference in Gibbs free energy between reactants and a transition state.
  - If  $\Delta G^\ddagger$  is large, few collisions occur with sufficient energy to reach the transition state; reaction is slow.
  - If  $\Delta G^\ddagger$  is small, many collisions occur with sufficient energy to reach the transition state; reaction is fast.

6

## Energy Diagrams

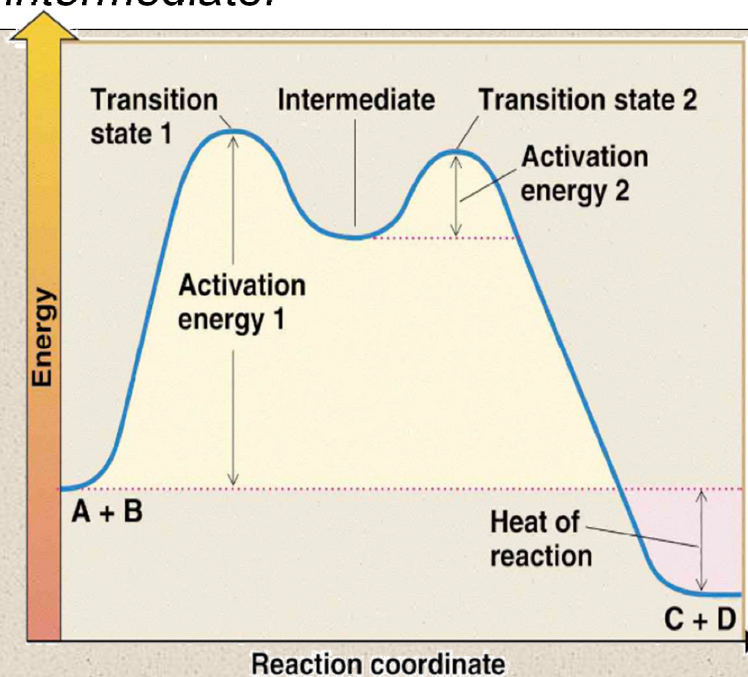
- An energy diagram for a one-step reaction with no intermediate.



7

## Energy Diagrams

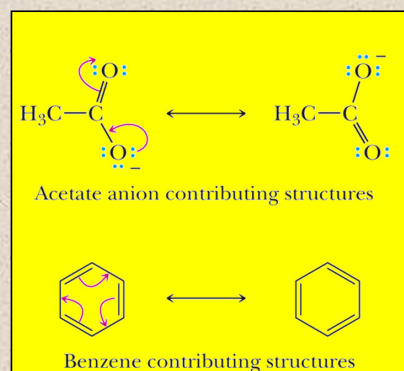
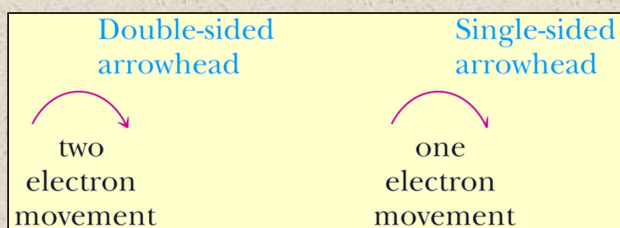
- An energy diagram for a two-step reaction with one intermediate.



8

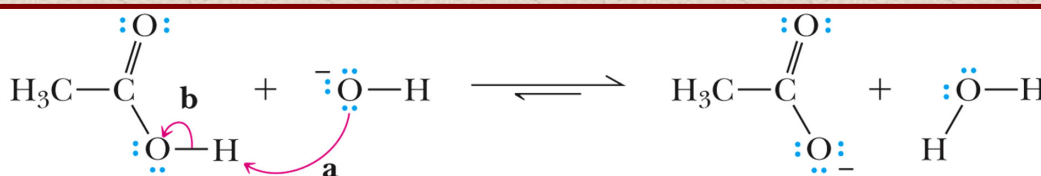
## Electron Pushing

- Organic chemists use a technique called **electron pushing**, alternatively called **arrow pushing**, to depict the flow of electrons during a chemical reaction.
- Rule 1:** Arrows are used to indicate movement of electrons.



## Electron Pushing

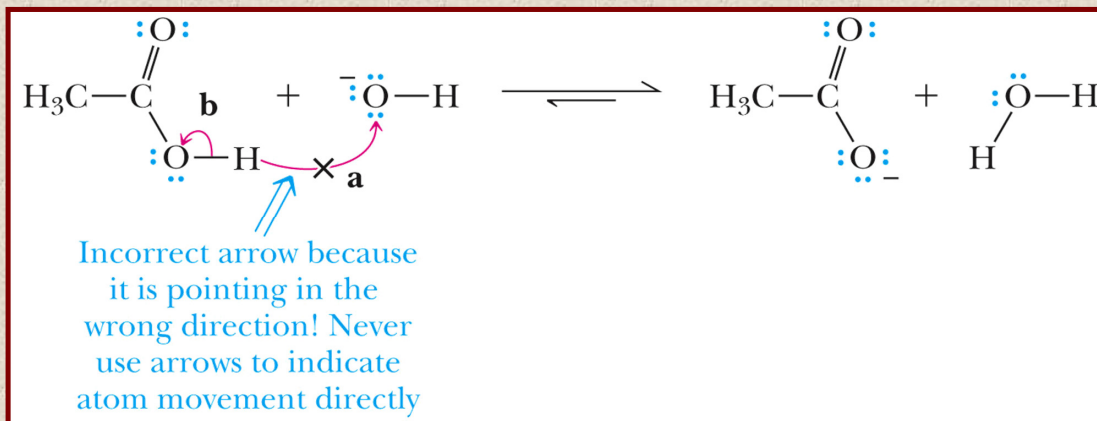
- Rule 2:** Arrows are **never** used to indicate the movement of atoms.



Correct use of arrows to indicate electron movement during a reaction

## Electron Pushing

- **Rule 2:** Arrows are **never** used to indicate the movement of atoms.



11

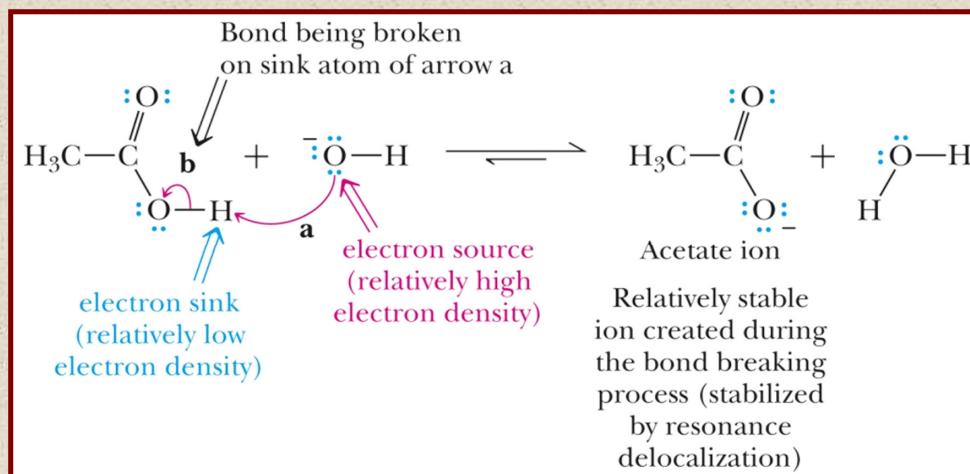
## Electron Sources & Sinks

- **Rule 3** Arrows always start at an electron **source** and end at an **electron sink**.
  - **Electron source:** Most commonly a  $\pi$  bond or a lone pair of electrons on an atom.
  - **Electron sink:** An atom in a molecule or ion that can accept a new bond or a lone pair of electrons.

12

## Electron Sources & Sinks

- **Rule 4** Bond breaking will occur to avoid overfilling valence (hypervalence) on an atom serving as an electron sink



13

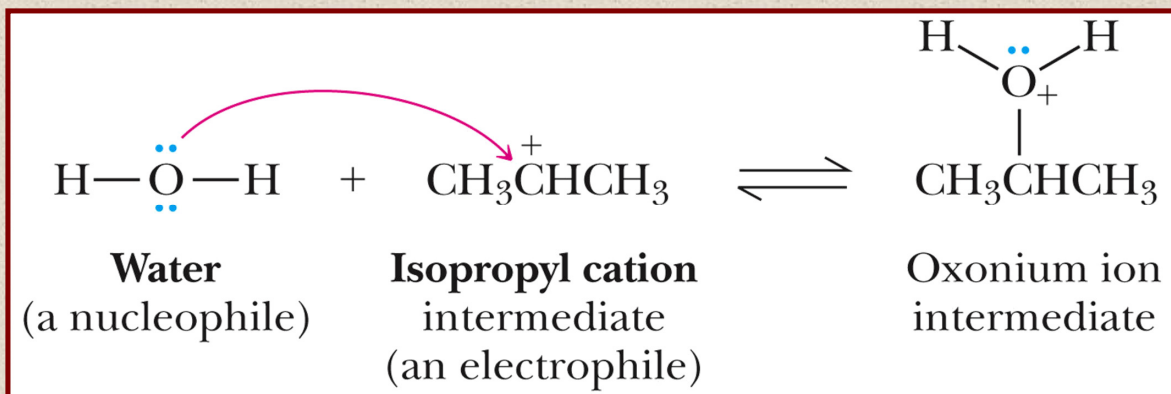
## Patterns of e<sup>-</sup> Movement

1. Redistribution of  $\pi$  bonds and/or lone pairs.
2. Formation of a new  $\sigma$  bond from a lone pair or a  $\pi$  bond.
3. Breaking a  $\sigma$  bond to give a new lone pair or a  $\pi$  bond.

14

## Mechanisms: Make-a-bond

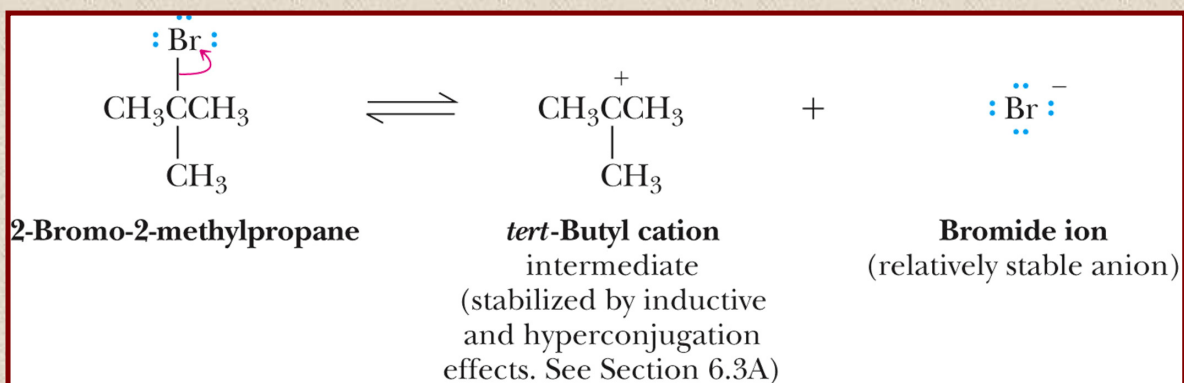
- Pattern 1:** Make a new bond between a nucleophile (source for an arrow) and an electrophile (sink for an arrow).



15

## Mechanisms: Break-a-bond

- Pattern 2:** Break a bond so that relatively stable molecules or ions are created.

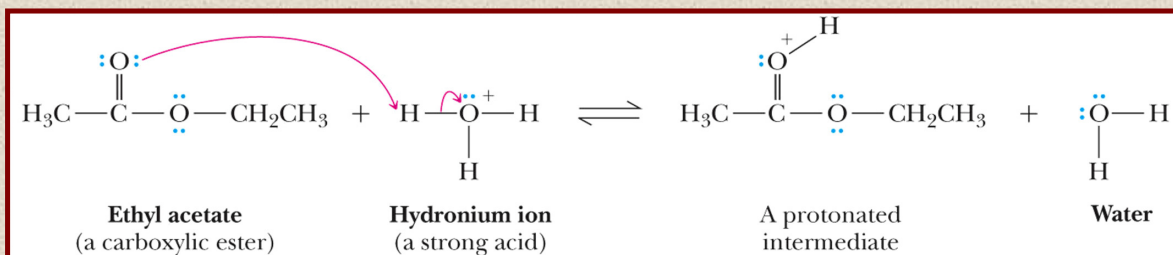


16



## Proton transfer

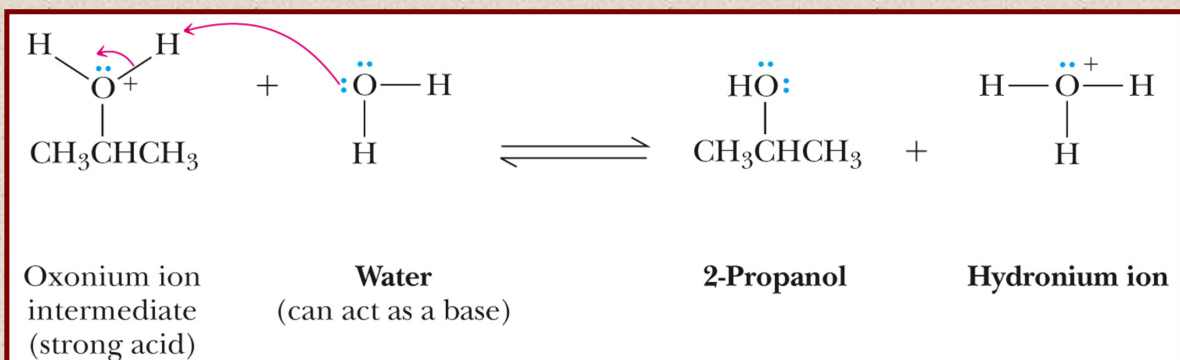
- Pattern 3: Add a proton** Use this pattern when there is a strong acid present or a molecule that has a strongly basic functional group.



17

## Proton transfer

- Pattern 4: Take a proton away.** Use this pattern when a molecule has a strongly acidic proton or there is a strong base present.



18

## Electrophilic Additions

- **Hydrohalogenation** using HCl, HBr, HI
- **Hydration** using H<sub>2</sub>O in the presence of H<sub>2</sub>SO<sub>4</sub>
- **Halogenation** using Cl<sub>2</sub>, Br<sub>2</sub>
- **Halohydrination** using HOCl, HOBr
- **Oxymercuration** using Hg(OAc)<sub>2</sub>, H<sub>2</sub>O followed by reduction

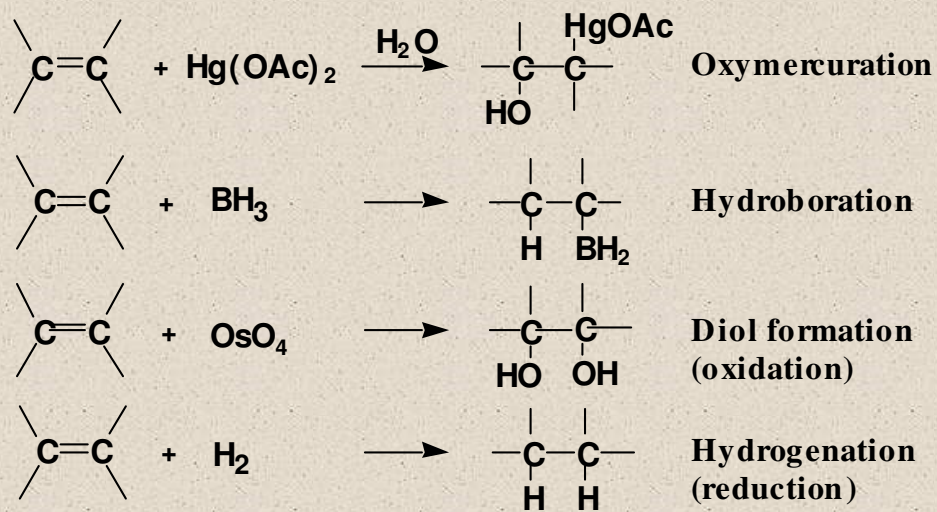
19

## Characteristic Reactions

Reaction	Descriptive Name(s)
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array} + \text{HCl} \quad (\text{HX}) \quad \longrightarrow \quad \begin{array}{c} \text{H} \\   \\ -\text{C}-\text{C}- \\   \quad   \\ \quad \text{Cl(X)} \end{array}$	<b>Hydrochlorination</b> (hydrohalogenation)
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array} + \text{H}_2\text{O} \quad \longrightarrow \quad \begin{array}{c} \text{H} \\   \\ -\text{C}-\text{C}- \\   \quad   \\ \quad \text{OH} \end{array}$	<b>Hydration</b>
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array} + \text{Br}_2 \quad (\text{X}_2) \quad \longrightarrow \quad \begin{array}{c} (\text{X})\text{Br} \\   \\ -\text{C}-\text{C}- \\   \quad   \\ \quad \text{Br(X)} \end{array}$	<b>Bromination</b> (halogenation)
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array} + \text{Br}_2 \quad (\text{X}_2) \quad \xrightarrow{\text{H}_2\text{O}} \quad \begin{array}{c} \text{HO} \\   \\ -\text{C}-\text{C}- \\   \quad   \\ \quad \text{Br(X)} \end{array}$	<b>Halohydrin formation</b> (Bromohydrin formation)

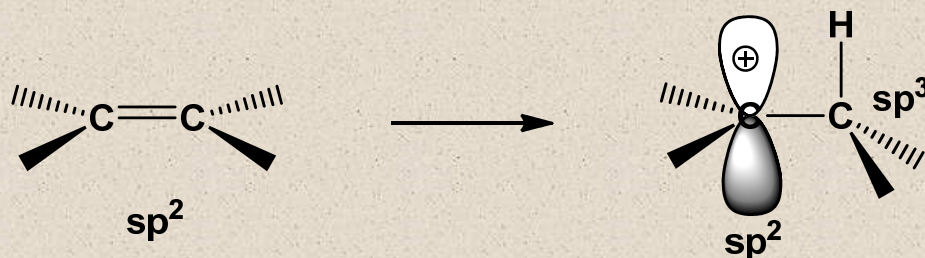
20

## Characteristic Reactions



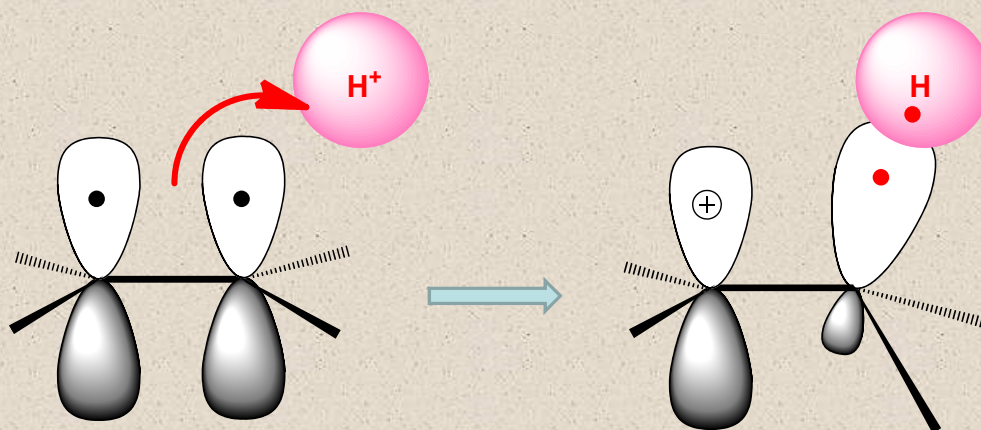
21

## Protonation of Alkene



22

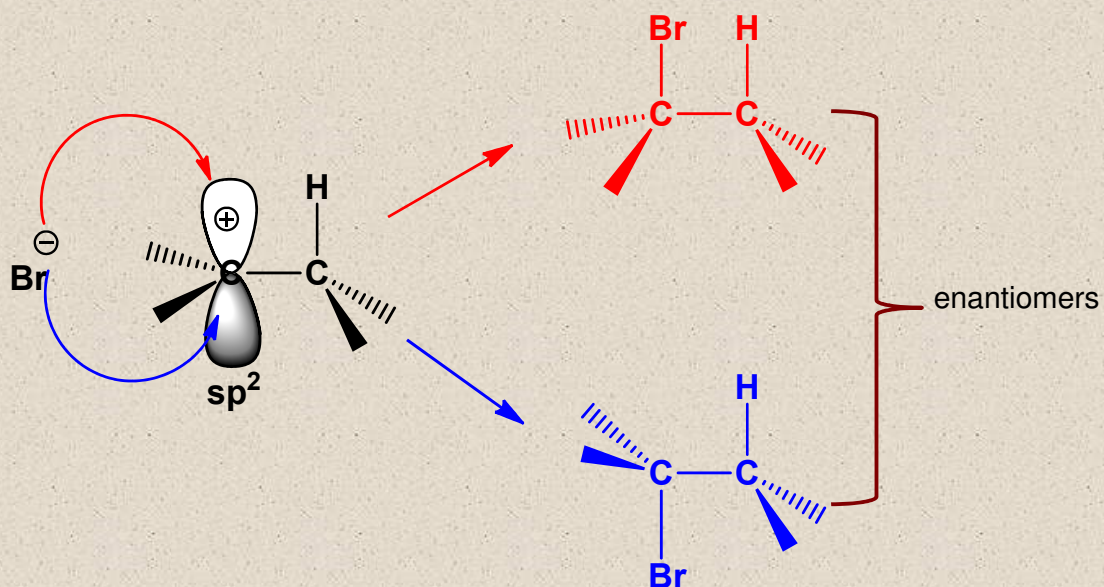
## Protonation of Alkene



A Carbocation is formed

23

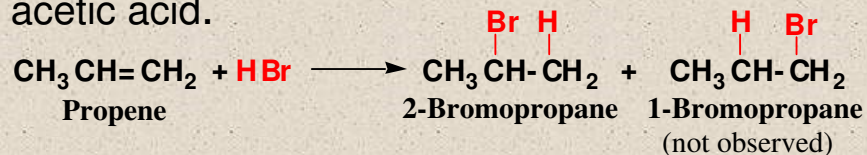
## Bromide addition



24

## Addition of HX

- Carried out with pure reagents or in a polar solvent such as acetic acid.



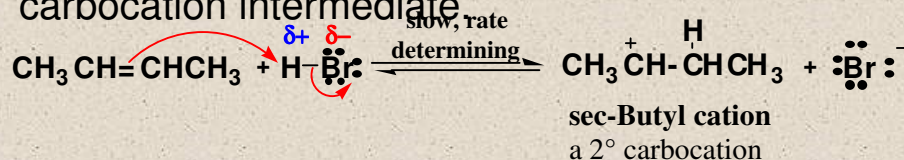
- Addition is regioselective
  - Regioselective reaction:** An addition or substitution reaction in which one product is formed *in preference* to all others that might be formed.
  - Markovnikov's rule:** In the addition of HX or H<sub>2</sub>O to an alkene, H adds to the carbon of the double bond having the greater number of hydrogens.

25

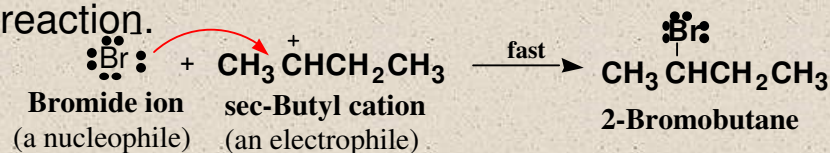
## HBr + 2-Butene

- A two-step mechanism

Step 1: Proton transfer from HBr to the alkene gives a carbocation intermediate



Step 2: Reaction of the sec-butyl cation (an electrophile) with bromide ion (a nucleophile) completes the reaction.



26

## Carbocations

**Carbocation:** A species in which a carbon atom has only six electrons in its valence shell and bears a positive charge.

Carbocations:

1. Are classified as 1°, 2°, or 3° depending on the number of carbons bonded to the carbon bearing the + charge.
2. **Are electrophiles; that is, they are electron-loving.**
3. Are Lewis acids.

27

## Carbocations

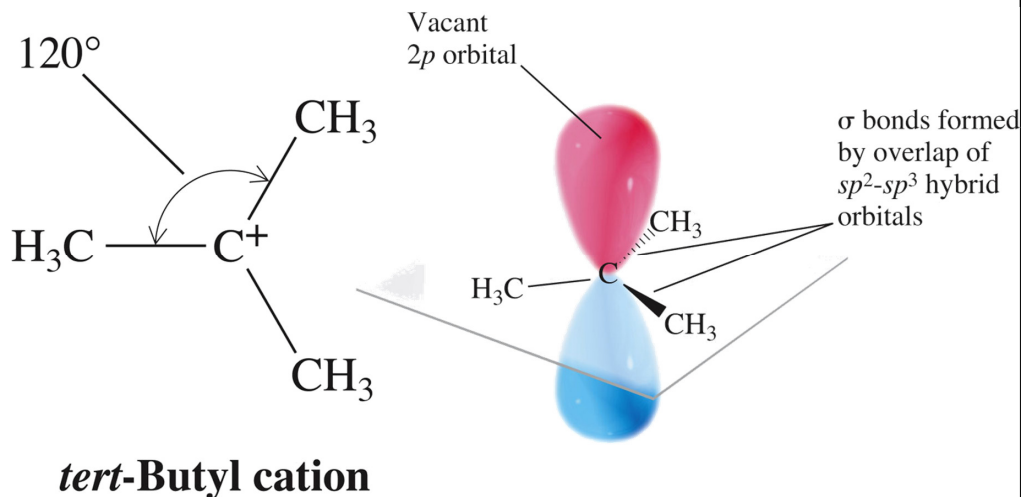
Carbocations:

4. Have bond angles of approximately 120° about the positively charged carbon.
5. Use  $sp^2$  hybrid orbitals to form sigma bonds from carbon to the three attached groups.
6. The unhybridized  $2p$  orbital lies perpendicular to the sigma bond framework and contains no electrons.

28

## Carbocations

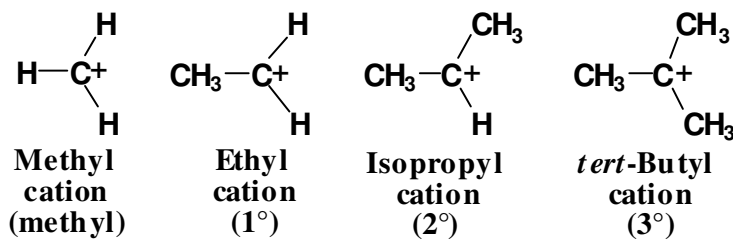
- The structure of the *tert-butyl cation*.



29

## Carbocation Stability

– relative stability



Increasing carbocation stability  $\rightarrow$

– Methyl and primary carbocations are so unstable that they are never observed *in solution*.

30

## Carbocation Stability

To account for the relative stability of carbocations- assume **that alkyl groups bonded to a positively charged carbon are electron releasing** and thereby delocalize the positive charge of the cation.

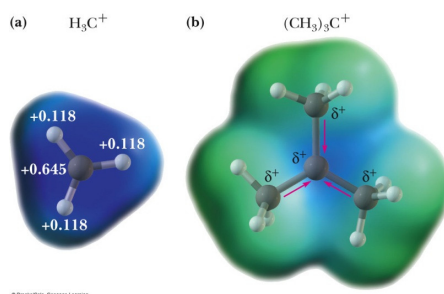
This electron-releasing ability of alkyl groups arises from

- (1) the inductive effect, and
- (2) hyperconjugation.

31

## The Inductive Effect

- The positively charged carbon polarizes electrons of adjacent sigma bonds toward it.
- The positive charge on the cation is thus delocalized over nearby atoms.
- The larger the volume over which the positive charge is delocalized, the greater the stability of the cation.



32

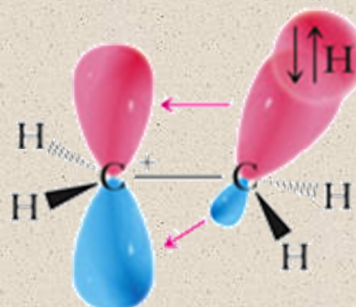


## Hyperconjugation

- Involves partial overlap of the  $\sigma$ -bonding orbital of an adjacent C-H or C-C bond with the vacant  $2p$  orbital of the cationic carbon.
- The result is delocalization of the positive charge.

(a)

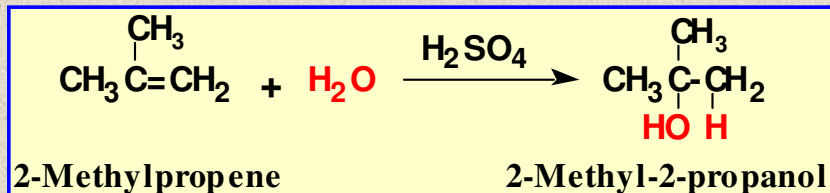
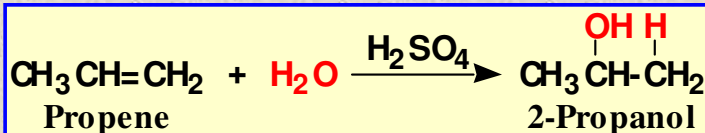
Cartoon diagram of the ethyl cation. There is delocalization of C—H bonding electrons into the empty  $2p$  orbital of the positively charged carbon. The orbital that results from this delocalization contains two electrons (see (b)).



33

## Addition of H<sub>2</sub>O

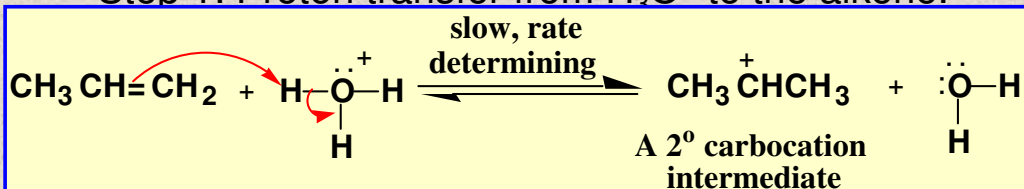
- Addition of water is called hydration.
- Acid-catalyzed hydration of an alkene is regioselective; hydrogen adds preferentially to the less substituted carbon of the double bond (to the carbon bearing the greater number of hydrogens).
- HOH adds in accordance with Markovnikov's rule.



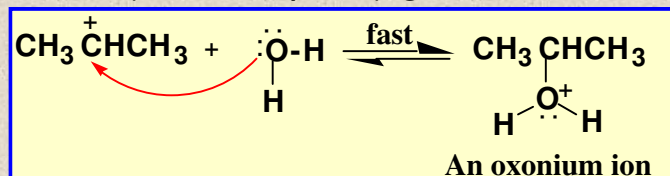
34

## Addition of H<sub>2</sub>O

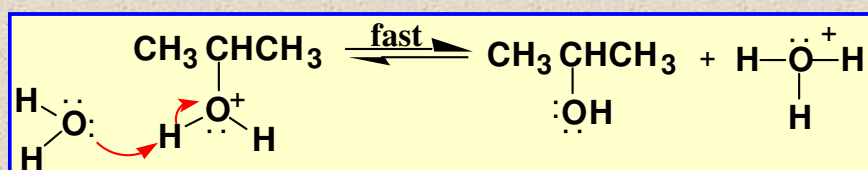
- Step 1: Proton transfer from H<sub>2</sub>O<sup>+</sup> to the alkene.



- Step 2: Reaction of the carbocation (an electrophile) with water (a nucleophile) gives an oxonium ion.



- Step 3: Proton transfer to water gives the alcohol.



35

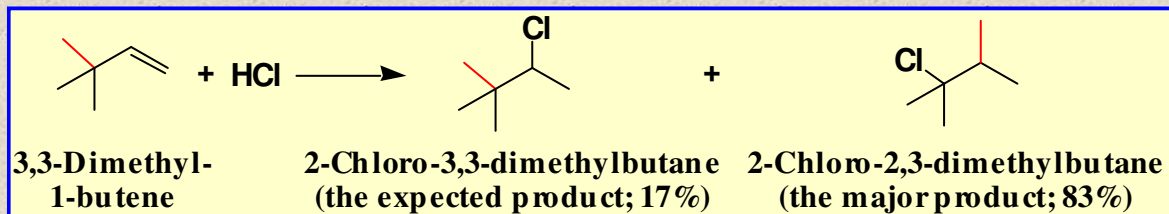
## Carbocation Rearrangements

- In electrophilic addition to alkenes, there is the possibility for rearrangement if a carbocation is involved.
- **Rearrangement:** A change in connectivity of the atoms in a product compared with the connectivity of the same atoms in the starting material.

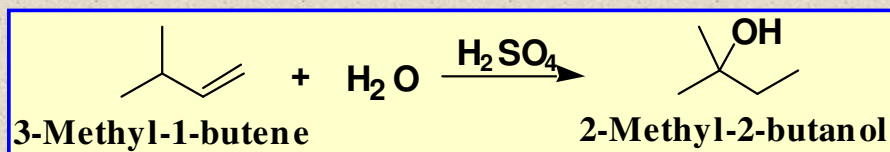
36

## Carbocation Rearrangements

– In addition of HCl to an alkene.



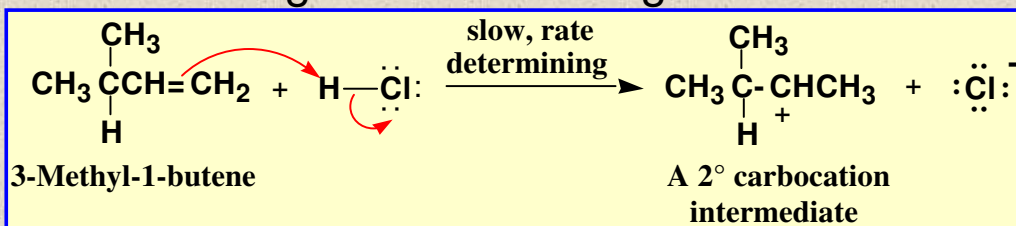
– In acid-catalyzed hydration of an alkene.



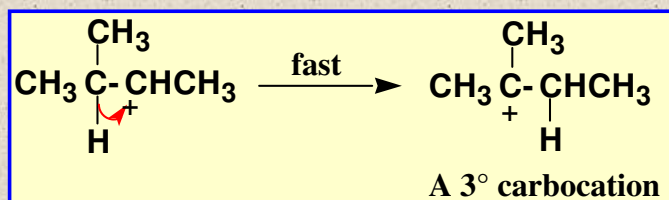
37

## Carbocation Rearrangements

– The driving force is rearrangement of a less



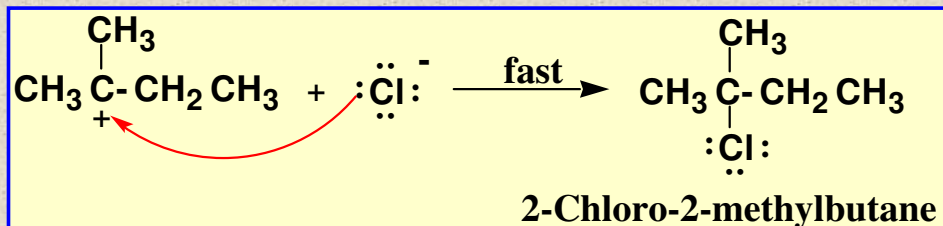
– The less stable 2° carbocation rearranges to a more stable 3° carbocation by 1,2-shift of a hydride ion.



38

## Carbocation Rearrangements

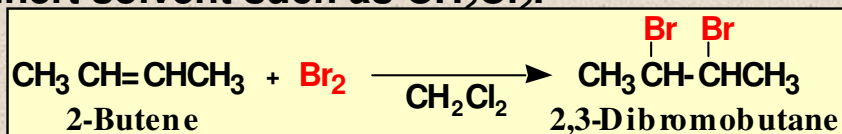
- Reaction of the more stable carbocation (an electrophile) with chloride ion (a nucleophile) completes the reaction.



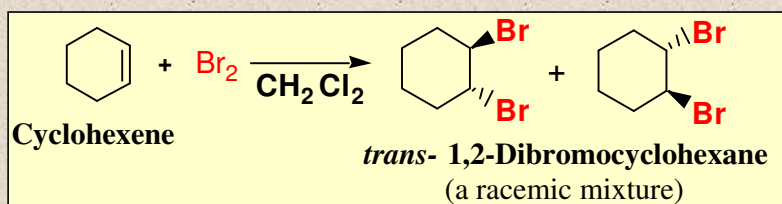
39

## Additions of Cl<sub>2</sub> and Br<sub>2</sub>

- Carried out with either the pure reagents **or in an inert solvent such as CH<sub>2</sub>Cl<sub>2</sub>.**



- Addition of bromine or chlorine to a cycloalkene gives a *trans*-dihalocycloalkane as a racemic mixture.

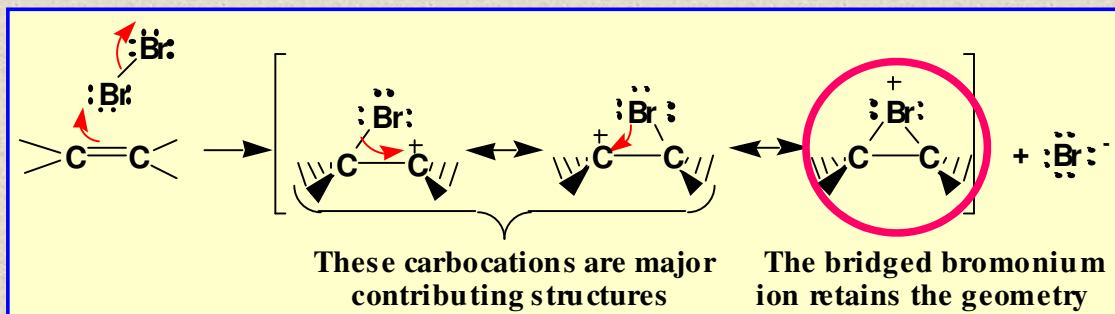


- Addition occurs with **anti stereoselectivity**; halogen atoms add from the opposite face of the double bond

40

## Additions of Cl<sub>2</sub> and Br<sub>2</sub>

- **Step 1:** Formation of a bridged bromonium ion intermediate.

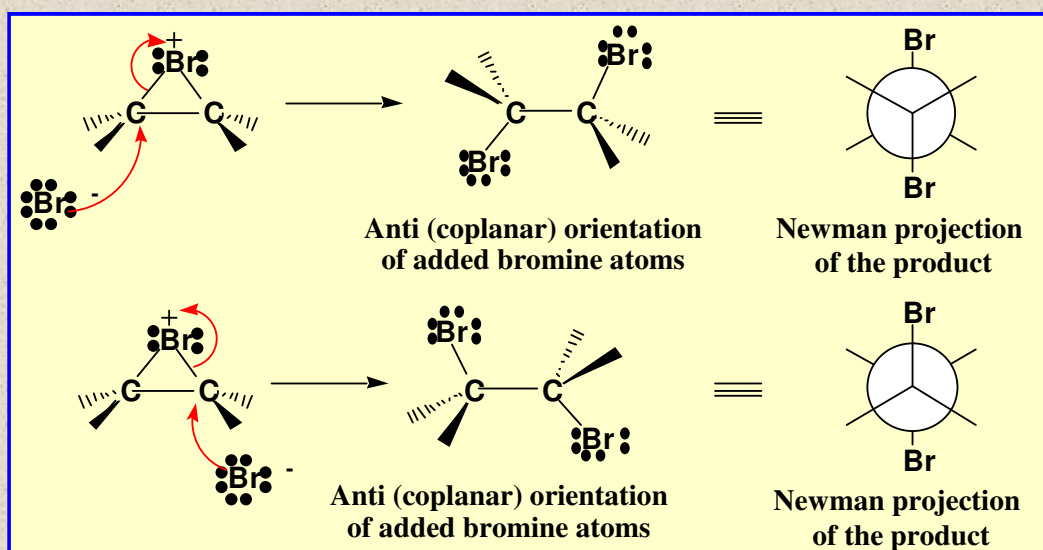


Draw the bridged Structure!!!

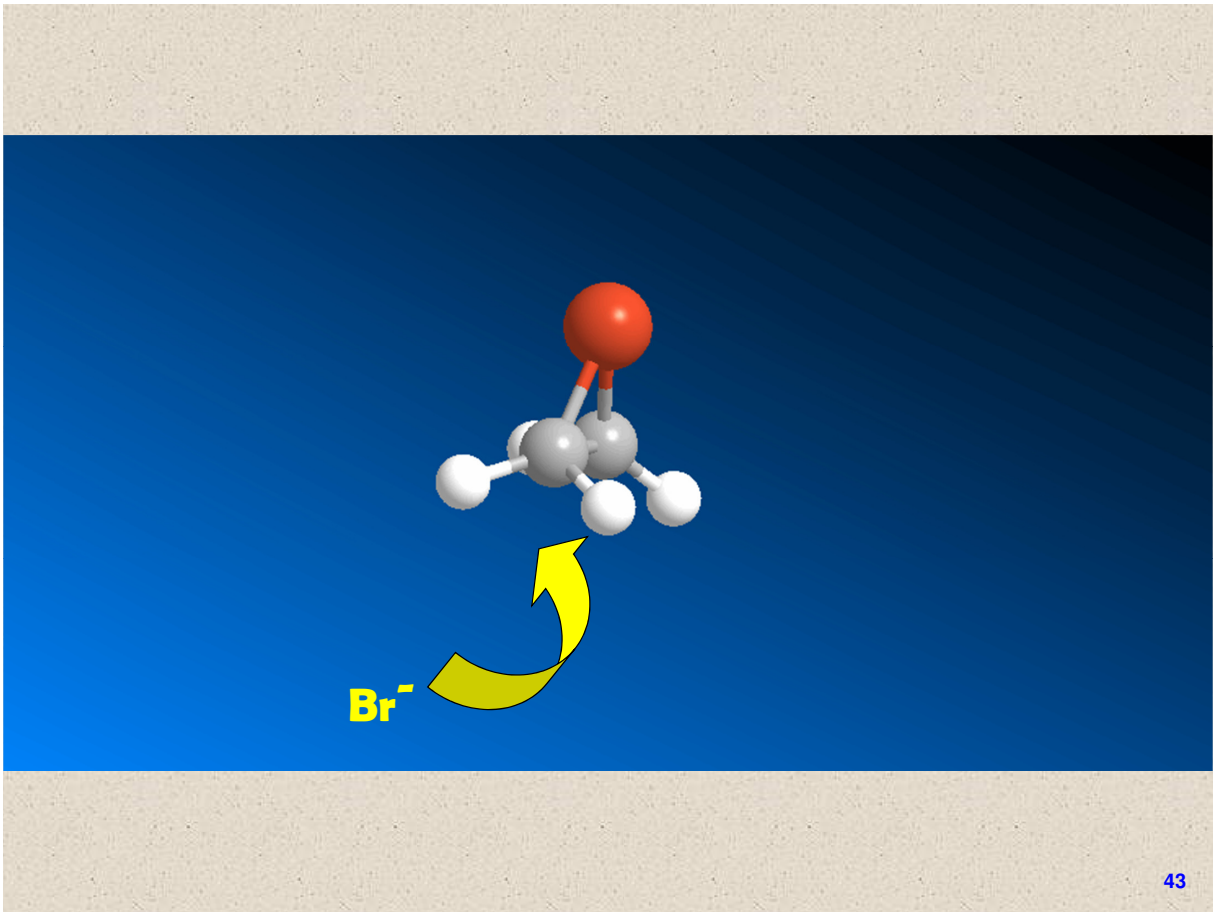
41

## Additions of Cl<sub>2</sub> and Br<sub>2</sub>

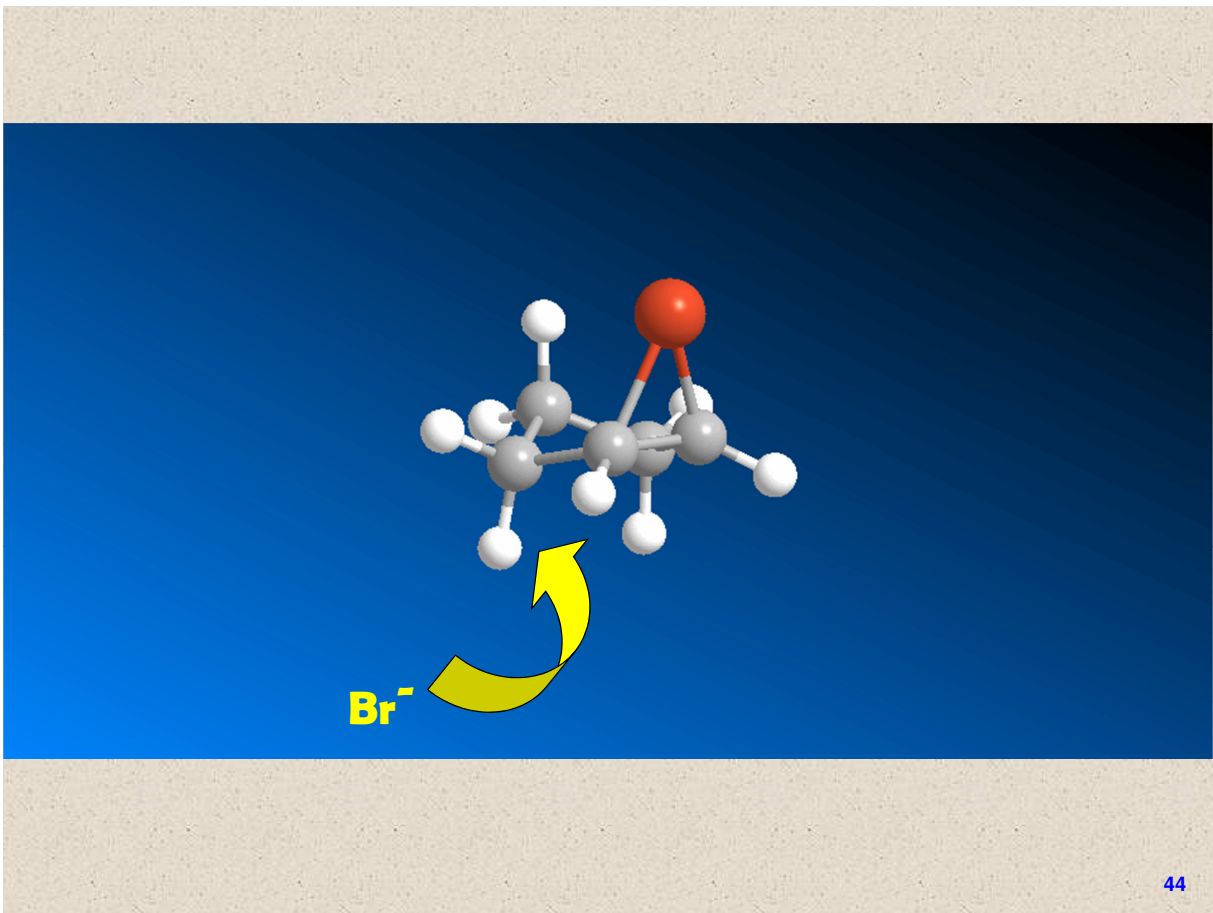
- **Step 2:** Attack of halide ion (a nucleophile) from the opposite side of the bromonium ion (an electrophile) opens the three-membered ring to give the product.



42



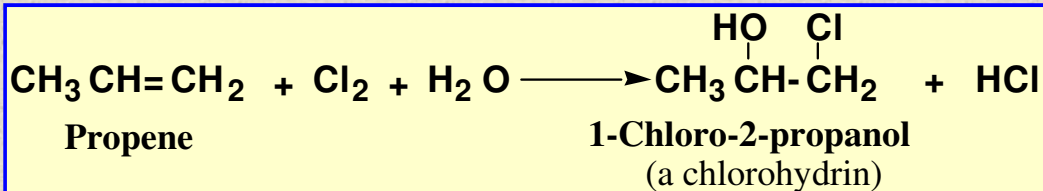
43



44

## Additions of HOCl and HOBr

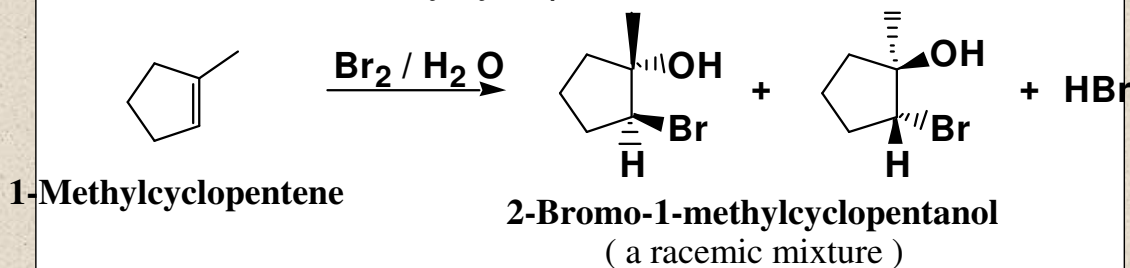
- Treatment of an alkene with Br<sub>2</sub> or Cl<sub>2</sub> in water forms a halohydrin.
- **Halohydrin:** A compound containing -OH and -X on adjacent carbons.



45

## Additions of HOCl and HOBr

- Reaction is both regioselective (OH adds to the more substituted carbon) and anti stereoselective.
- Both selectivities are illustrated by the addition of HOBr to 1-methylcyclopentene.

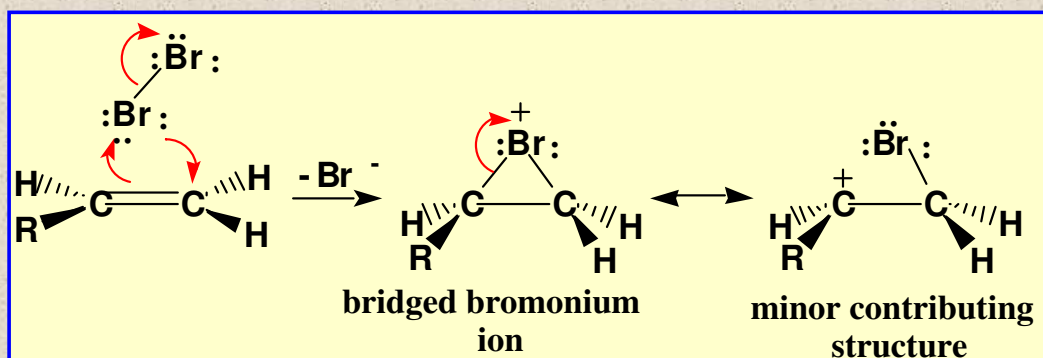


- To account for the regioselectivity and the anti stereoselectivity, chemists propose a three-step mechanism.

46

## Additions of HOCl and HOBr

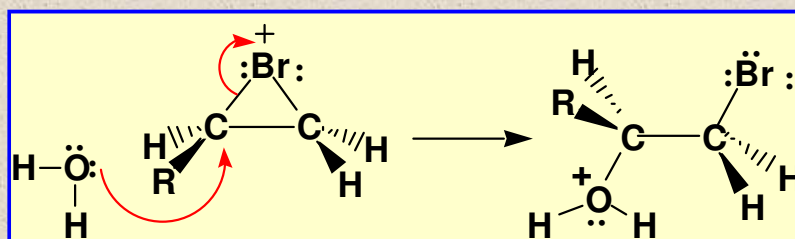
**Step 1:** Formation of a bridged halonium ion intermediate



47

## Additions of HOCl and HOBr

**Step 2:** Attack of H<sub>2</sub>O on the more substituted carbon opens the three-membered ring.

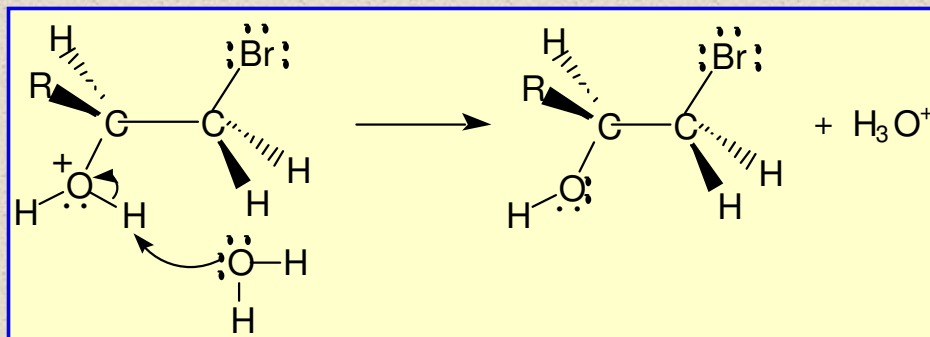


48

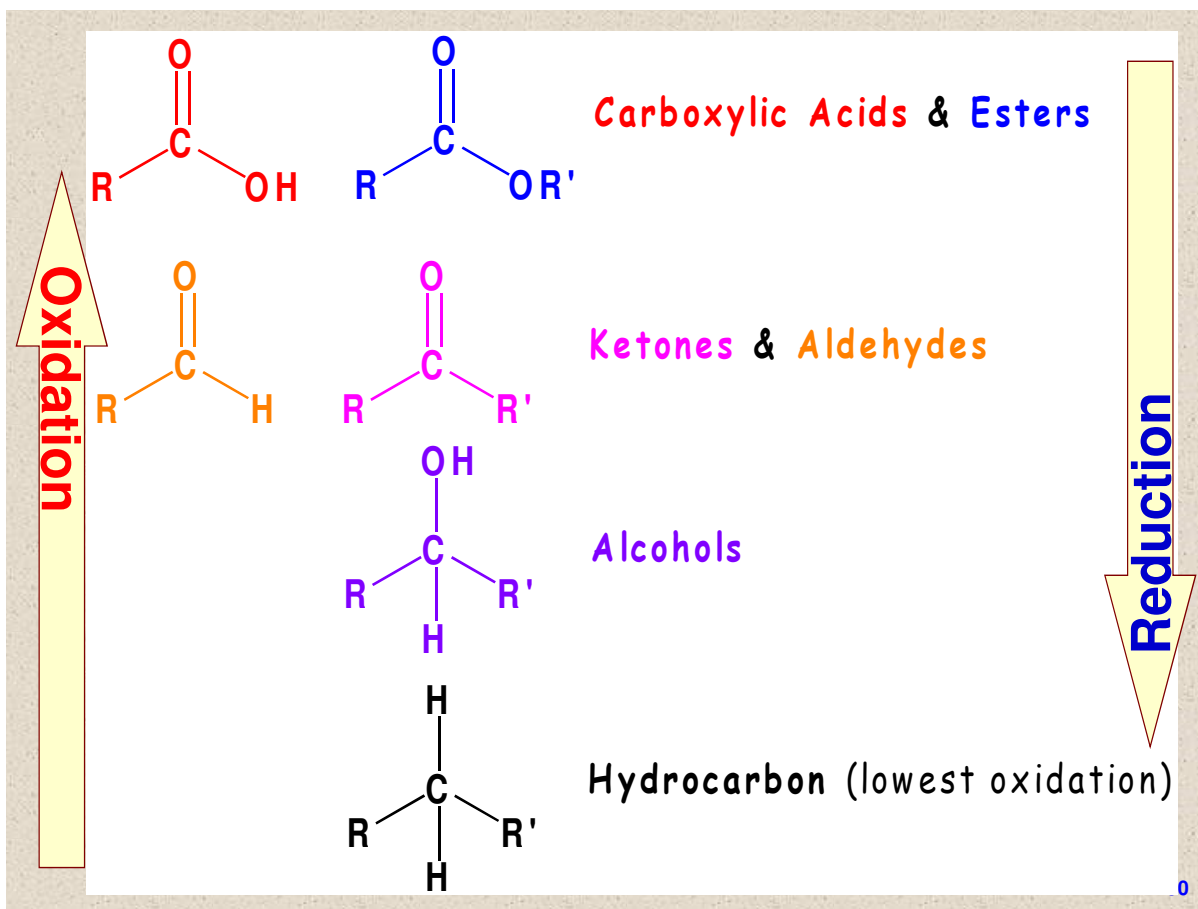


## Additions of HOCl and HOBr

- **Step 3:** Proton transfer to  $\text{H}_2\text{O}$  completes the reaction



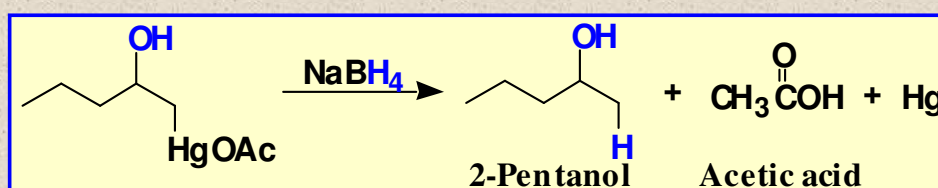
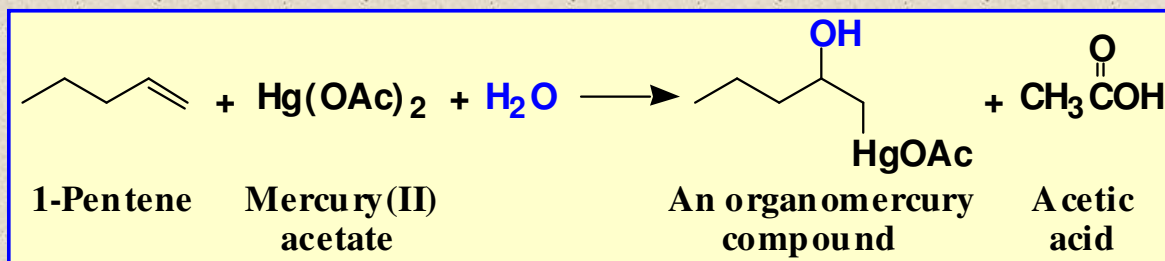
49



0

## Oxymercuration/Reduction

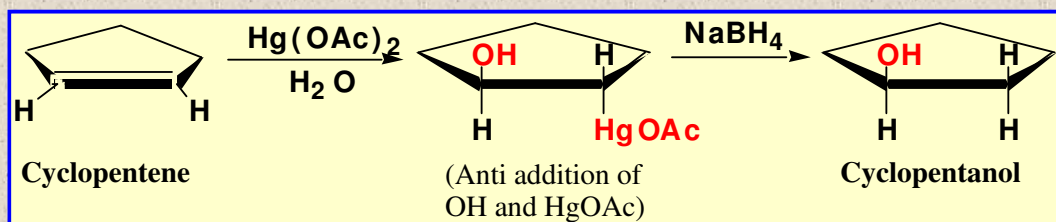
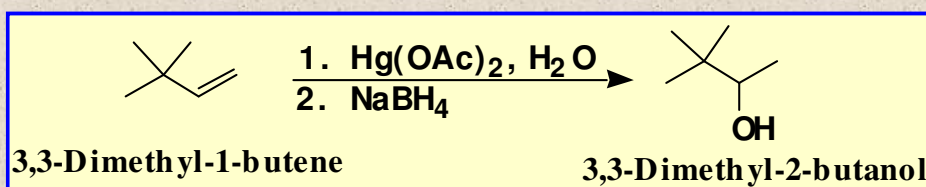
- Oxymercuration followed by reduction results in **hydration of a carbon-carbon double bond.**



51

## Oxymercuration/Reduction

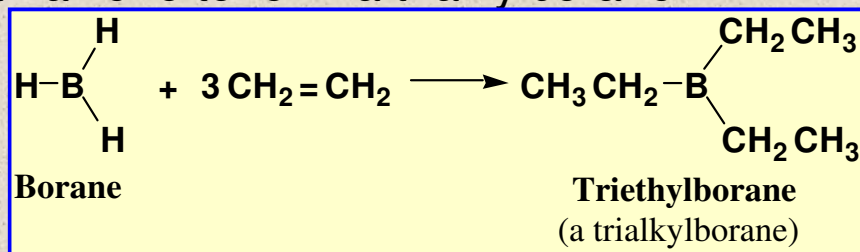
- An important feature of oxymercuration/reduction is that it occurs without rearrangement.**



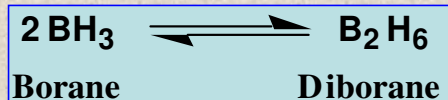
52

## Hydroboration/Oxidation

- **Hydroboration:** The addition of borane,  $\text{BH}_3$ , to an alkene to form a trialkylborane.



- Borane dimerizes to diborane,  $\text{B}_2\text{H}_6$ .

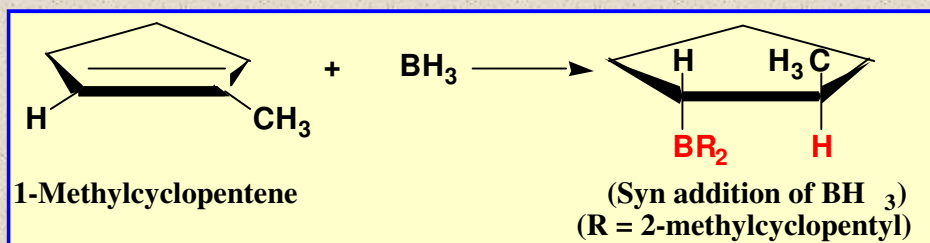


Not exam material

53

## Hydroboration/Oxidation

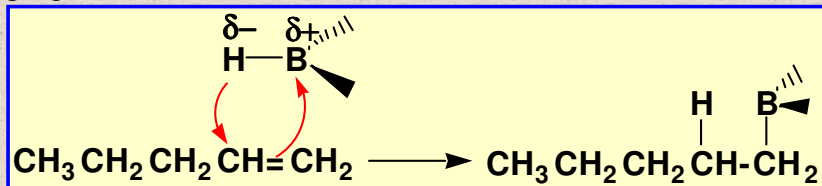
- Hydroboration is both
  - regioselective (boron bonds to the less hindered carbon)
  - and syn stereoselective.



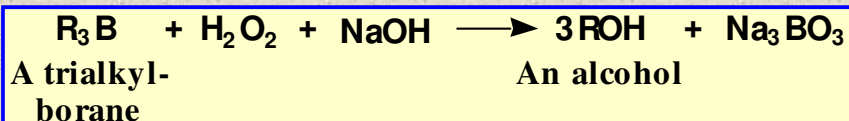
54

## Hydroboration/Oxidation

- Concerted regioselective and syn stereoselective addition of B and H to the carbon-carbon double bond.



- Trialkylboranes are rarely isolated.
- Oxidation with alkaline hydrogen peroxide gives an alcohol and sodium borate.



55

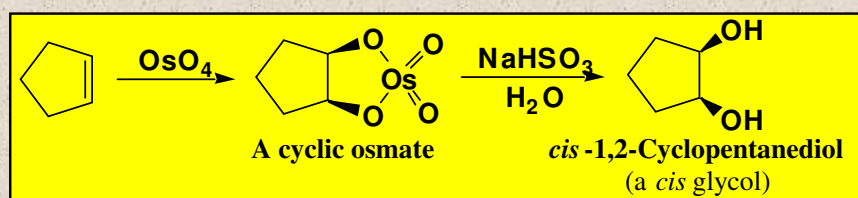
## Oxidation/Reduction

- **Oxidation:** The loss of electrons.
  - Alternatively, the loss of H, the gain of O, or both.
- **Reduction:** The gain of electrons.
  - Alternatively, the gain of H, the loss of O, or both.

56

## Oxidation with OsO<sub>4</sub>

- OsO<sub>4</sub> oxidizes an alkene to a glycol, a compound with OH groups on adjacent carbons.
  - Oxidation is syn stereoselective.



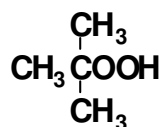
57

## Oxidation with OsO<sub>4</sub>

- OsO<sub>4</sub> is both expensive and highly toxic.
- It is used in catalytic amounts with another oxidizing agent to reoxidize its reduced forms and, thus, recycle OsO<sub>4</sub>. Two commonly used oxidizing agents are



Hydrogen  
peroxide

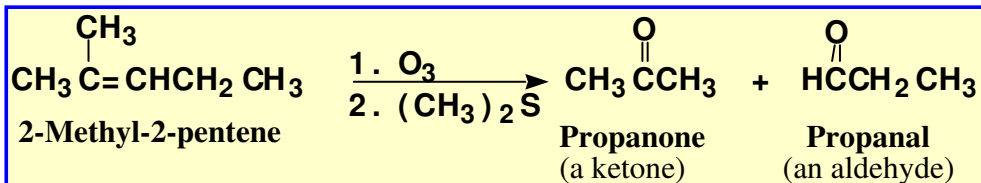


*tert*-Butyl hydroperoxide  
(*t*-BuOOH)

58

## Oxidation with O<sub>3</sub>

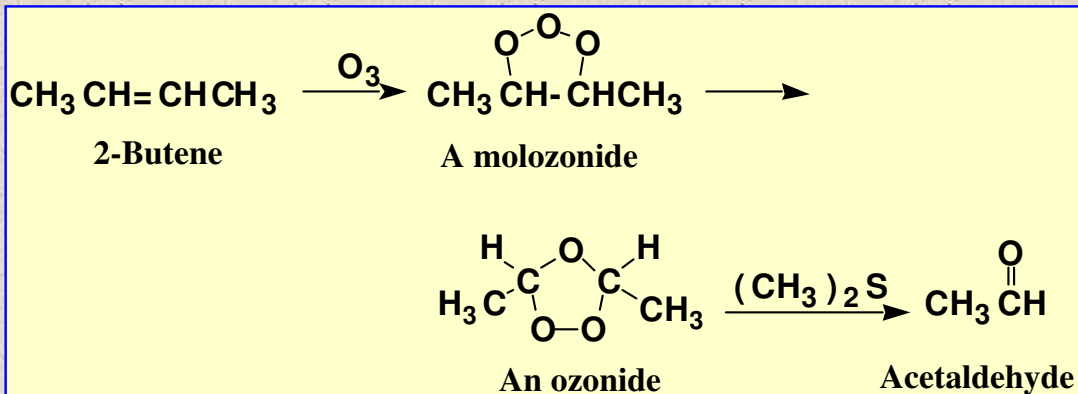
- Treatment of an alkene with ozone followed by a weak reducing agent cleaves the C=C and forms two carbonyl groups in its place. In the following example, the weak reducing agent is dimethylsulfide, (CH<sub>3</sub>)<sub>2</sub>S.



59

## Oxidation with O<sub>3</sub>

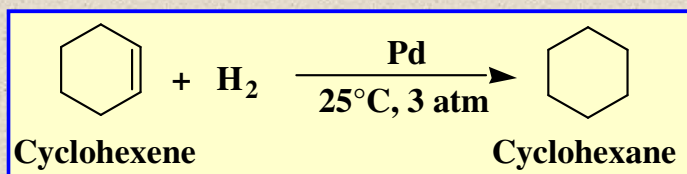
- The initial product is a molozonide which rearranges to an isomeric ozonide.



60

## Reduction of Alkenes

- Most alkenes react with  $\text{H}_2$  in the presence of a transition metal catalyst to give alkanes.

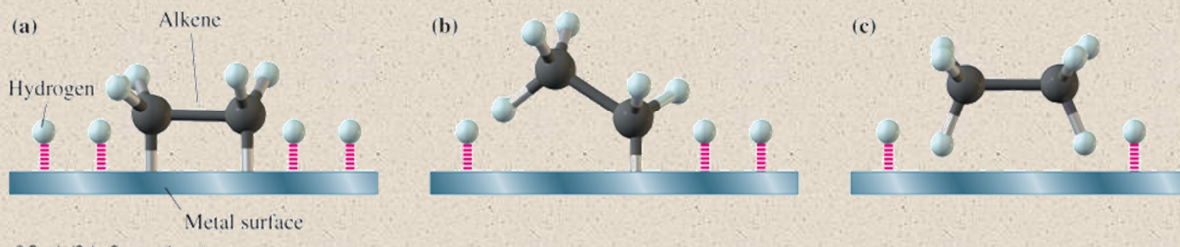


- Commonly used catalysts are Pt, Pd, Ru, and Ni.
- The process is called **catalytic reduction** or, alternatively, **catalytic hydrogenation**.
- Addition occurs with **syn stereoselectivity**.

61

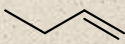




## Reduction of Alkenes

- Mechanism of catalytic hydrogenation.



62

## $\Delta H^\circ$ of Hydrogenation

Name	Structural Formula	$\Delta H^\circ$ [kJ (kcal)/mol]
Ethylene	$\text{CH}_2=\text{CH}_2$	-137 (-32.8)
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	-126 (-30.1)
1-Butene		-127 (-30.3)
<i>cis</i> -2-Butene		-120 (-28.6)
<i>trans</i> -2-Butene		-115 (-27.6)
2-Methyl-2-butene		-113 (-26.9)
2,3-Dimethyl-2-butene		-111 (-26.6)

63

## $\Delta H^\circ$ of Hydrogenation

- Reduction of an alkene to an alkane is exothermic.
  - There is net conversion of one pi bond to two sigma bond.
- $\Delta H^\circ$  depends on the degree of substitution of the carbon atoms of the double bond.
  - The greater the substitution, the lower the value of  $\Delta H^\circ$  i.e. greater substitution is more stable
- $\Delta H^\circ$  for a *trans* alkene is lower than that of an isomeric *cis* alkene.
  - A *trans* alkene is more stable than a *cis* alkene.

64