Organic Chemistry, *Fourth Edition*

Janice Gorzynski Smith
University of Hawai'i

Chapter 10
Alkenes

Prepared by Layne A. Morsch
The University of Illinois - Springfield

Alkenes

Introduction : Structure, Degrees of Unsaturation, Nomenclature, Physical Properties

Preparation of Alkenes

Addition Reactions: HX
  Hydration
 **Halogenation**
  Halohydrin Formation
  Hydroboration-Oxidation

1. Alkene Structure

- **Alkenes are also called olefins.**

- **Alkenes contain a carbon-carbon double bond.**

- **Terminal alkenes have the double bond at the end of the carbon chain.**

- **Internal alkenes have at least one carbon atom bonded to each end of the double bond.**

- **Cycloalkenes contain a double bond in a ring.**

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Alkene

$$C=C$$

double bond   terminal alkene   internal alkene   cycloalkene
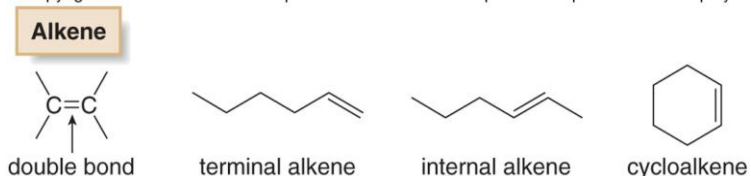
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Alkene Hybridization

- **Recall that the double bond consists of a π bond and a σ bond.**

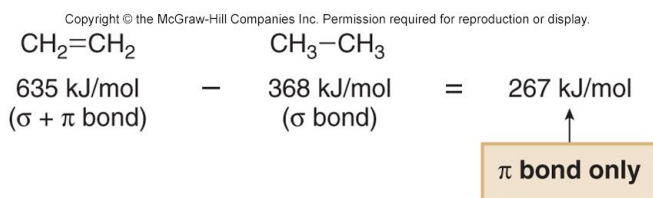- **Each carbon is sp^2 hybridized and trigonal planar, with bond angles of approximately 120°.**

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π bond

H   H
  C=C   =   120°   =   H   H
H   H   C   C
ethylene sp^2 hybridized   H   H

                                   σ bond
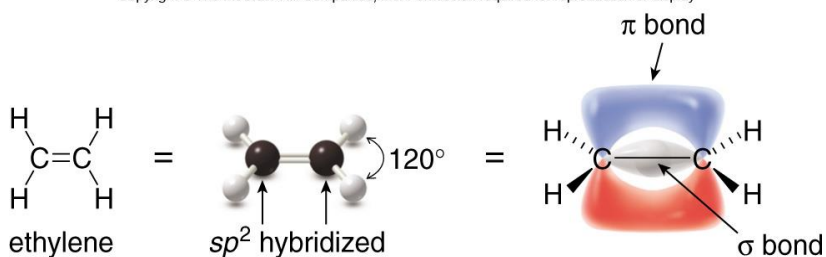
4

Reactivity of alkenes
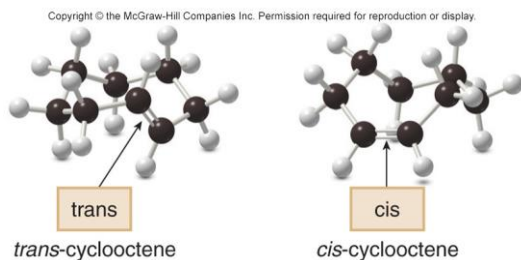
- **Bond dissociation energies** of the C-C bonds in ethane (a σ bond only) and ethylene (one σ and one π bond) can be used to estimate the strength of the π component of the double bond.
- **The π bond is much weaker** than the σ bond of a C-C double bond, making it much more easily broken.
- Therefore, **alkenes undergo many reactions** that alkanes do not.

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$$CH_2=CH_2 \qquad\qquad CH_3-CH_3$$

$$635 \text{ kJ/mol} \quad - \quad 368 \text{ kJ/mol} \quad = \quad 267 \text{ kJ/mol}$$
$$(\sigma + \pi \text{ bond}) \qquad\qquad (\sigma \text{ bond})$$

π **bond only**

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Cyclic Alkenes

- **Cycloalkenes having fewer than eight carbon atoms have a cis geometry.**
- **A trans-cycloalkene must have a carbon chain long enough to connect the ends of the double bond without introducing too much strain.**
- **trans-Cyclooctene is the smallest, isolable trans cycloalkene, but it is considerably less stable than cis-cyclooctene, making it one of the few alkenes having a higher energy trans isomer.**

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trans

cis

trans-cyclooctene   *cis*-cyclooctene

6

3

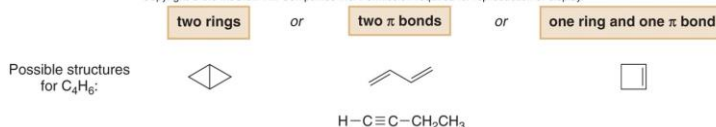**Table 10.1** Properties of the Carbon–Carbon Double Bond

Property	Result
Restricted rotation	• **The rotation around the C−C double bond is restricted.** Rotation can occur only if the π bond breaks and then re-forms, a process that is unfavorable (Section 8.2B).
Stereoisomerism	• Whenever the two groups on each end of a C=C are different from each other, two diastereomers are possible. *Cis-* and *trans-*2-butene (drawn at the bottom of Table 10.1) are diastereomers (Section 8.2B).
Stability	• **Trans** alkenes are generally more stable than **cis** alkenes. • **The stability of an alkene increases as the number of R groups on the C=C increases** (Section 8.2C).

1-butene   *cis*-2-butene   *trans*-2-butene

Increasing stability

2. Calculating Degrees of Unsaturation

- **An acyclic alkene has the general structural formula C_nH_{2n}.**
- **Alkenes are unsaturated hydrocarbons because they have fewer than the maximum number of hydrogen atoms per carbon.**
- **Cycloalkanes also have the general formula C_nH_{2n}.**
- **Each π bond or ring removes two hydrogen atoms from a molecule, and this introduces one degree of unsaturation.**
- **The number of degrees of unsaturation for a given molecular formula can be calculated by comparing the <u>actual number of H atoms</u> in a compound to the <u>maximum number of H atoms possible</u> for the number of carbons present if the molecule were an <u>acyclic alkane</u>.**
- **This procedure gives the total number of rings and/or π bonds in a molecule.**

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two rings	*or*	two π bonds	*or*	one ring and one π bond

Possible structures for C_4H_6:

$H-C\equiv C-CH_2CH_3$

Degrees of Unsaturation for Molecules Containing Heteroatoms

- **Ignore O atoms in the molecule (this divalent atom is a linker and has no effect on degree of unsaturation).**

- **Add number of <u>halogens</u> to number of H's (they are equivalent to H).**

- **Subtract 1 H for each <u>N present</u> (N's two connections allows extra H).**

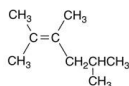- **E.g., $C_6H_{10}OCl_3N$ is equivalent to C_6H_{12}.**
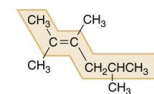
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3. Naming of alkenes

HOW TO Name an Alkene

Example Give the IUPAC name of the following alkene:

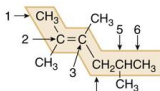**Step [1]** Find the longest chain that contains *both* carbon atoms of the double bond.

6 C's in the longest chain

hex*ane* - - - → hex*ene*

- Change the *-ane* ending of the parent alkane to *-ene*.

Step [2] Number the carbon chain to give the double bond the lower number, and apply all other rules of nomenclature.
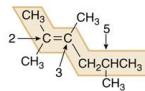
a. **Number** the chain, and name using the *first number* assigned to the C=C.

- Number the chain to put the C=C at C2, not C4.

2-hexene
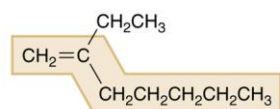
b. **Name** and **number** the substituents.

three methyl groups at C2, C3, and C5

Answer: 2,3,5-trimethyl-2-hexene
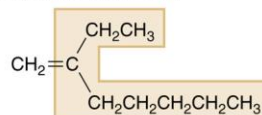
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Naming Alkenes and Alkenols

Example 1

CH_2CH_3

$CH_2=C$

$CH_2CH_2CH_2CH_2CH_3$

7 C's ----→ heptene

Both C's of the C=C are contained in this long chain.

Correct: 2-ethyl-1-heptene

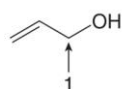CH_2CH_3

$CH_2=C$

$CH_2CH_2CH_2CH_2CH_3$

8 C's
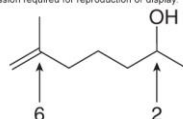
Both C's of the C=C are NOT contained in this long chain.

Incorrect

- **Compounds that contain both a double bond and a hydroxy group are named as alkenols and the chain (or ring) is numbered to give the OH group the lower number.**

Example 2

OH

OH

1

6   2

2-propen-1-ol   **6-methyl-6-hepten-2-ol**

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Naming Polyenes and Cyclic Alkenes

- **Compounds with two double bonds are named as dienes by changing the "-ane" ending of the parent alkane to the suffix "-adiene".**
- **Compounds with three double bonds are named as trienes, and so forth.**
- **In naming cycloalkenes, the double bond is located between C1 and C2, and the "1" is usually omitted in the name.**
- **The ring is numbered clockwise or counterclockwise to give the first substituent the lower number.**

Example 3

1

CH_3

1-methylcyclopentene

1

CH_3

3
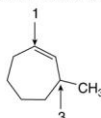
3-methylcycloheptene

2 1

CH_3

CH_3

6
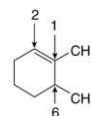
1,6-dimethylcyclohexene

[Number clockwise beginning at the C=C and place the CH₃ at C3.]

[Number counterclockwise beginning at the C=C and place the first CH₃ at C1.]

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Cis and Trans Isomers of Alkenes

- **Alkenes having one alkyl group bonded to each carbon atom can be differentiated using the prefixes – cis and trans.**
    - **cis has the two alkyl groups on the <u>same side </u>of the double bond.**
    - **trans has the two alkyl groups on <u>opposite sides </u>of the double bond.**
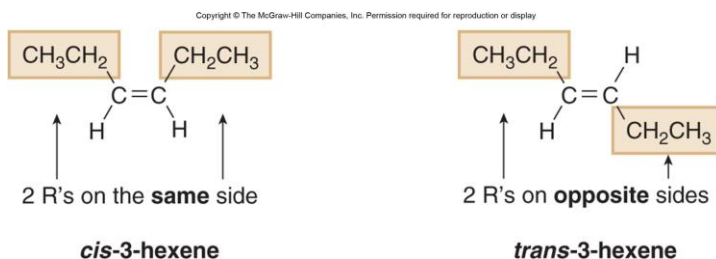
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CH_3CH_2 CH_2CH_3

C=C

H   H

2 R's on the **same** side

***cis*-3-hexene**

CH_3CH_2 H

C=C

H CH_2CH_3

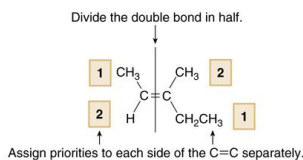2 R's on **opposite** sides

***trans*-3-hexene**

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HOW TO Assign the Prefixes *E* and *Z* to an Alkene

Step [1] Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R,S* nomenclature (Section 5.6).

- Divide the double bond in half, and assign the numbers **1** and **2** to indicate the relative priority of the two groups on each end—the higher priority group is labeled **1,** and the lower priority group is labeled **2**.

Divide the double bond in half.

1 CH_3 CH_3 **2**

C=C

2 H CH_2CH_3 **1**

Assign priorities to each side of the C=C separately.

Step [2] Assign *E* or *Z* based on the location of the two higher priority groups (1).

Two higher priority groups on **opposite** sides

1 CH_3 CH_3 **2**

C=C

2 H CH_2CH_3 **1**

***E* isomer**

(2*E*)-3-methyl-2-pentene

Two higher priority groups on the **same** side

1 CH_3 CH_2CH_3 **1**

C=C

2 H CH_3 **2**

***Z* isomer**

(2*Z*)-3-methyl-2-pentene
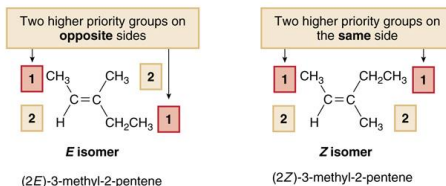
- The ***E*** isomer has the two higher priority groups on the **opposite sides.**
- The ***Z*** isomer has the two higher priority groups on the **same side.**

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Common Names of Alkenes and Alkene Substituents

- **Some alkene or alkenyl substituents have common names.**
- **The simplest alkene, $CH_2=CH_2$, named in the IUPAC system as ethene, is often called ethylene.**

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methylene group   vinyl group   allyl group

Figure 10.3

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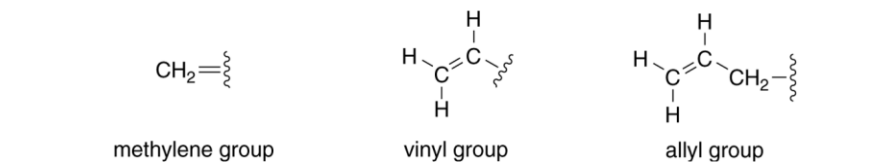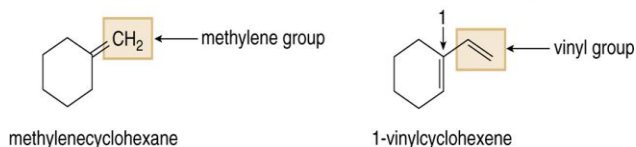CH₂ ← methylene group   1 ← vinyl group

methylenecyclohexane   1-vinylcyclohexene

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4. Physical Properties of Alkenes

- **Most alkenes exhibit only weak van der Waals interactions, so their physical properties are similar to alkanes of comparable molecular weight.**
- **Alkenes have low melting points and boiling points.**
- **Melting and boiling points increase as the number of carbons increases due to increased surface area.**
- **Alkenes are soluble in organic solvents and insoluble in water.**
- **The C_{sp^3}–C_{sp^2} single bond between an alkyl group and one of the double bond carbons of an alkene is slightly polar because the sp^3 hybridized alkyl carbon donates electron density to the sp^2 hybridized alkenyl carbon.**

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δ^+
CH_3 ← sp^3 hybridized C 25% s-character
=C δ^- This R group **donates** electron density.

sp^2 hybridized C 33% s-character
This C **accepts** electron density.

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Cis/Trans Differ in Physical Properties

- A consequence of the alkene dipole is that cis and trans isomeric alkenes often have somewhat different physical properties.
- *cis*-2-Butene has a higher boiling point (4 °C) than *trans*-2-butene (1 °C).
- In the cis isomer, the two C_{sp^3}–C_{sp^2} bond dipoles reinforce each other, yielding a small net molecular dipole.
- In the trans isomer, the two bond dipoles cancel.

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more polar isomer → a small net dipole
cis-2-butene
higher bp

no net dipole ← less polar isomer
trans-2-butene
lower bp

Useful Products Formed From Ethylene

Figure 10.4

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polyethylene
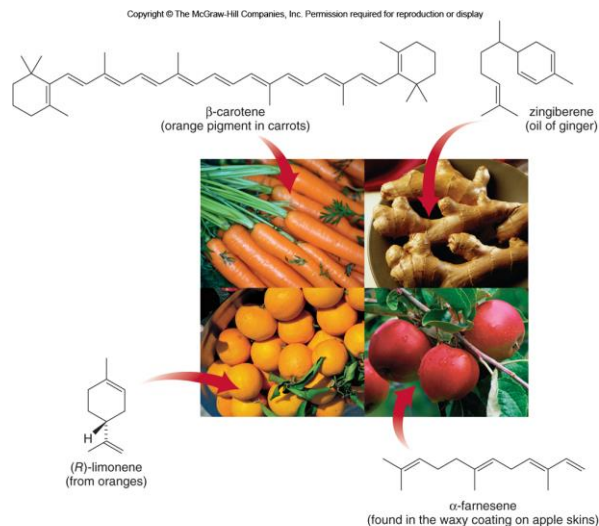(packaging, bottles, films)

CH_3CH_2OH
ethanol
(solvent, fuel additive)

$CH_2=CHCl$ → poly(vinyl chloride)
(insulation, films, pipes)

$C=C$
ethylene

$HOCH_2CH_2OH$
ethylene glycol
(antifreeze)

$CH_2=CHC_6H_5$

$CH_2=CH$
$OCOCH_3$
→ poly(vinyl acetate)
(paints, adhesives)

polystyrene
(Styrofoam, molded plastics)

Naturally Occurring Alkenes

Figure 10.5

β-carotene
(orange pigment in carrots)

zingiberene
(oil of ginger)

(R)-limonene
(from oranges)

α-farnesene
(found in the waxy coating on apple skins)

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Fatty Acids

- **Triacylglycerols** are hydrolyzed to glycerol and three fatty acids of general structure RCOOH.

H_2O
(H^+ or ^-OH)
or
enzymes

triacylglycerol

glycerol

fatty acids

These fatty acids have **12–20 C's.**
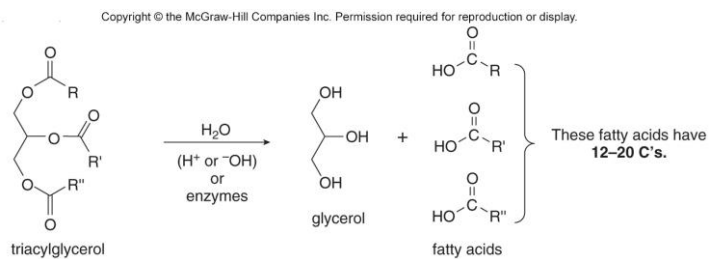
- **Saturated fatty acids** have no double bonds in their long hydrocarbon chains, and unsaturated fatty acids have one or more double bonds in their hydrocarbon chains.

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Table 10.2 The Effect of Double Bonds on the Melting Point of Fatty Acids

Name	Structure	Mp (°C)
Stearic acid (0 C=C)		69
Oleic acid (1 C=C)		4
Linoleic acid (2 C=C)		−5
Linolenic acid (3 C=C)		−11

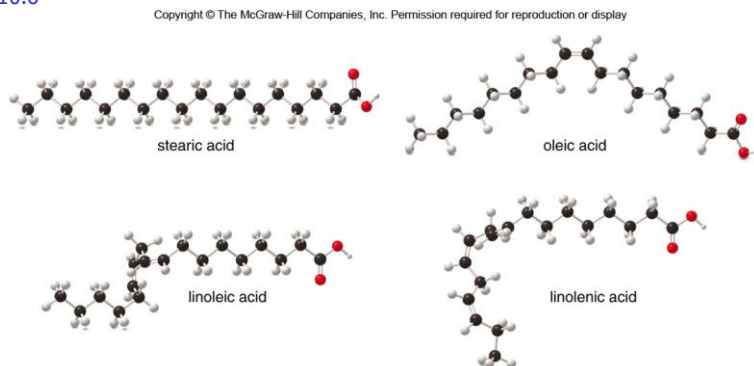Increasing number of double bonds

- **Increasing** the number of **double bonds** in the fatty acid side chains **decreases** the **melting point** of the **triacylglycerol**.

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3-D Structure of C$_{18}$ Fatty Acids

- **The larger the number of Z double bonds, the more kinks in the hydrocarbon chain.**
- **This causes poorer stacking and less van der Waals interactions, leading to lower melting points.**

Figure 10.6

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stearic acid

oleic acid

linoleic acid

linolenic acid

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Triacylglycerols

- **Fats** and **oils** are both triacylglycerols, but with different physical properties.
- **Fats** have <u>higher melting points</u>—they are solids at room temperature.
- **Oils** have <u>lower melting points</u>—they are liquids at room temperature.
- The composition (saturated vs. unsaturated) of the three fatty acids in the triacylglycerol determines whether it is a fat or an oil.

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Properties of Fatty Acids

- **Fats** are derived from fatty acids having <u>few or no double bonds</u>.
- **Oils** are derived from fatty acids having a <u>larger number of double</u> bonds.
- **Saturated fats** are typically obtained <u>from animal sources</u>, whereas unsaturated oils are common in vegetable sources.
- An <u>exception</u> to this generalization is <u>coconut oil</u>, which is largely composed of saturated alkyl side chains.

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Alkenes

Introduction : Structure, Degrees of Unsaturation,
Nomenclature, Physical Properties

Preparation of Alkenes

Addition Reactions: HX
Hydration
Halogenation
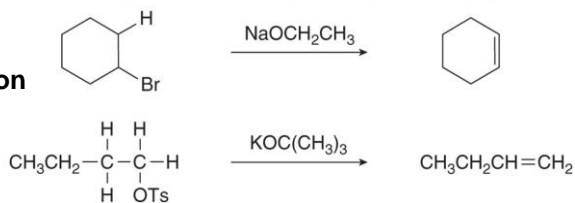Halohydrin Formation
Hydroboration-Oxidation

Preparation of Alkenes

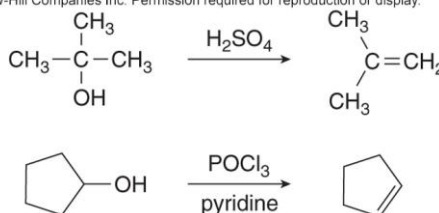- **Alkenes can be prepared from alkyl halides, tosylates, and alcohols via elimination reactions.**

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Chapter 8
Dehydrohalogenation

Chapter 9
Dehydydration

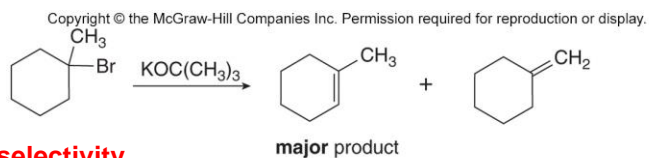Copyright © the McGraw-Hill Companies Inc. Permission required for reproduction or display.

Regioselectivity and Stereoselectivity
of Alkene Formation

• **The most stable alkene (Zaitsev product) is usually formed as the major product.**

Regioselectivity

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Stereoselectivity
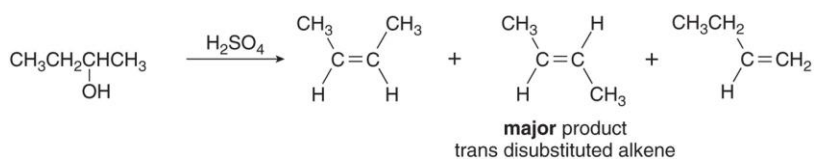
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Alkenes

Introduction : Structure, Degrees of Unsaturation, Nomenclature, Physical Properties

Preparation of Alkenes

Addition Reactions: HX
                        Hydration
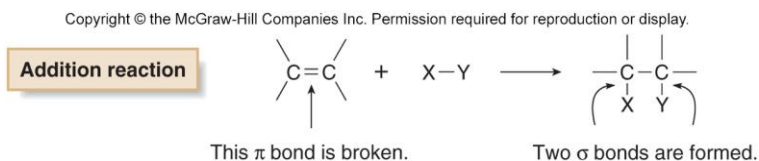   **Halogenation**
                        Halohydrin Formation
                        Hydroboration-Oxidation

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Addition Reactions

- **The characteristic reaction of alkenes in addition—the π bond is broken and two new σ bonds are formed.**

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Addition reaction	$\underset{/}{\overset{\backslash}{C}}=\underset{\backslash}{\overset{/}{C}}$ + X—Y ⟶ —C—C— with X Y

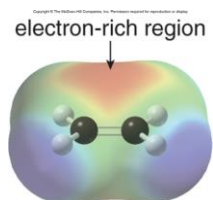This π bond is broken.   Two σ bonds are formed.

- **Alkenes are electron rich, with the electron density of the π bond concentrated above and below the plane of the molecule.**
  - **Therefore, alkenes act as nucleophiles and react with electrophiles.**
  - **Simple alkenes do not react with nucleophiles or bases, reagents that are themselves electron rich.**
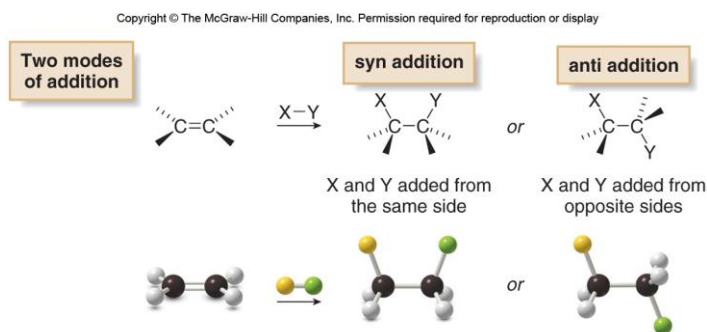
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Electrostatic Potential Plot of Ethylene

- **The red electron-rich region of the π bond is located above and below the plane of the molecule.**

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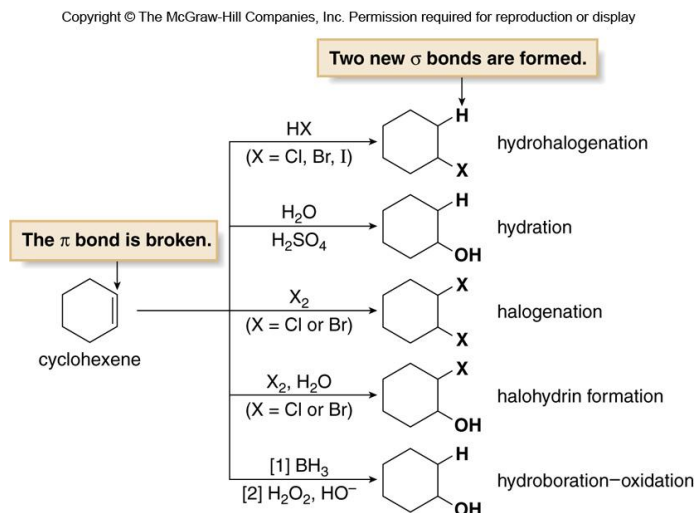electron-rich region

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Syn and Anti Addition to Alkenes

- **Because the carbon atoms of a double bond are both trigonal planar, the elements of <u>X and Y can be added</u> to them from the <u>same side or from opposite sides</u>.**
  - *Syn addition* **takes place when both X and Y are added from the <u>same side</u>.**
  - *Anti addition* **takes place when X and Y are added from <u>opposite sides</u>.**

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Addition Reactions of Cyclohexene

Figure 10.8

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1. Hydrohalogenation—Electrophilic Addition   of HX

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Hydrohalogenation

$$\begin{array}{c} \backslash \quad / \\ C=C \\ / \quad \backslash \end{array} \quad + \quad \begin{array}{c} \delta^+ \quad \delta^- \\ H-X \end{array} \quad \longrightarrow \quad \begin{array}{c} | \quad | \\ -C-C- \\ | \quad | \\ H \quad X \end{array}$$

(X = Cl, Br, I)

This π bond is broken.

HX is added.

alkyl halide
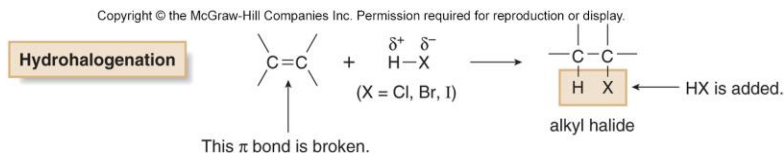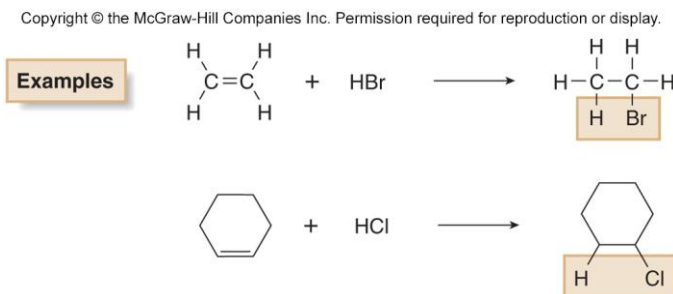
- **Two bonds** are <u>broken</u> in this reaction—the weak π bond of the alkene and the HX bond—and **two new σ bonds** are <u>formed</u>—one to H and one to X.
- **Recall that the H-X bond is polarized, with a partial positive charge on H.**
- **Because the <u>electrophilic H</u> end of HX is <u>attracted</u> to the <u>electron-rich double bond</u>, these reactions are called electrophilic additions.**

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How to Draw the Products of an Addition Reaction

- **Locate the C-C double bond.**
- **Identify the σ bond of the reagent that breaks.**
- **<u>Break</u> the π bond of the alkene and the σ bond of the reagent**
- **<u>Form</u> two new σ bonds to the C atoms of the double bond.**

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Examples

$$\begin{array}{c} H \quad \quad H \\ \backslash \quad \quad / \\ C=C \\ / \quad \quad \backslash \\ H \quad \quad H \end{array} \quad + \quad HBr \quad \longrightarrow \quad \begin{array}{c} H \quad H \\ | \quad | \\ H-C-C-H \\ | \quad | \\ H \quad Br \end{array}$$
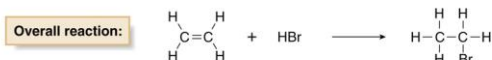
+ HCl ⟶

34

17

Heat of Formation for Electrophilic Addition

- **Addition reactions are exothermic because the <u>two σ bonds formed</u> in the product are stronger than the <u>σ and π bonds broken</u> in the reactants.**

Example

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$\Delta H°$ calculation:

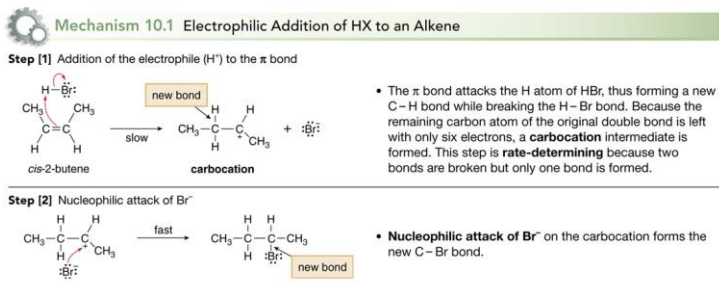| [1] Bonds broken		[2] Bonds formed		[3] Overall $\Delta H°$ =
	$\Delta H°$ (kJ/mol)		$\Delta H°$ (kJ/mol)	sum in Step [1] + sum in Step [2]
$CH_2=CH_2$ π bond	+267	$BrCH_2CH_2-H$	−410	
H−Br	+368	CH_3CH_2-Br	−285	+635 kJ/mol −695 kJ/mol
total	+635 kJ/mol	total	−695 kJ/mol	
	Energy needed to break bonds.		Energy released in forming bonds.	$\Delta H° = -60$ kJ/mol
[Values taken from Appendix C.]				The reaction is exothermic.

35

Mechanism of Electrophilic Addition

- **The mechanism of electrophilic addition consists of two successive Lewis acid-base reactions.**
  - **Step [1] – the alkene is the Lewis base that donates an electron pair to H-Br, the Lewis acid.**
  - **Step [2] – Br⁻ is the Lewis base that donates an electron pair to the carbocation, the Lewis acid.**

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Mechanism 10.1 Electrophilic Addition of HX to an Alkene

Step [1] Addition of the electrophile (H⁺) to the π bond

- The π bond attacks the H atom of HBr, thus forming a new C – H bond while breaking the H – Br bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

Step [2] Nucleophilic attack of Br⁻

- **Nucleophilic attack of Br⁻** on the carbocation forms the new C – Br bond.

36

18

Energy Diagram for Electrophilic Addition

- **Each step has its own energy barrier with a transition state energy maximum.**
- **Since step [1] has a higher energy transition state, it is rate-determining.**
- **ΔH° for step [1] is positive because more bonds are broken than formed, whereas ΔH° for step [2] is negative because only bond making occurs.**

Figure 10.10

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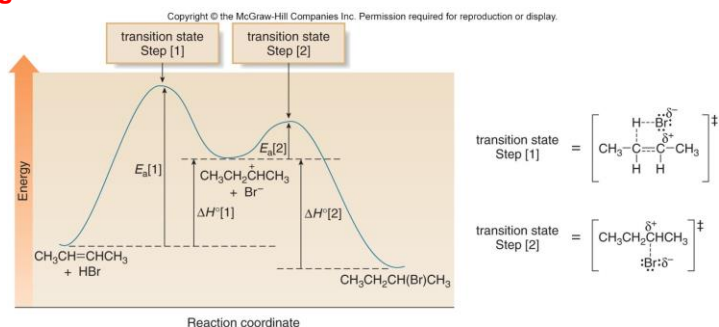
- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.

37

Markovnikov's Rule

- **With an unsymmetrical alkene, HX can add to the double bond to give two constitutional isomers, but only one is actually formed:**
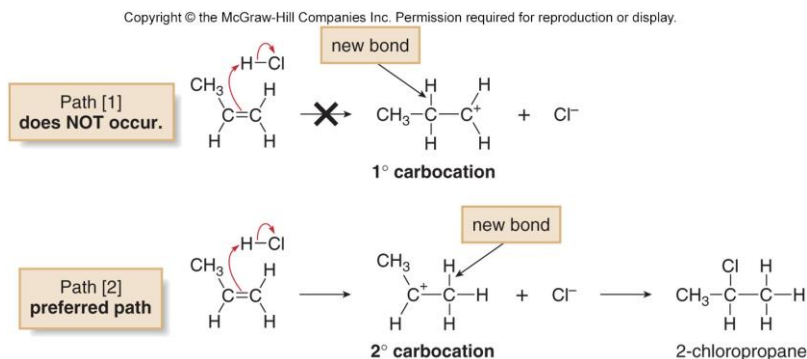

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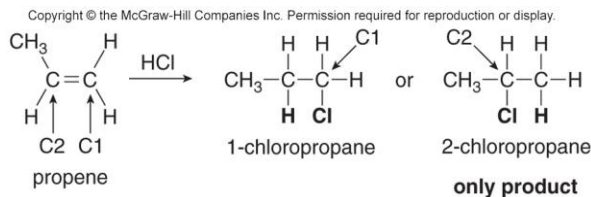
- **Markovnikov's rule states that in the addition of HX to an unsymmetrical alkene, the H atom adds to the less substituted carbon atom—that is, the carbon that has the greater number of H atoms to begin with.**

38

Carbocation Stability and Markovnikov's Rule

- **The basis of Markovnikov's rule is the formation of a carbocation in the rate-determining step of the mechanism.**
- **In the addition of HX to an unsymmetrical alkene, the H atom is added to the less substituted carbon to form the more stable, more substituted carbocation.**

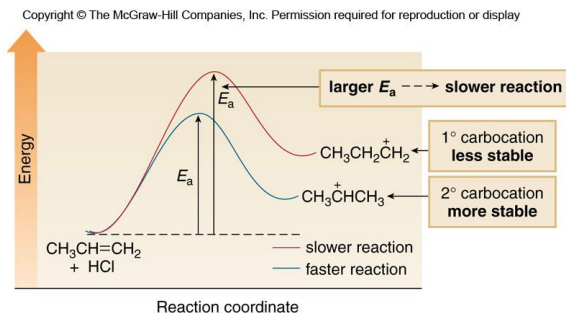Copyright © the McGraw-Hill Companies Inc. Permission required for reproduction or display.

Path [1] does NOT occur.

new bond

CH_3–C–C$^+$ + Cl$^-$

1° carbocation

Path [2] preferred path

new bond

CH_3–C$^+$–C–H + Cl$^-$ → CH_3–C–C–H

2° carbocation   2-chloropropane

39

Hammond Postulate and Electrophilic Addition

- **According to the Hammond postulate, the blue path is faster because formation of the carbocation is an endothermic process.**
- **Thus, the transition state to form the more stable 2° carbocation is lower in energy.**
- **The E_a for formation of the more stable 2° carbocation is lower than the E_a for formation of the 1° carbocation.**
    - **The 2° carbocation is formed faster.**

Figure 10.11

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larger E_a – – → slower reaction

E_a

$CH_3CH_2\overset{+}{C}H_2$ ← 1° carbocation less stable

E_a

$CH_3\overset{+}{C}HCH_3$ ← 2° carbocation more stable

$CH_3CH=CH_2$ + HCl

—— slower reaction
—— faster reaction

Energy

Reaction coordinate
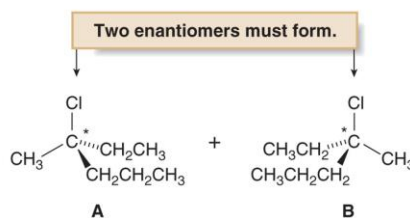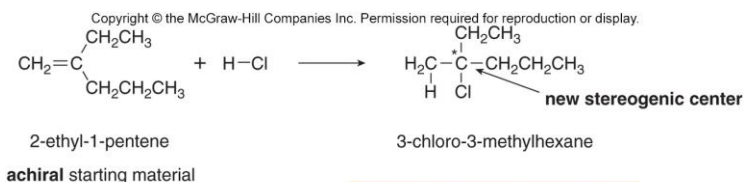
40

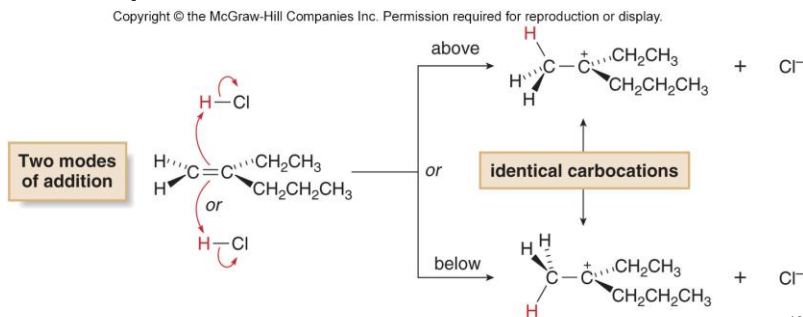**20**

Stereochemistry of Electrophilic Addition

- Recall that **trigonal planar** atoms react with reagents <u>from two directions</u> with equal probability.
- **Achiral starting materials** yield <u>achiral products</u>.
- Sometimes new stereogenic centers are formed from **hydrohalogenation**.

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2-ethyl-1-pentene

achiral starting material

3-chloro-3-methylhexane

new stereogenic center

Two enantiomers must form.

A   B

41

a. Stereochemistry of Carbocation Formation

- The mechanism of hydrohalogenation illustrates **why two enantiomers** are formed.
- Initial addition of **H$^+$ occurs from either side** of the planar double bond.
- Both modes of addition generate the same **achiral carbocation**.
- Either representation of this carbocation can be used to draw the second step of the mechanism.

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above

Two modes of addition

or

below

identical carbocations

42

21

b. Stereochemistry of Nucleophilic Attack

- **Nucleophilic attack of Cl⁻ on the trigonal planar carbocation also occurs from two different directions, forming two products, A and B, having a new stereogenic center.**
- **A and B are enantiomers.**
- **Since attack from either direction occurs with equal probability, a racemic mixture of A and B is formed.**
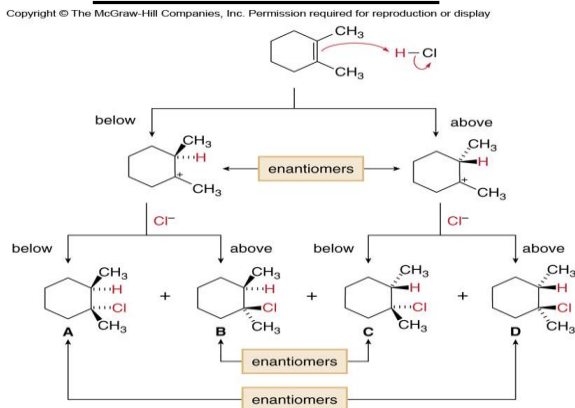

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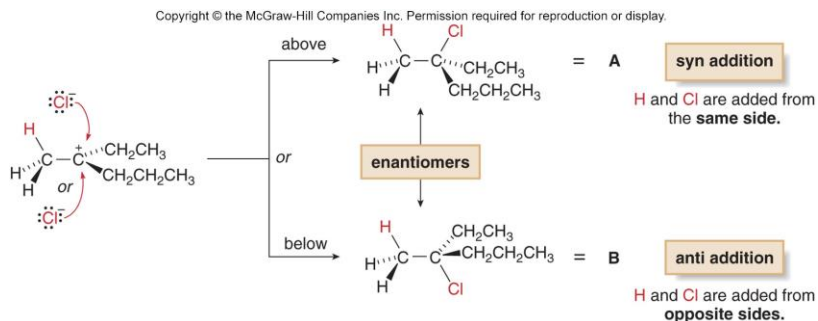
43

Reaction of 1,2-dimethylcyclohexene with HCl

- **Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers.**
- **Four stereoisomers are formed:**
  - **Compounds A and D are enantiomers.**
 - **Compounds B and C are enantiomers.**

Figure 10.12

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Hydrohalogenation—Summary

Table 10.3 Summary: Electrophilic Addition of HX to Alkenes

	Observation
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	• Syn and anti addition occur.

2. Hydration—Electrophilic Addition of Water

• **Hydration** is the <u>addition of water</u> to an alkene to form an alcohol.
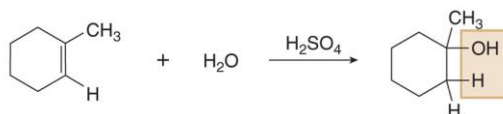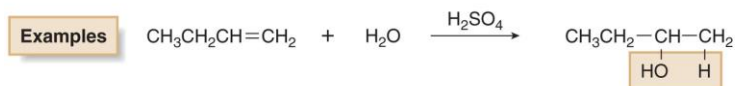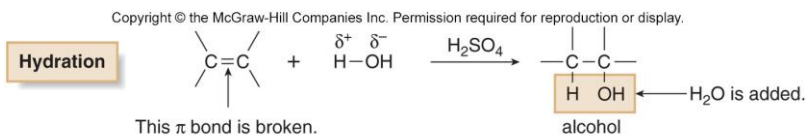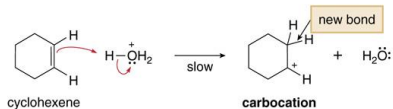
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Mechanism of Hydration

Mechanism 10.2 Electrophilic Addition of H_2O to an Alkene—Hydration

**Step [1]** Addition of the electrophile (H^+) to the π bond

- The π bond attacks H_3O^+, thus forming a new C–H bond while breaking the H–O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

Step [2] Nucleophilic attack of H_2O
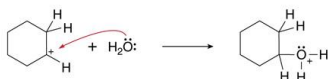
- **Nucleophilic attack of H_2O** on the carbocation forms the new C–O bond.

Step [3] Loss of a proton
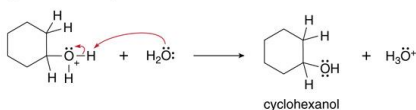
- Removal of a proton with a base (H_2O) forms a neutral alcohol. Because the acid used in Step [1] is regenerated in Step [3], hydration is **acid-catalyzed.**

3. Electrophilic Addition of Alcohols

- **Alcohols add to alkenes, forming ethers by the same mechanism.**

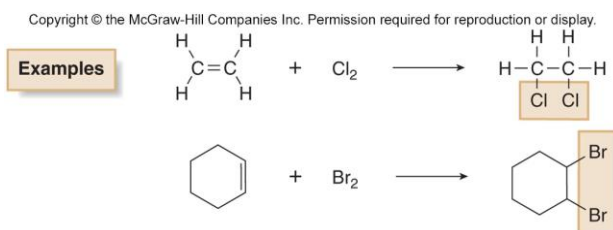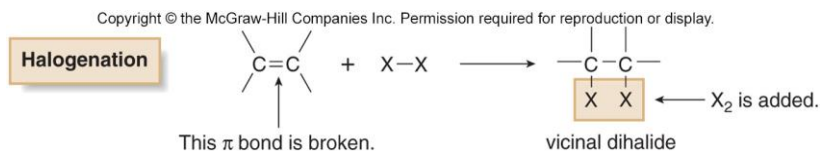**Example: addition of CH$_3$OH to 2-methylpropene, forms *tert*-butyl methyl ether (MTBE), a high octane fuel additive.**

tert-butyl methyl ether
MTBE
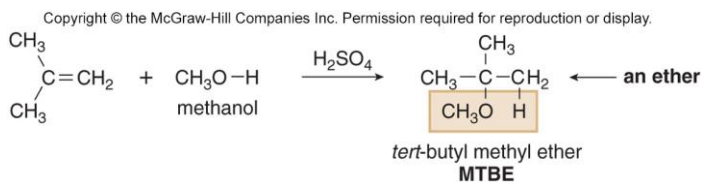
4. Halogenation—Electrophilic Addition of Halogen

- **Halogenation is the addition of X_2 (X = Cl or Br) to an alkene to form a vicinal dihalide.**

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Halogenation

$$C=C + X-X \longrightarrow -\overset{|}{C}-\overset{|}{C}-$$

This π bond is broken.

X X ← X_2 is added.

vicinal dihalide

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Examples

$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} + Cl_2 \longrightarrow H-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H$$

cyclohexene + Br_2 ⟶ cyclohexane with Br, Br

49

Halogenation Details

- **Halogens add to π bonds because halogens are polarizable.**

- **The electron-rich double bond induces a dipole in an approaching halogen molecule, making one halogen atom electron deficient and the other electron rich ($X^{\delta+}$—$X^{\delta-}$).**

- **The electrophilic halogen atom is then attracted to the nucleophilic double bond, making addition possible.**

- **Two facts demonstrate that halogenation follows a different mechanism from that of hydrohalogenation or hydration.**
  - **No rearrangements occur.**
  - **Only anti addition of X_2 is observed.**

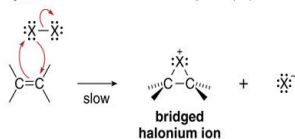 **These facts suggest that carbocations are not intermediates.**

50

25

Halogenation Mechanism

Mechanism 10.3 Addition of X_2 to an Alkene—Halogenation

Step [1] Addition of the electrophile (X^+) to the π bond

bridged halonium ion

- Four bonds are broken or formed in this step: the electron pair in the π bond and a lone pair on a halogen atom are used to form two new C–X bonds. The X–X bond is also cleaved heterolytically, forming X^-. This step is rate-determining.
- The three-membered ring containing a positively charged halogen atom is called a **bridged halonium ion.** This strained three-membered ring is highly unstable, making it amenable to opening of the ring in the second step.

Step [2] Nucleophilic attack of X^-

leaving group

nucleophile →

new bond
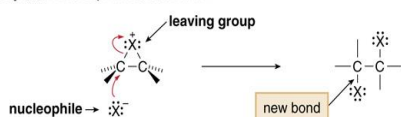
- **Nucleophilic attack of X^-** opens the ring of the halonium ion, forming a new C–X bond and relieving the strain in the three-membered ring.

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Stability of Cation Intermediates

- **Carbocations** are unstable because they have only six electrons that surround carbon.
- **Halonium** ions are unstable because of ring strain.

no octet

carbocation

angle strain

bridged
halonium ion

52

26
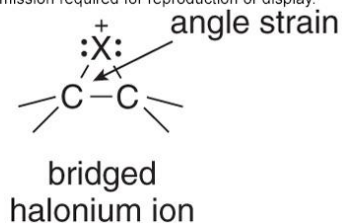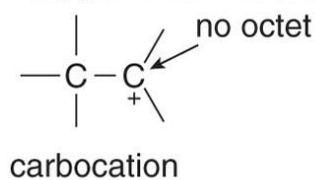
Stereochemistry of Halonium Formation

- **Chlorination of cyclopentene affords <u>both enantiomers</u> of *trans*-1,2-dichlorocyclopentane, with no cis products.**
- **Step [1]: Initial addition of the electrophile Cl$^+$ from (Cl$_2$) occurs from either side of the planar double bond to form a bridged chloronium ion.**

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Example 1
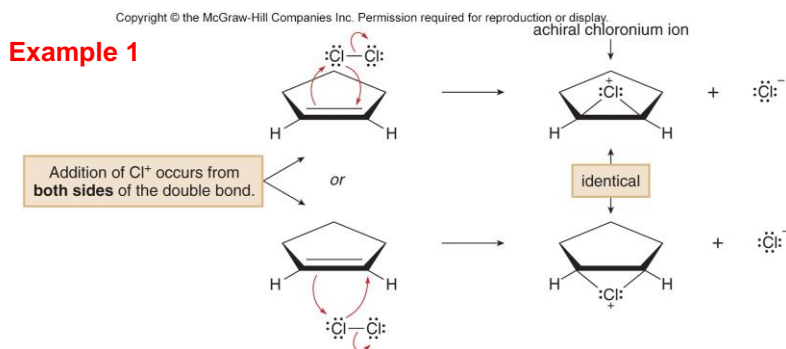
53

Stereochemistry of Halonium Ring Opening

- **Step [2]: nucleophilic attack of Cl$^-$ must occur from the backside.**
- **Since the nucleophile attacks from below and the leaving group departs from above, the two Cl atoms in the product are oriented trans to each other.**
- **Backside attack occurs with equal probability at either carbon of the three-membered ring to yield a racemic mixture.**

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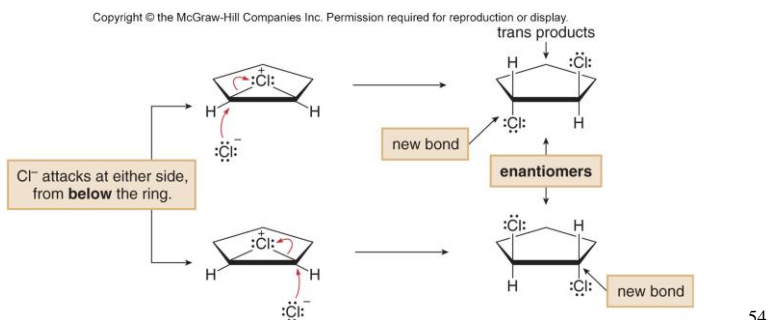
54

Stereochemical output

Example 2: *cis*-2-Butene yields two enantiomers

cis-2-butene $\xrightarrow{Br_2}$

enantiomers
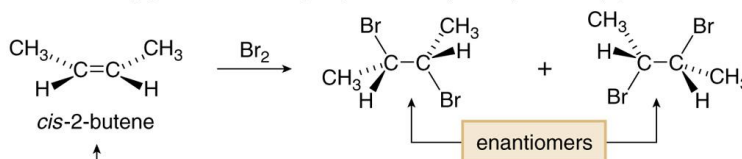
Example 3: *trans*-2-butene yields a single achiral meso compound.

achiral alkenes

trans-2-butene $\xrightarrow{Br_2}$

an achiral **meso** compound
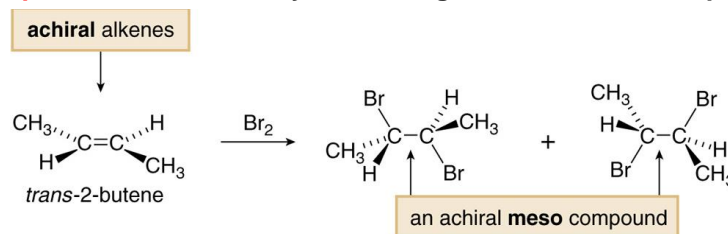
55

5. Halohydrin Formation

- **Treatment of an alkene with a halogen X_2 and H_2O forms a halohydrin by addition of the groups of X and OH to the double bond.**

General reaction

$C=C$ + X—X $\xrightarrow{H_2O}$ —C—C—
X OH ← X and OH added

(X = Cl or Br)

This π bond is broken.

halohydrin

Example

$C=C$ $\xrightarrow[H_2O]{Cl_2}$ H—C—C—H
Cl OH

chlorohydrin

56

28

Mechanism of Halohydrin Formation

Mechanism 10.4 Addition of X and OH—Halohydrin Formation

Step [1] Addition of the electrophile (X⁺) to the π bond

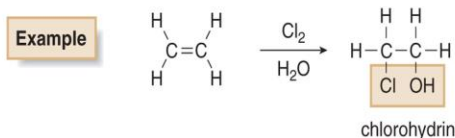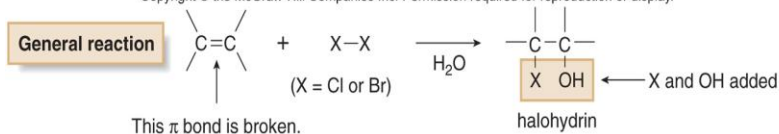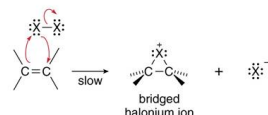- Four bonds are broken or formed in this step: the electron pair in the π bond and a lone pair on a halogen atom are used to form two new C−X bonds in the bridged halonium ion. The X−X bond is also cleaved heterolytically, forming X⁻. This step is rate-determining.

Steps [2] and [3] Nucleophilic attack of H₂O and loss of a proton
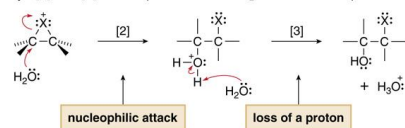
- **Nucleophilic attack of H₂O** opens the halonium ion ring, forming a new C−O bond. Subsequent loss of a proton forms the neutral halohydrin.

nucleophilic attack   loss of a proton

- **Even though X⁻ is formed in step [1] of the mechanism, its concentration is small compared to H₂O (often the solvent), so H₂O and not X⁻ is the nucleophile.**

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Generating Bromine in Halohydrin Formation

- **Although the combination of Br₂ and H₂O effectively forms bromohydrins from alkenes, other reagents can also be used.**
- **Bromohydrins are also formed with *N*-bromosuccinimide (NBS) in aqueous DMSO [(CH₃)₂S=O].**
- **In H₂O, NBS decomposes to form Br₂, which then goes on to form a bromohydrin by the same reaction mechanism.**

N-bromosuccinimide
NBS

$$\ce{C=C} \xrightarrow[\text{DMSO, H2O}]{\text{NBS}} \text{bromohydrin}$$
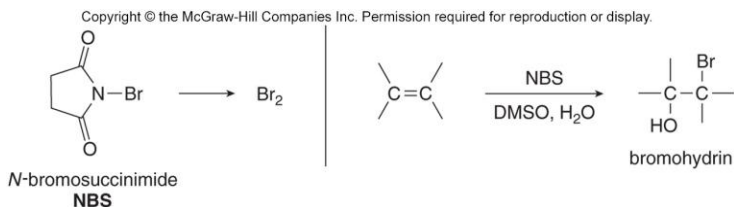
58

Anti Stereochemistry in Halohydrin Formation

- **Because the bridged halonium ion is opened by <u>backside attack of H_2O</u>, addition of X and OH occurs in an anti fashion and trans products are formed.**

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anti addition of Br and OH

trans enantiomers
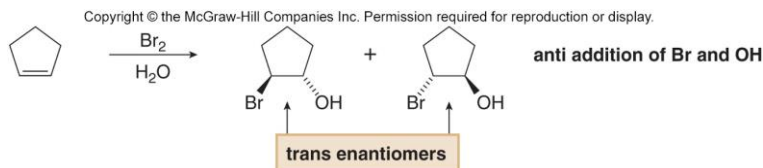
Anti Stereochemistry in Halohydrin Formation

- **With unsymmetrical alkenes, the preferred product has the electrophile X+ bonded to the <u>less substituted carbon</u>, and the nucleophile (H_2O) bonded to the <u>more substituted carbon</u>.**

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This product is formed.

NOT

The electrophile (Br^+) ends up on the **less substituted C.**
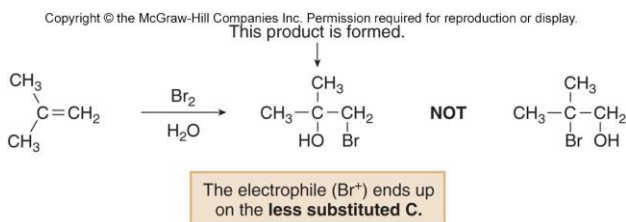
Regiochemistry of Halohydrin Formation

- **As in the acid catalyzed ring opening of epoxides, nucleophilic attack occurs at the <u>more substituted carbon</u> end of the bridged halonium ion because that carbon is better able to accommodate the <u>partial positive charge</u> in the transition state.**

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nucleophilic attack at the
more substituted C
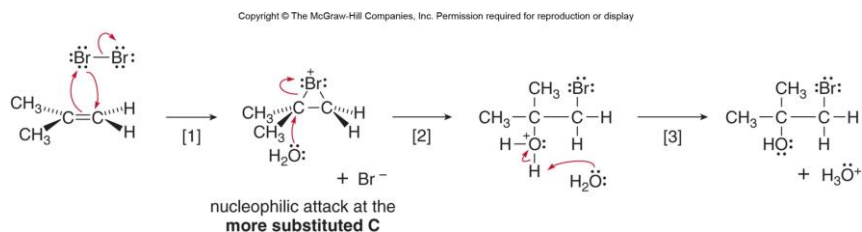
Summary of Halohydrin Formation

Table 10.4 Summary: Conversion of Alkenes to Halohydrins	
	Observation
Mechanism	• The mechanism involves three steps. • The rate-determining step forms a bridged halonium ion. • No rearrangements can occur.
Regioselectivity	• The electrophile X^+ bonds to the less substituted carbon.
Stereochemistry	• Anti addition occurs.

Halohydrin Use in Synthesis

- **Halohydrins have been used in the synthesis of many naturally occurring compounds.**
- **Key steps in the synthesis of estrone, a female sex hormone, are illustrated below.**

Figure 10.14
The synthesis of estrone
from a chlorohydrin
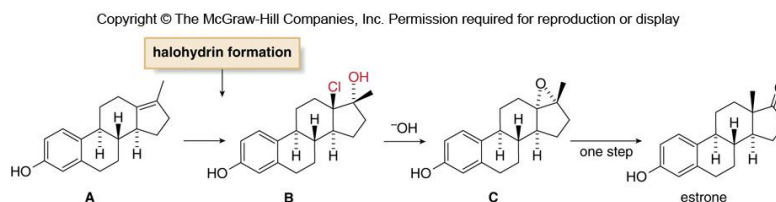
- Chlorohydrin **B**, prepared from alkene **A** by addition of Cl and OH, is converted to epoxide **C** with base. **C** is converted to estrone in one step.

63

6. Hydroboration–Oxidation

- **Hydroboration–oxidation is a two-step reaction sequence that converts an alkene into an <u>alcohol</u>.**
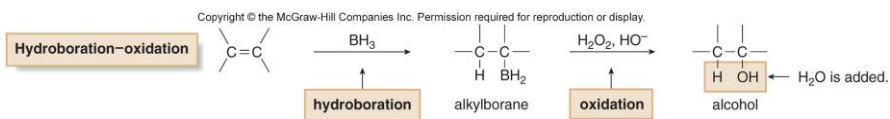
- *Hydroboration* is the addition of borane (BH_3) to an alkene, forming an alkylborane.
- *Oxidation* converts the C–B bond of the alkylborane to a C–O bond.

64

Borane and Hydroboration

- **BH_3** is a reactive gas that exists mostly as a <u>dimer</u>, <u>diborane</u> **(<u>B_2H_6</u>).**
- **Borane** is a strong <u>Lewis acid</u> that reacts readily with Lewis bases.
- **For ease of handling in the laboratory, it is commonly used as a complex with tetrahydrofuran (THF).**

$$BH_3 \quad + \quad \overset{\cdot\cdot}{O} \longrightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{B}}-\overset{+}{O}$$

borane   tetrahydrofuran $BH_3 \cdot THF$

THF

Lewis acid   **Lewis base**

- **Step [1]:** hydroboration–oxidation is the addition of the elements of H and BH_2 to the π bond of the alkene, forming an intermediate alkylborane.

Hydroboration

$$\overset{}{\underset{}{C=C}} \xrightarrow{BH_3} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

     H BH_2 ← These elements are added.

alkylborane

65

Hydroboration Mechanism

- **The proposed mechanism involves concerted addition of <u>H and BH_2</u> from the same side of the planar double bond: the π bond and H-BH_2 bond are broken as two new σ bonds are formed.**
- **Because four atoms are involved, the transition state is said to be four-centered.**
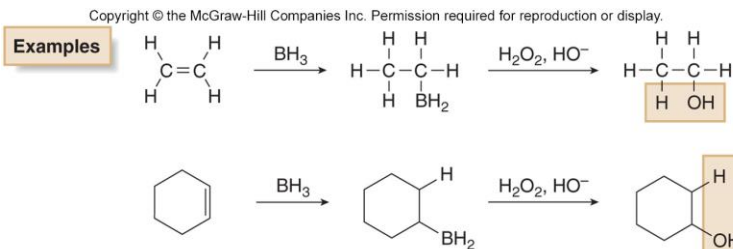
Mechanism 10.5 Addition of H and BH_2—Hydroboration

One step The π bond and H–BH_2 bonds break as the C–H and C–B bonds form.

$$\overset{}{\underset{H-BH_2}{C=C}} \longrightarrow \left[\overset{C\cdots C}{\underset{H\cdots BH_2}{}} \right]^{\ddagger} \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{BH_2}{C}}-$$

            transition state   **syn addition**
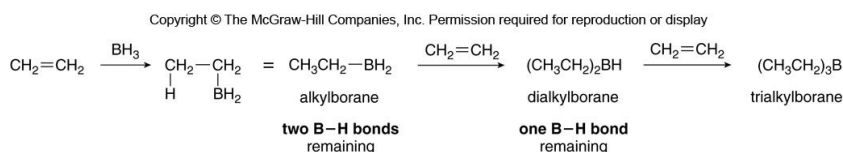
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Reactivity of Borane During Hydroboration

- **Because the alkylborane formed by the reaction with one equivalent of alkene still has <u>two B-H bonds</u>, it can react with two more equivalents of alkene to form a trialkylborane.**
- **We often draw hydroboration as if addition stopped after one equivalent of alkene reacts with BH_3.**
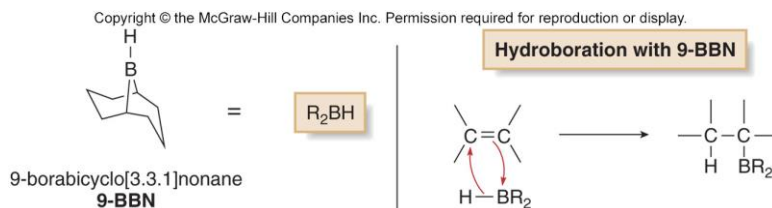- **Instead all three B-H bonds actually react with three equivalents of an alkene to form a trialkylborane.**

Figure 10.15

$CH_2=CH_2 \xrightarrow{BH_3}$ $\underset{\substack{| \\ H \quad BH_2}}{CH_2-CH_2}$ $= CH_3CH_2-BH_2 \xrightarrow{CH_2=CH_2} (CH_3CH_2)_2BH \xrightarrow{CH_2=CH_2} (CH_3CH_2)_3B$

alkylborane   dialkylborane   trialkylborane

two B−H bonds remaining   **one B−H bond** remaining

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Other Sources of B-H for Hydroboration
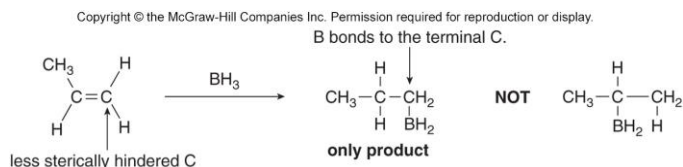
- **Since only one B-H bond is needed for hydroboration, commercially available dialkylboranes having the general structure R_2BH are sometimes used <u>instead of BH_3</u>.**
- **A common example is 9-borabicyclo[3.3.1]nonane (9-BBN).**

9-borabicyclo[3.3.1]nonane
9-BBN

$= \boxed{R_2BH}$

Hydroboration with 9-BBN

$C=C$ $H-BR_2$ $\longrightarrow$ $\underset{\substack{| \quad | \\ H \quad BR_2}}{-C-C-}$

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Regiochemistry of Hydroboration

- **With unsymmetrical alkenes, the boron atom bonds to the less substituted carbon atom.**

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B bonds to the terminal C.

$$CH_3 \quad H$$
$$C=C \xrightarrow{\;BH_3\;} CH_3-\underset{H}{\overset{H}{C}}-\underset{BH_2}{CH_2} \quad \textbf{NOT} \quad CH_3-\underset{BH_2}{\overset{H}{C}}-\underset{H}{CH_2}$$
$$H \quad H$$

less sterically hindered C

only product

- **This regioselectivity can be explained by considering steric factors.**

- **The larger boron atom bonds to the less sterically hindered, more accessible carbon atom.**

# Electronic Factors Affecting Regiochemistry of Hydroboration

- **Electronic factors are also used to explain this regioselectivity.**

- **If bond making and bond breaking are not completely symmetrical, boron bears a δ- charge in the transition state and carbon bears a δ+ charge.**

- **Since alkyl groups stabilize a positive charge, the more stable transition state has the partial positive charge on the more substituted carbon.**

Example of Regiochemistry of Hydroboration

Figure 10.16

The CH$_3$ group stabilizes the partial positive charge.

more stable transition state

preferred product

less stable transition state
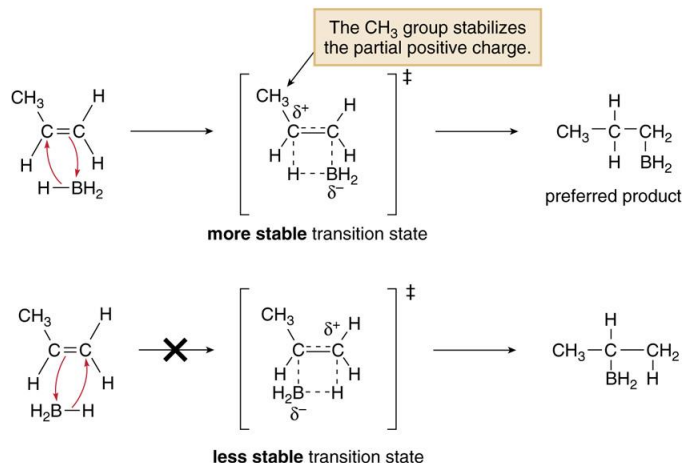
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Oxidation Following Hydroboration

- **Step [2]: alkylboranes react <u>rapidly with water</u> and spontaneously burn when exposed to air, they are oxidized**, without isolation, with <u>basic hydrogen peroxide</u> (H$_2$O$_2$, $^-$OH).
- <u>Oxidation</u> replaces the **C-B bond with a C-O bond**, forming a new OH group with retention of configuration.

Oxidation

H$_2$O$_2$, HO$^-$

retention of configuration
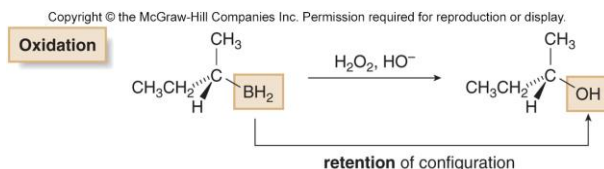
- **The overall result of this two-step sequence is syn addition of the elements of H and OH to a double bond in an <u>"anti-Markovnikov"</u> fashion.**
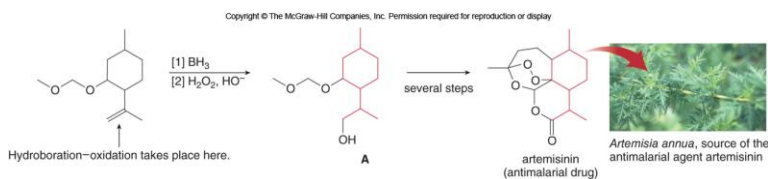
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Summary of Hydroboration—Oxidation

Table 10.5 Summary: Hydroboration–Oxidation of Alkenes

	Observation
Mechanism	• The addition of H and BH_2 occurs in one step. • No rearrangements can occur.
Regioselectivity	• The OH group bonds to the less substituted carbon atom.
Stereochemistry	• Syn addition occurs. • OH replaces BH_2 with retention of configuration.

Example of Hydroboration-Oxidation in Synthesis

- **Hydroboration-oxidation is one step toward making the antimalarial drug artemisinin**

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[1] BH_3
[2] H_2O_2, HO^-

several steps

Hydroboration–oxidation takes place here.

OH
A

artemisinin
(antimalarial drug)

Artemisia annua, source of the antimalarial agent artemisinin

© Henriette Kress

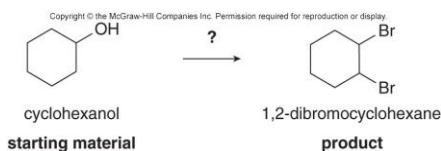• The carbon atoms of artemisinin that come from alcohol **A** are indicated in red.

Keeping Track of Reactions

- **1st Learn the basic type of reaction for a functional group.**
  - **This provides overall organization to the reactions.**
- **2nd Learn the specific reagents for each reaction.**
  - **It helps to classify each reagent according the its properties.**
    - **Is it an acid or base?**
    - **Is it a nucleophile or electrophile?**
    - **Is it an oxidizing or reducing agent?**

- **Finally, you MUST practice these reactions over and over again by writing them. It is not enough just to look at them.**
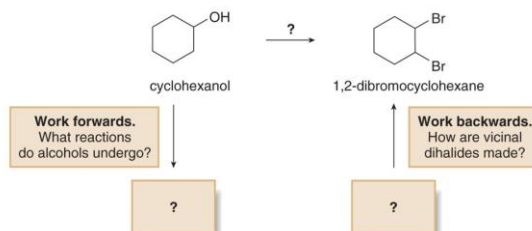
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Use of Alkenes in Synthesis

- **Suppose we wish to synthesize 1,2-dibromocyclohexane from cyclohexanol.**

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cyclohexanol
starting material

1,2-dibromocyclohexane
product

To solve this problem we must:

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- Work backwards from the product by asking: What type of reactions introduce the functional groups in the product?
- Work forwards from the starting material by asking: What type of reactions does the starting material undergo?
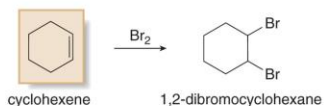

cyclohexanol

1,2-dibromocyclohexane

Work forwards.
What reactions do alcohols undergo?

Work backwards.
How are vicinal dihalides made?

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Retrosynthetic Analysis

Working backwards from the product to determine the starting material from which it is made is called retrosynthetic analysis.

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Working backwards:

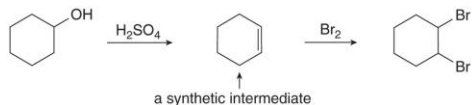[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene.**

cyclohexene → (Br₂) → 1,2-dibromocyclohexane

Working forwards:

[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene.**

cyclohexanol → (H_2SO_4) → cyclohexene
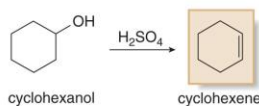
Cyclohexene is called a **synthetic intermediate,** or simply an **intermediate,** because it is the **product of one step and the starting material of another.** We now have a two-step sequence to convert cyclohexanol to 1,2-dibromocyclohexane, and the synthesis is complete. Take note of the central role of the alkene in this synthesis.

A two-step synthesis

OH → (H_2SO_4) → a synthetic intermediate → (Br_2) → Br, Br

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