Organic Chemistry, *Fourth Edition*

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Chapter 10
Alkenes

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The University of Illinois - Springfield

Alkenes

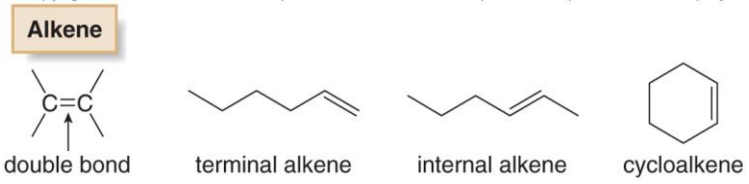
Introduction : Structure, Degrees of Unsaturation, Nomenclature, Physical Properties

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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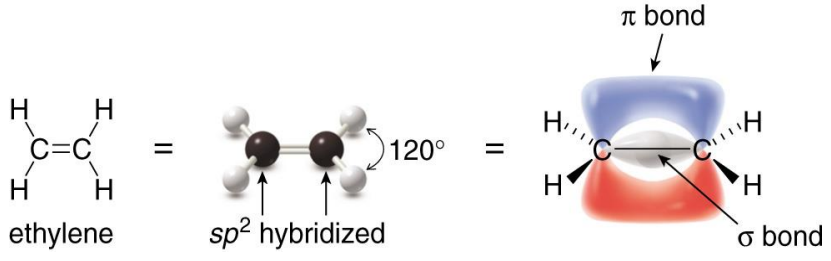
Alkene Hybridization

- **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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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.**

$CH_2=CH_2$		CH_3-CH_3		
635 kJ/mol ($\sigma + \pi$ bond)	−	368 kJ/mol (σ bond)	=	267 kJ/mol

π bond only

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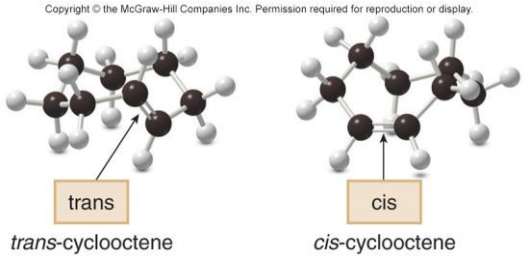
Cyclic Alkenes

- **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.**



trans-cyclooctene *cis*-cyclooctene

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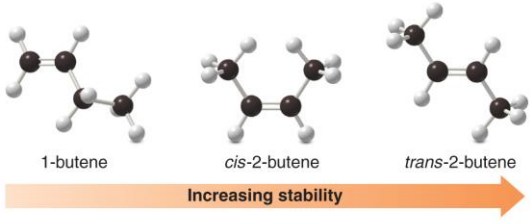
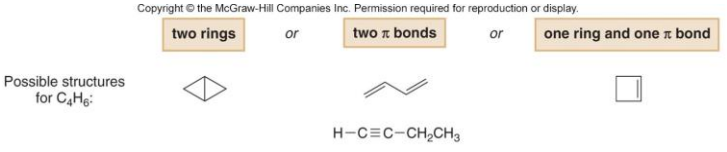
Table 10.1 Properties of the Carbon–Carbon Double Bond

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 actual number of H atoms in a compound to the maximum number of H atoms possible for the number of carbons present if the molecule were an acyclic alkane.**
- **This procedure gives the total number of rings and/or π bonds in a molecule.**



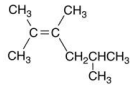
Degrees of Unsaturation for Molecules Containing Heteroatoms

- **Ignore O atoms in the molecule (this divalent atom is a linker and has no effect on degree of unsaturation).**
- **Add number of halogens to number of H's (they are equivalent to H).**
- **Subtract 1 H for each N present (N's two connections allows extra H).**
- **E.g., $C_6H_{10}OCl_3N$ is equivalent to C_6H_{12}.**

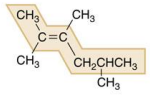
3. Naming of alkenes

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.



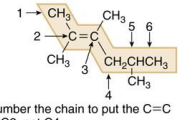
6 C's in the longest chain

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.

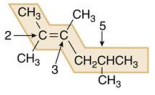
a. **Number** the chain, and name using the ***first*** **number** assigned to the C=C.



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

2-hexene

b. **Name** and **number** the substituents.

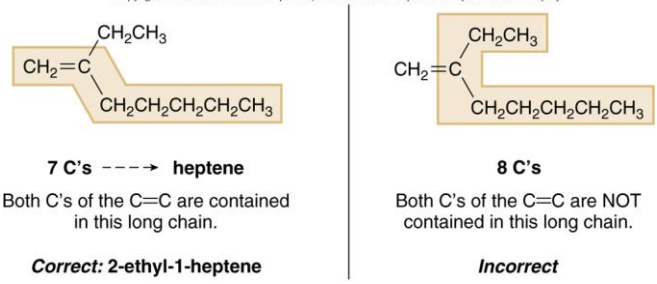


three methyl groups at C2, C3, and C5

Answer: 2,3,5-trimethyl-2-hexene

Naming Alkenes and Alkenols

Example 1



- **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

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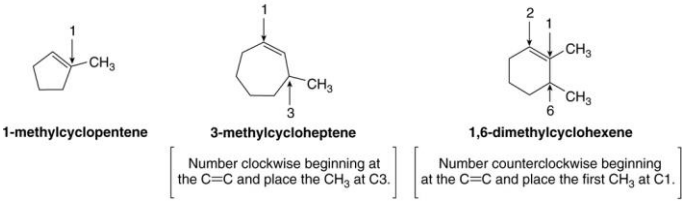
Naming Polyenes and Cyclic Alkenes

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

Example 3



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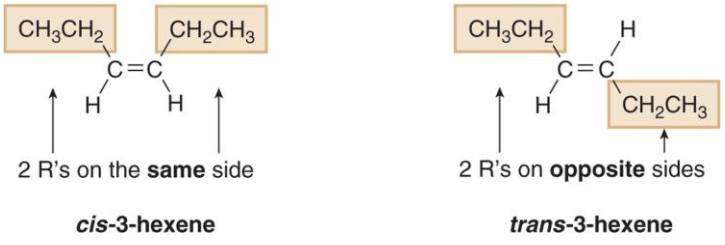
Cis and Trans Isomers of Alkenes

- **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 same side of the double bond.**
  - **trans has the two alkyl groups on opposite sides of the double bond.**



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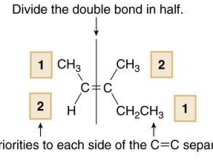
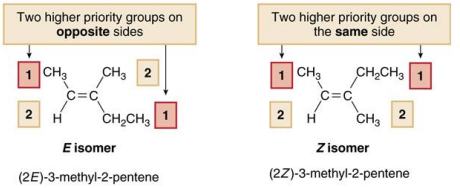
HOW TO Assign the Prefixes *E* and *Z* to an Alkene

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.**



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



- 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.

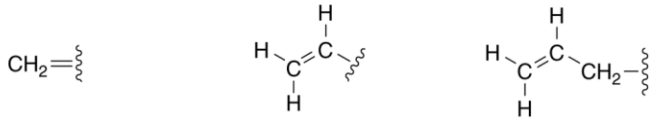
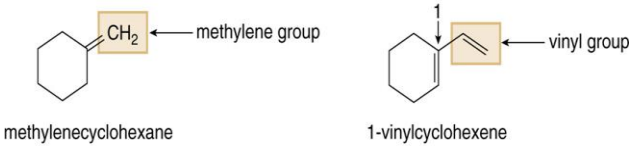


Figure 10.3



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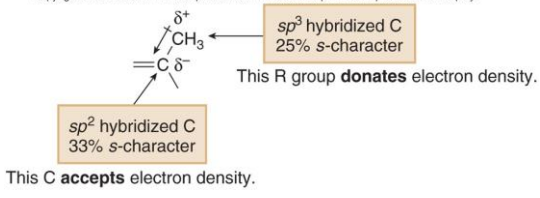
4. Physical Properties of Alkenes

- 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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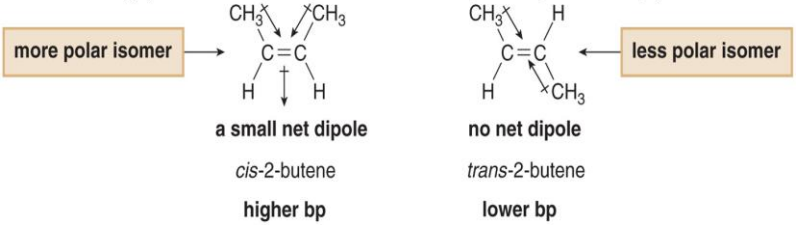
Cis/Trans Differ in Physical Properties

- **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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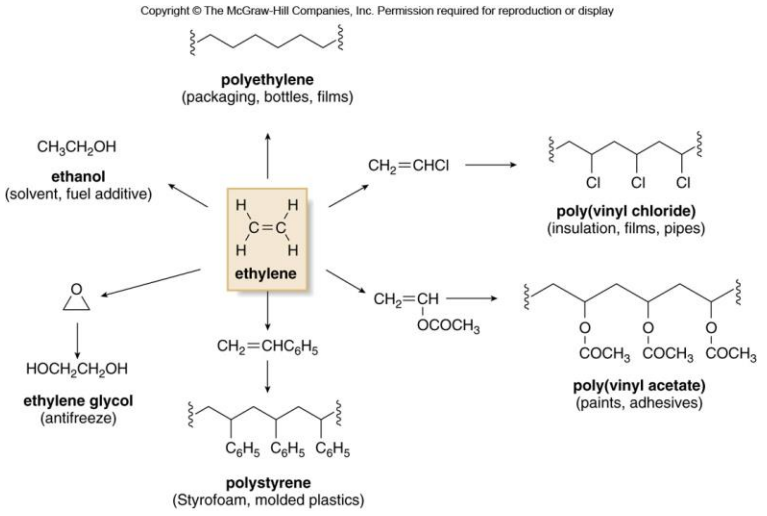
Useful Products Formed From Ethylene

Figure 10.4



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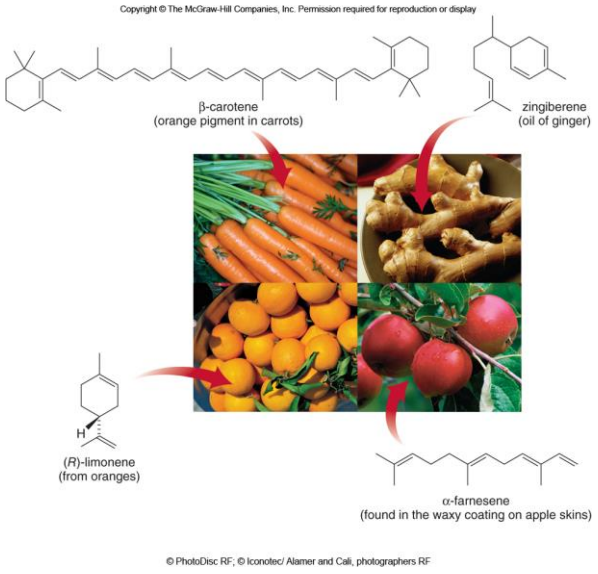
Naturally Occurring Alkenes

Figure 10.5



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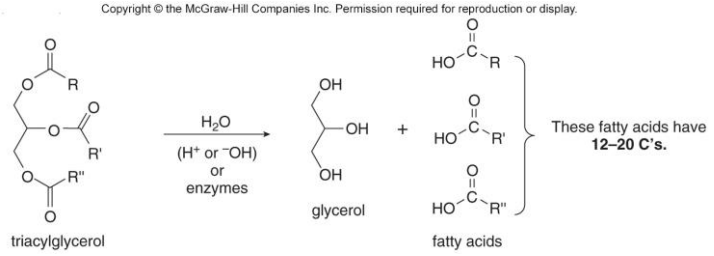
Fatty Acids

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



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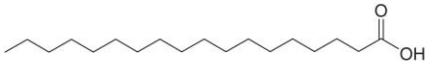
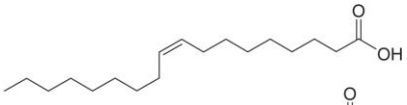
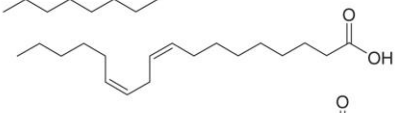
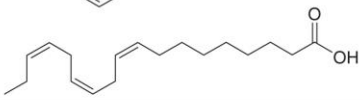
Table 10.2 The Effect of Double Bonds on the Melting Point of Fatty Acids

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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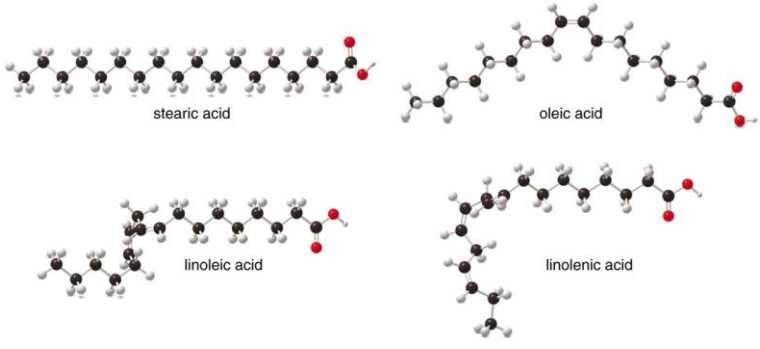
3-D Structure of C_{18} Fatty Acids

- **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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Triacylglycerols

- **Fats and oils are both triacylglycerols, but with different physical properties.**
- **Fats have higher melting points—they are solids at room temperature.**
- **Oils have lower melting points—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 few or no double bonds.**
- **Oils are derived from fatty acids having a larger number of double bonds.**
- **Saturated fats are typically obtained from animal sources, whereas unsaturated oils are common in vegetable sources.**
- **An exception to this generalization is coconut oil, which is largely composed of saturated alkyl side chains.**

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Alkenes

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Hydroboration-Oxidation

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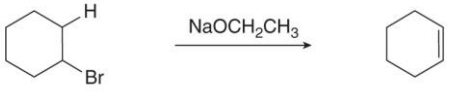
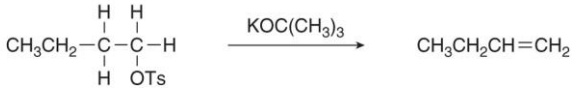
Preparation of Alkenes

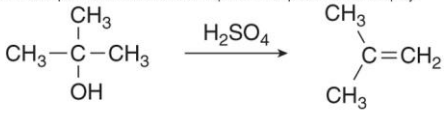
- **Alkenes can be prepared from alkyl halides, tosylates, and alcohols via elimination reactions.**

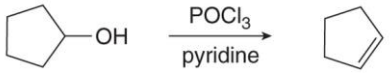
Chapter 8
Dehydrohalogenation





Chapter 9
Dehydydration





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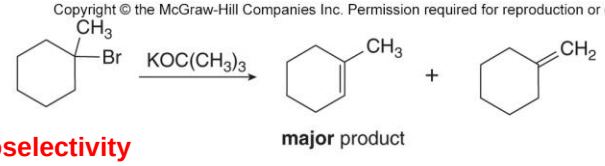
Regioselectivity and Stereoselectivity of Alkene Formation

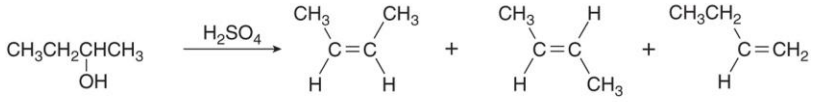
- **The most stable alkene (Zaitsev product) is usually formed as the major product.**

Regioselectivity



major product

Stereoselectivity



major product
trans disubstituted alkene

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Alkenes

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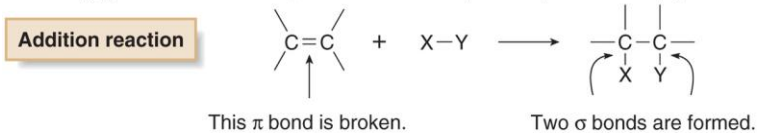
Addition Reactions

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



- **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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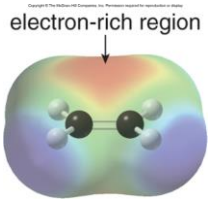
Electrostatic Potential Plot of Ethylene

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



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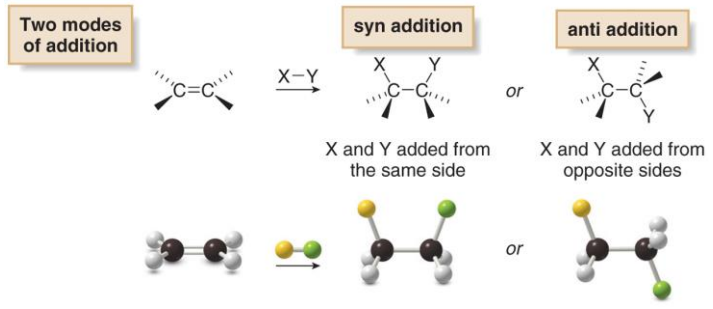
Syn and Anti Addition to Alkenes

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



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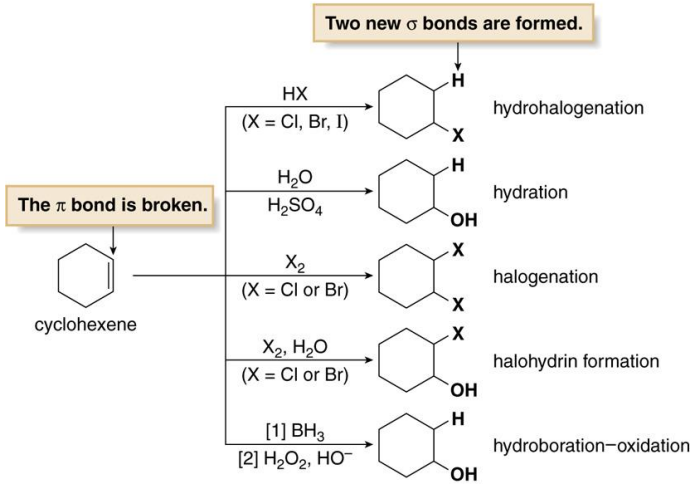
Addition Reactions of Cyclohexene

Figure 10.8



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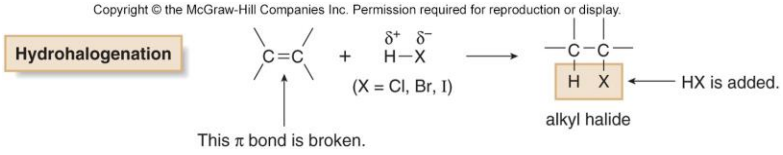
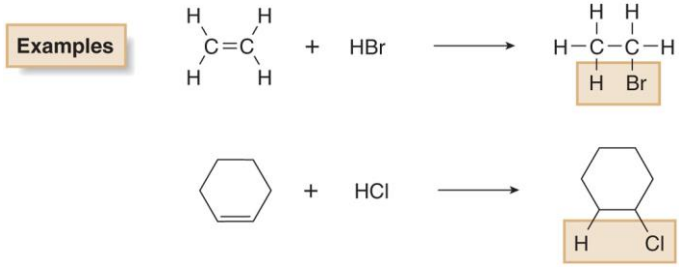
1. Hydrohalogenation—Electrophilic Addition of HX



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

How to Draw the Products of an Addition Reaction

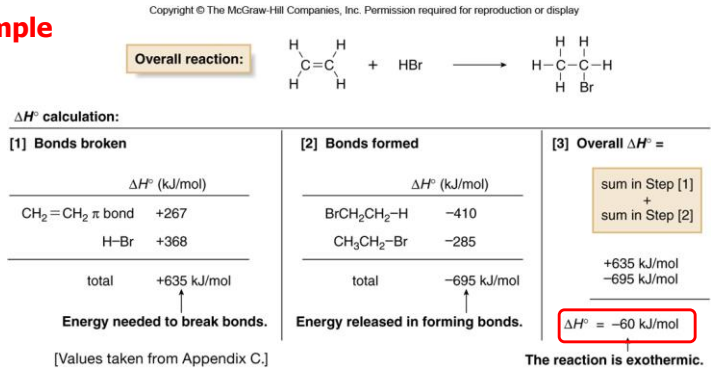
- **Locate the C-C double bond.**
- **Identify the σ bond of the reagent that breaks.**
- **Break the π bond of the alkene and the σ bond of the reagent**
- **Form two new σ bonds to the C atoms of the double bond.**



Heat of Formation for Electrophilic Addition

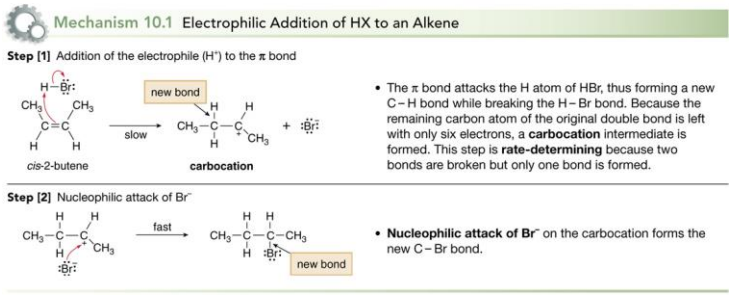
- **Addition reactions are exothermic because the two σ bonds formed in the product are stronger than the σ and π bonds broken in the reactants.**

Example



Mechanism of Electrophilic Addition

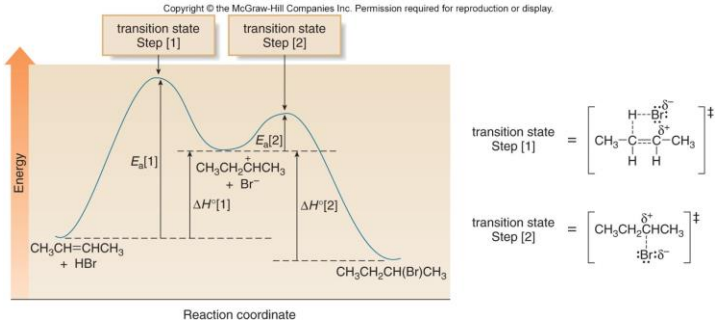
- **The mechanism of electrophilic addition consists of two successive Lewis acid-base reactions.**
  - **Step [1] – the alkene is the Lewis base that donates an electron pair to H-Br, the Lewis acid.**
  - **Step [2] – Br^- is the Lewis base that donates an electron pair to the carbocation, the Lewis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



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.**

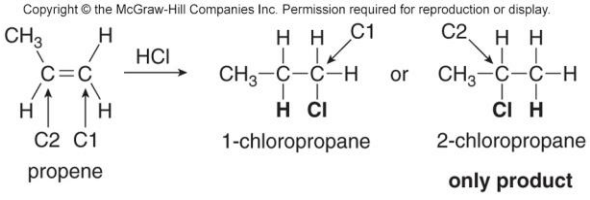
Figure 10.10



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

Markovnikov's Rule

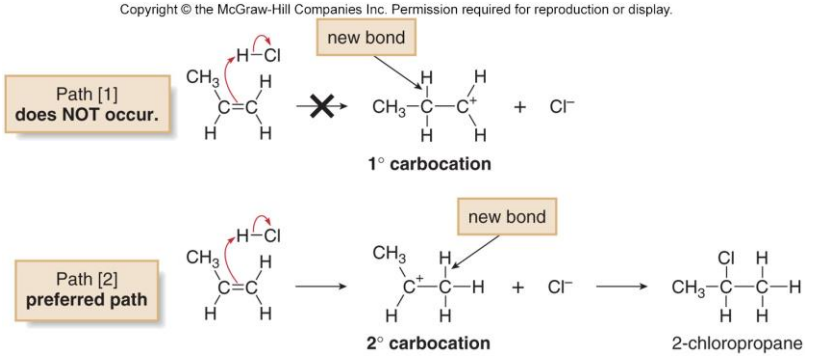
- **With an unsymmetrical alkene, HX can add to the double bond to give two constitutional isomers, but only one is actually formed:**



- **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.**

Carbocation Stability and Markovnikov's Rule

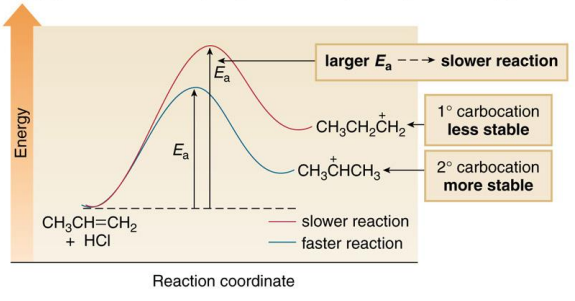
- The basis of Markovnikov's rule is the formation of a carbocation in the rate-determining step of the mechanism.
- In the addition of HX to an unsymmetrical alkene, the H atom is added to the less substituted carbon to form the more stable, more substituted carbocation.



Hammond Postulate and Electrophilic Addition

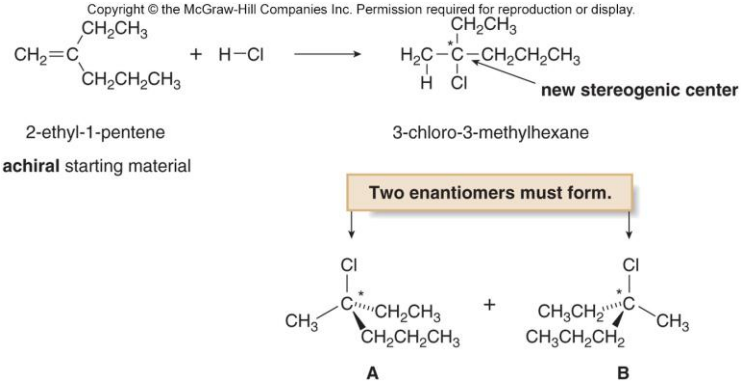
- According to the Hammond postulate, the blue path is faster because formation of the carbocation is an endothermic process.
- Thus, the transition state to form the more stable 2° carbocation is lower in energy.
- The E_a for formation of the more stable 2° carbocation is lower than the E_a for formation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

Figure 10.11



Stereochemistry of Electrophilic Addition

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



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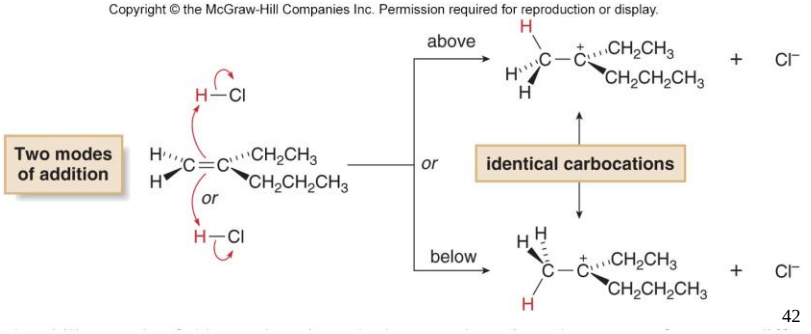
a. Stereochemistry of Carbocation Formation

- 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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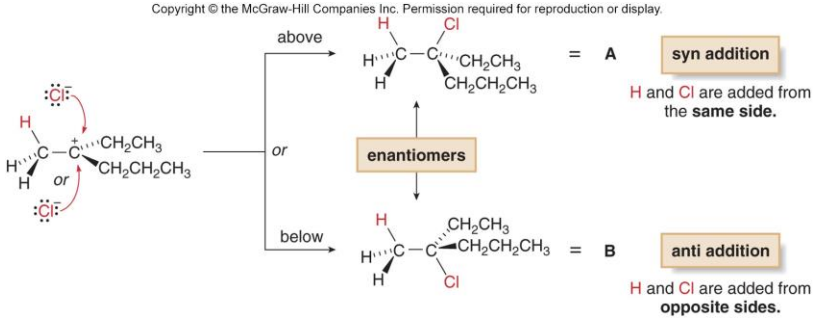
b. Stereochemistry of Nucleophilic Attack

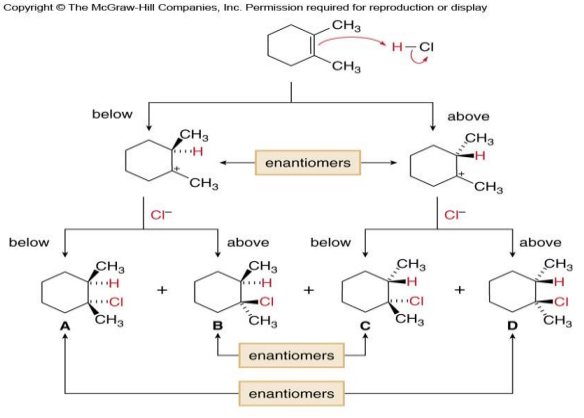
- Nucleophilic attack of Cl^- on the trigonal planar carbocation also occurs from two different directions, forming two products, A and B, having a new stereogenic center.
- A and B are enantiomers.
- Since attack from either direction occurs with equal probability, a racemic mixture of A and B is formed.



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



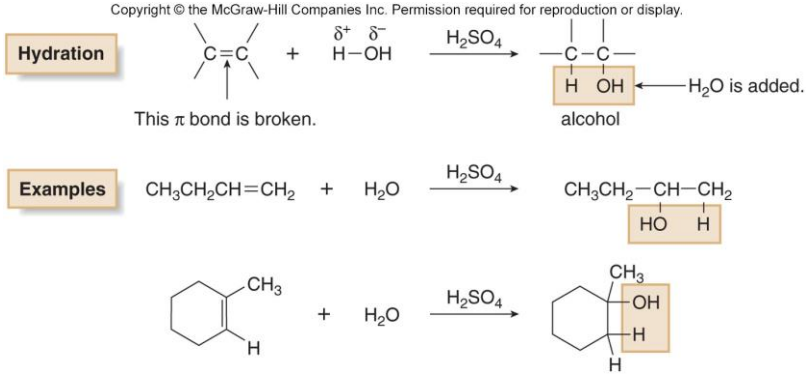
Hydrohalogenation—Summary

Table 10.3 Summary: Electrophilic Addition of HX to Alkenes

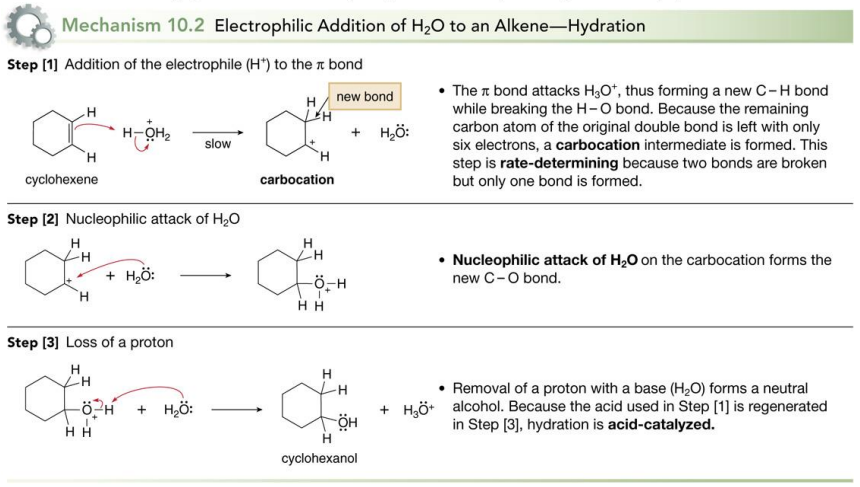
	Observation
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	•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

2. Hydration—Electrophilic Addition of Water

- **Hydration is the addition of water to an alkene to form an alcohol.**



Mechanism of Hydration



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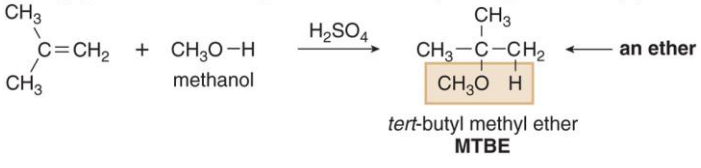
3. Electrophilic Addition of Alcohols

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

Example: addition of CH_3OH to 2-methylpropene, forms *tert*-butyl methyl ether (MTBE), a high octane fuel additive.



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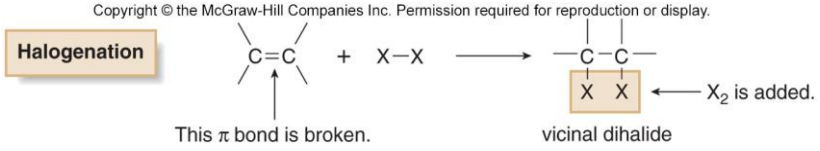
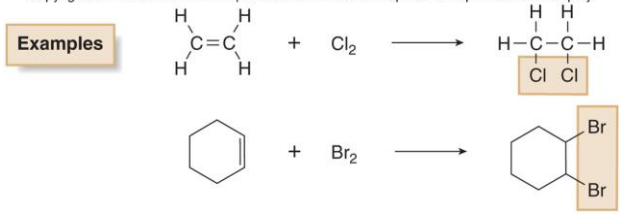
4. Halogenation—Electrophilic Addition of Halogen

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





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Halogenation 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.

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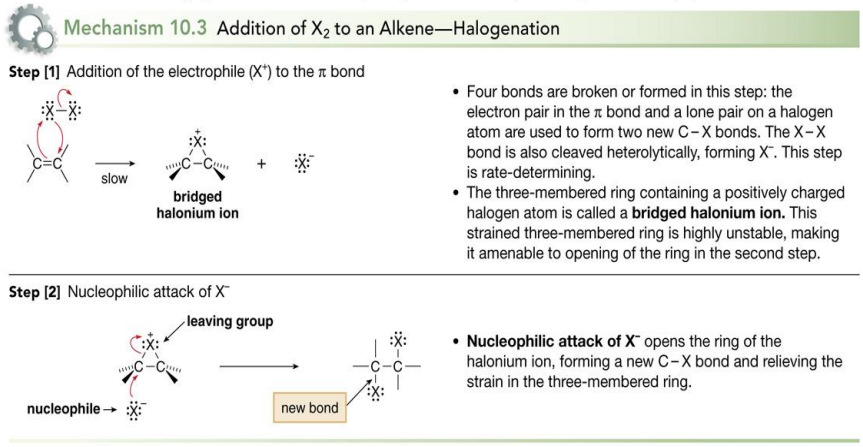
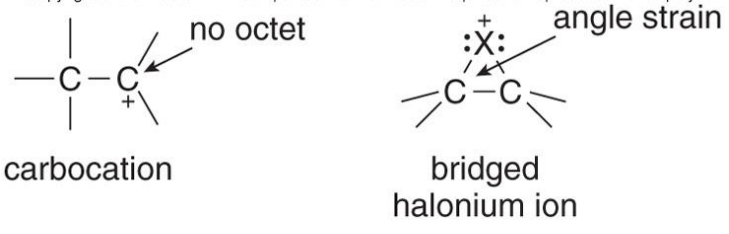
Halogenation Mechanism



Stability of Cation Intermediates

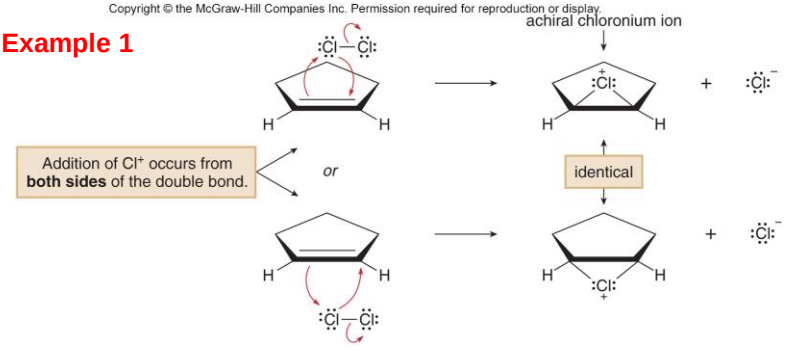
- **Carbocations are unstable because they have only six electrons that surround carbon.**
- **Halonium ions are unstable because of ring strain.**



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.

Example 1



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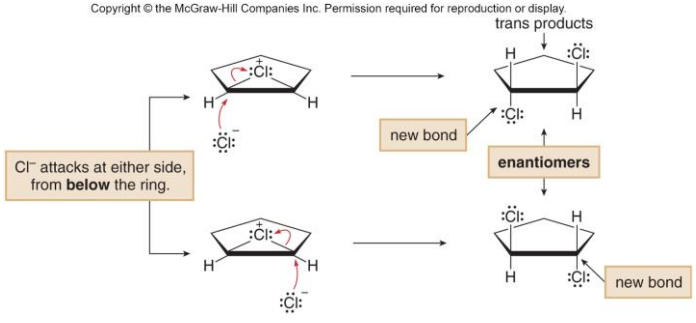
Stereochemistry of Halonium Ring Opening

- 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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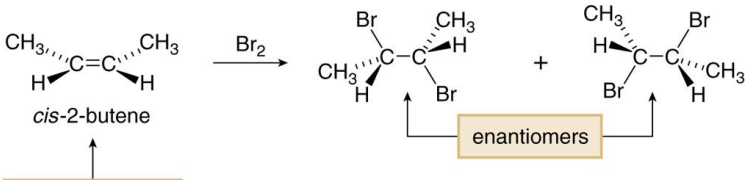
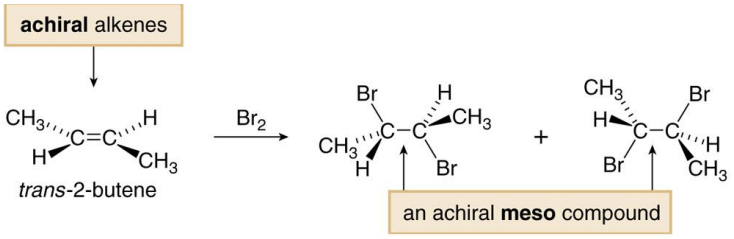
Stereochemical output

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



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



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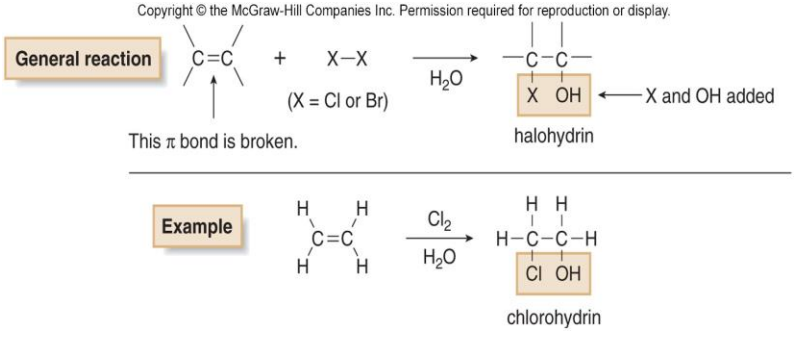
5. Halohydrin Formation

- **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.**



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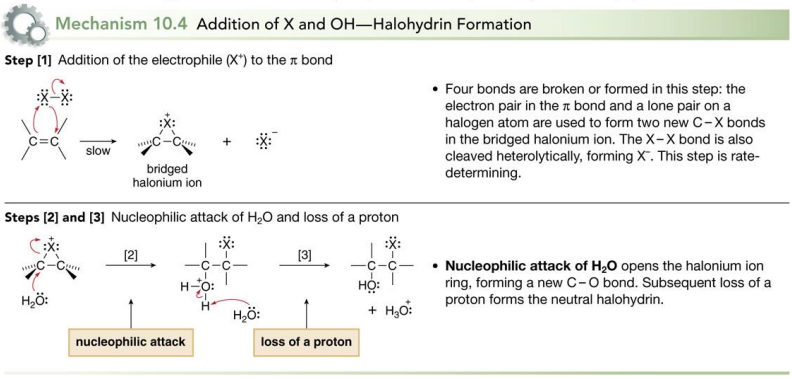
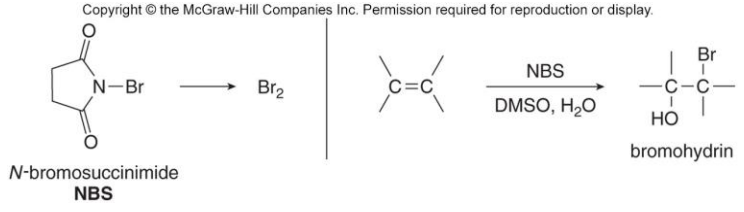
Mechanism of Halohydrin Formation



- **Even though X^- is formed in step [1] of the mechanism, its concentration is small compared to H_2O (often the solvent), so H_2O and not X^- is the nucleophile.**

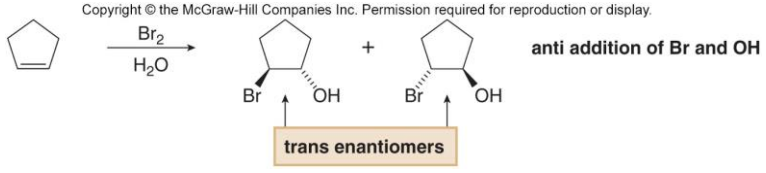
Generating Bromine in Halohydrin Formation

- **Although the combination of Br_2 and H_2O effectively forms bromohydrins from alkenes, other reagents can also be used.**
- **Bromohydrins are also formed with *N*-bromosuccinimide (NBS) in aqueous DMSO [$(CH_3)_2S{=}O$].**
- **In H_2O, NBS decomposes to form Br_2, which then goes on to form a bromohydrin by the same reaction mechanism.**



Anti Stereochemistry in Halohydrin Formation

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



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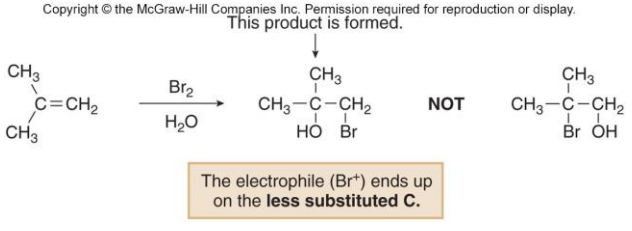
Anti Stereochemistry in Halohydrin Formation

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



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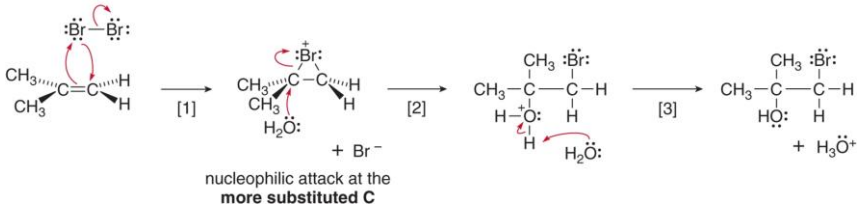
Regiochemistry of Halohydrin Formation

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



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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.

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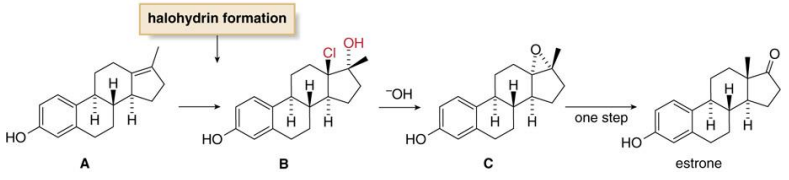
Halohydrin Use in Synthesis

- **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.

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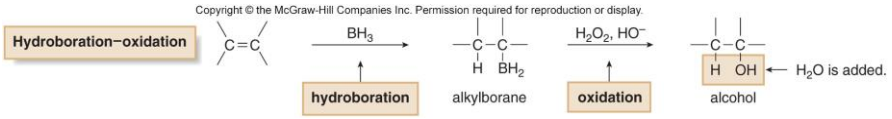
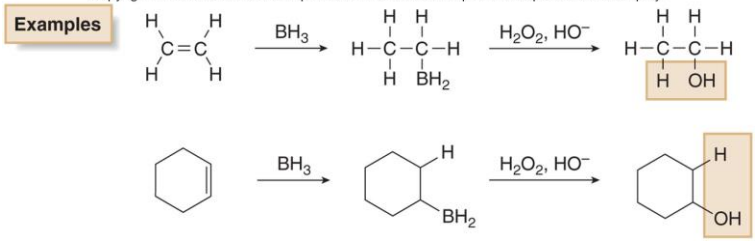
6. Hydroboration–Oxidation

- **Hydroboration–oxidation is a two-step reaction sequence that converts an alkene into an alcohol.**



- *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.



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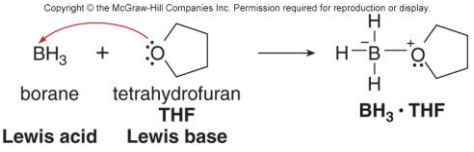
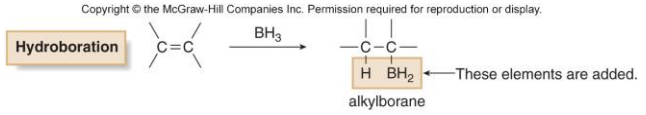
Borane and Hydroboration

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



- **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.**



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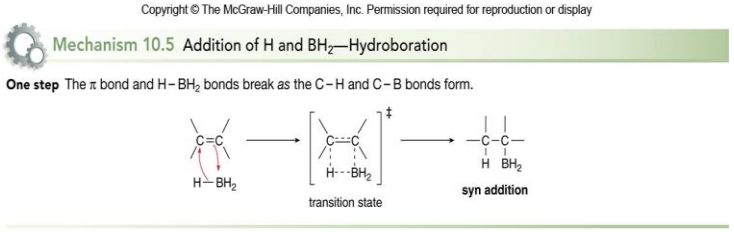
Hydroboration Mechanism

- **The proposed mechanism involves concerted addition of H and BH_2 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.**



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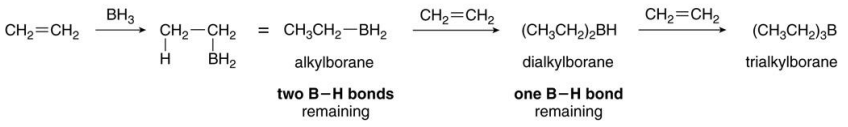
Reactivity of Borane During Hydroboration

- **Because the alkylborane formed by the reaction with one equivalent of alkene still has two B-H bonds, 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



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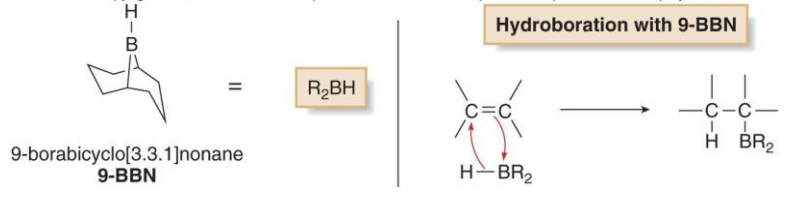
Other Sources of B-H for Hydroboration

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



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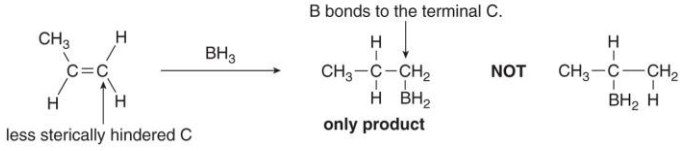
Regiochemistry of Hydroboration

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



- **This regioselectivity can be explained by considering steric factors.**
- **The larger boron atom bonds to the less sterically hindered, more accessible carbon atom.**

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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.**

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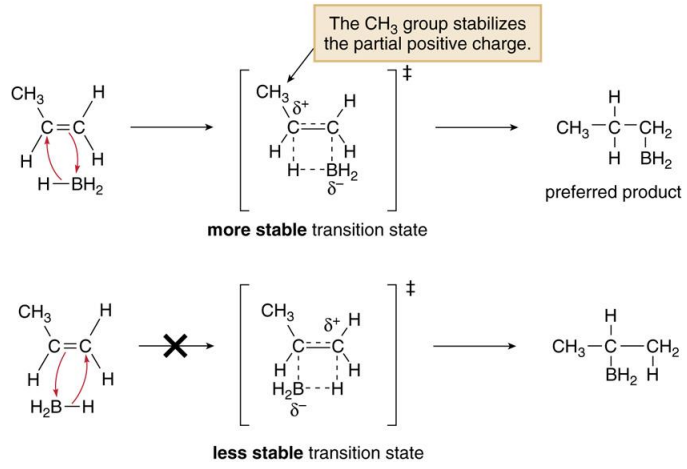
Example of Regiochemistry of Hydroboration

Figure 10.16



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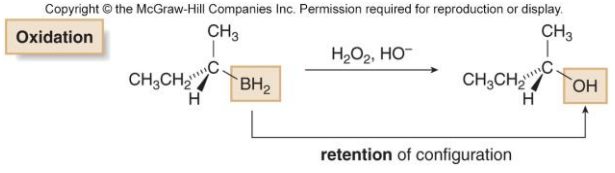
Oxidation Following Hydroboration

- **Step [2]: alkylboranes react rapidly with water and spontaneously burn when exposed to air, they are oxidized, without isolation, with basic hydrogen peroxide (H_2O_2, ^-OH).**
- **Oxidation replaces the C-B bond with a C-O bond, forming a new OH group with 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 "anti-Markovnikov" 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.

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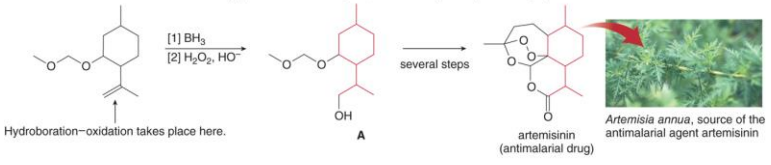
Example of Hydroboration-Oxidation in Synthesis

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



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

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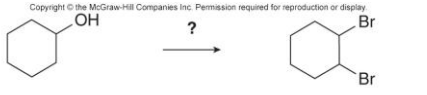
Keeping Track of Reactions

- **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.**

Use of Alkenes in Synthesis

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

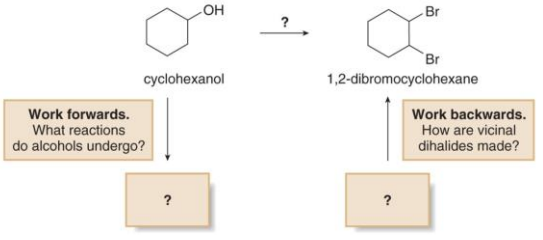


cyclohexanol — **starting material**

1,2-dibromocyclohexane — **product**

To solve this problem we must:

- 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?

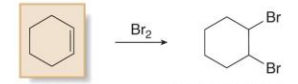


Retrosynthetic Analysis

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

Working backwards:

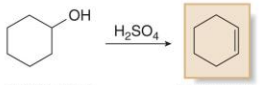
[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene.**



cyclohexene 1,2-dibromocyclohexane

Working forwards:

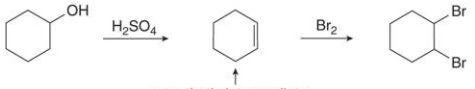
[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene.**



cyclohexanol 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



a synthetic intermediate

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