

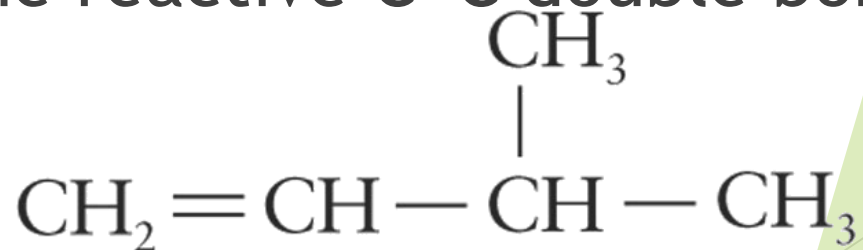
Organic Chemistry,
8th Edition
L. G. Wade, Jr.

Structure and Synthesis of Alkenes

Introduction to Alkenes

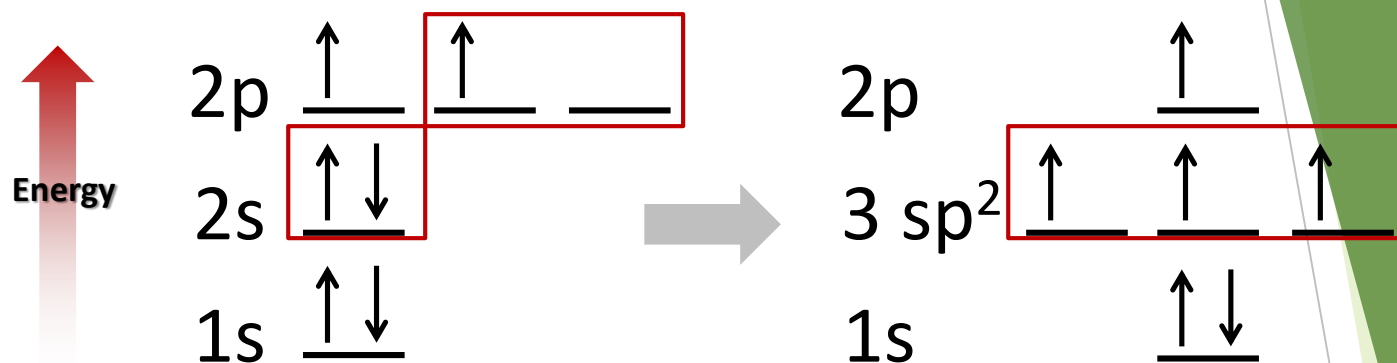
- ▶ Alkenes: Hydrocarbons with C=C double bonds.
- ▶ Alkenes are unsaturated.
- ▶ Alkenes also called olefins, meaning “oil-forming gas.”
- ▶ Alkene FG is the reactive C=C double bond.

Example:



3-methyl-1-butene

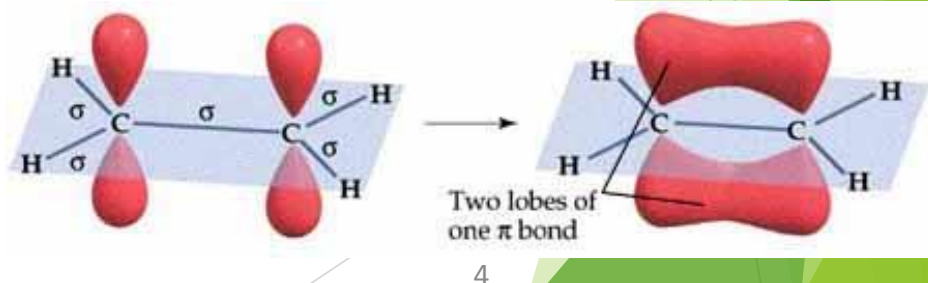
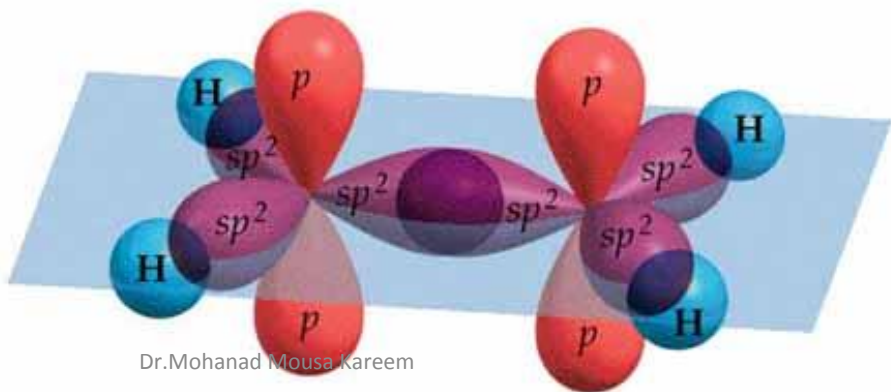
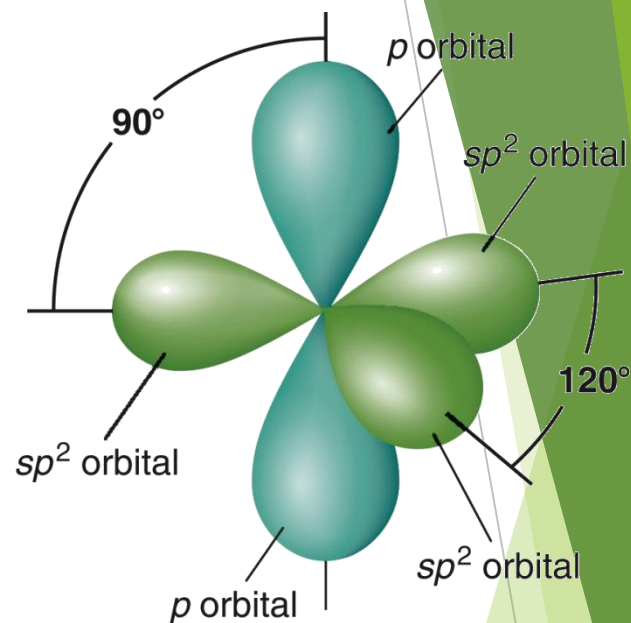
The Geometry of Alkenes



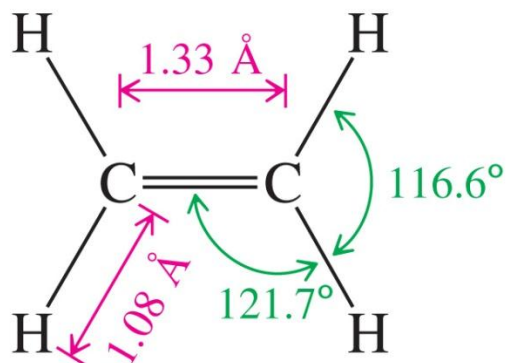
- ▶ In C=C bonds, sp^2 hybrid orbitals are formed by the carbon atoms, with one electron left in a $2p$ orbital.
- ▶ During hybridization, two of the $2p$ orbitals mix with the single $2s$ orbital to produce three sp^2 hybrid orbitals. One $2p$ orbital is not hybridized and remains unchanged.
- ▶ sp^2 hybrid orbitals have more s character than the sp^3 hybrid orbitals.

The Geometry of Alkenes (continued)

1. One bond (sigma, σ) is formed by overlap of two sp^2 hybrids.
2. Second bond (pi, π) is formed by connecting the electrons from 2 unhybridized p orbitals.
3. Trigonal planar molecular geometry.

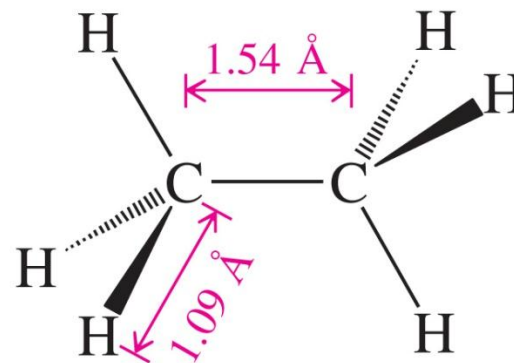


Bond Lengths and Angles



ethylene

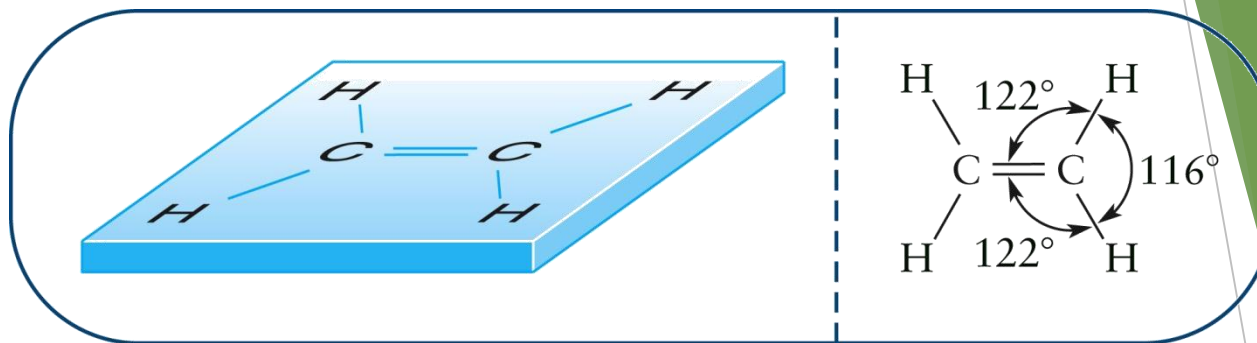
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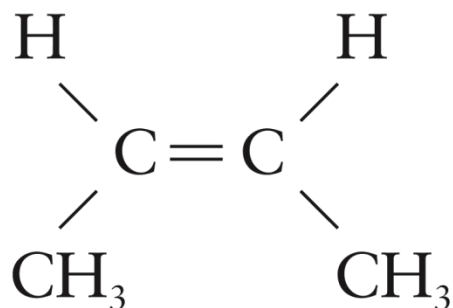
ethane

- ▶ Angles approximately 120°
- ▶ Pi overlap brings carbon atoms closer:
 - ▶ C-C bond length = 1.54 \AA
 - ▶ C=C bond length 1.33 \AA .
- ▶ Pi bonds weaker than sigma bonds

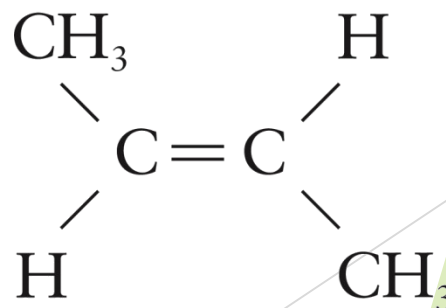
The Geometry of Alkenes (continued)



- ▶ Planar geometry of the sp^2 hybrid orbitals and pi bond locks the C=C bond firmly in place.
- ▶ No rotation around the carbon-carbon bond is possible without breaking the pi bond (264 kJ/mole).
- ▶ Cis and trans isomers cannot be interconverted.

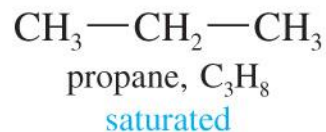


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cis-2-butene

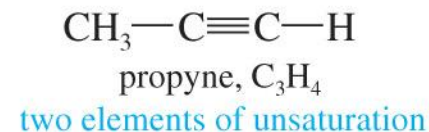
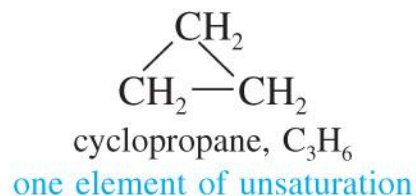
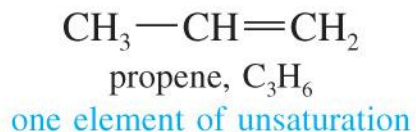


trans-2-butene

Elements of Unsaturation



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- ▶ **Unsaturation:** Structural element that decreases number of hydrogens in the molecule by 2.
- ▶ Also called *index of hydrogen deficiency*.
- ▶ Double bonds and rings are elements of unsaturation.
- ▶ Triples bonds also elements of unsaturation (like having 2 double bonds).

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Calculating Unsaturation

To calculate number of unsaturations:

- ▶ Find the number of hydrogens the carbons would have if the compounds were saturated (C_nH_{2n+2}).
- ▶ Subtract the actual number of hydrogens and divide by 2.
- ▶ This calculation cannot distinguish between unsaturations from multiple bonds and those from rings.

Example: Calculate the Un saturations for a Compound with Formula C₅H₈.

- ▶ Calculate the number of hydrogen atoms for a saturated compound with five carbons:

$$(2 \times C) + 2 \\ (2 \times 5) + 2 = 12$$

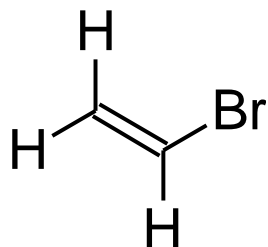
- ▶ Now subtract from this number the actual number of hydrogen atoms in the formula and divide by 2:

$$\frac{12 - 8}{2} = \frac{4}{2} = 2 \text{ unsaturations}$$

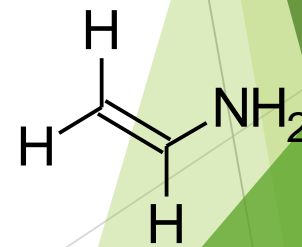
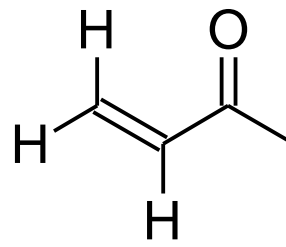
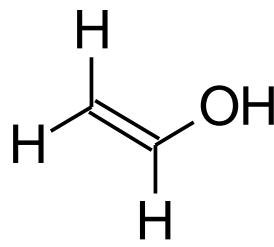
- ▶ The compound has two unsaturations. They can be two double bonds, two rings, one double bond and one ring, or 1 triple bond.

Elements of Unsaturation: Heteroatoms

- ▶ Halogens replace hydrogen atoms in hydrocarbons, so when calculating unsaturations, count halides as hydrogen atoms.
- ▶ Single bond oxygen does not change the C:H ratio, so ignore oxygen in the formula.
- ▶ Nitrogen is trivalent, so it acts like half a carbon. Add the number of nitrogen atoms when calculating unsaturations.



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Example: Calculate the Un saturations for a Compound with Formula C₄H₇Br.

- ▶ Calculate the number of hydrogens for a saturated compound with four carbons:

$$(2 \times C) + 2 + N \\ (2 \times 4) + 2 = 10$$

- ▶ Now subtract from this number the actual number of hydrogens in the formula and divide by 2. Remember to count halides as hydrogens:

$$\frac{10 - 8}{2} = \frac{2}{2} = 1 \text{ unsaturation}$$

Example: Calculate the Un saturations for a Compound with Formula C₆H₇N.

- ▶ First calculate the number of hydrogens for a saturated compound with six carbons. Add the number of nitrogens:

$$(2 \times C) + 2 + N$$
$$(2 \times 6) + 2 + 1 = 15$$

- ▶ Now subtract from this number the actual number of hydrogens in the formula and divide by 2:

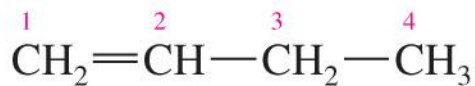
$$\frac{15 - 7}{2} = \frac{8}{2} = 4 \text{ unsaturations}$$

IUPAC Rules for Naming Alkenes

1. Name the longest chain that contains the double bond or double bonds. The name of the chain will end in *-ene*.
2. Number longest chain so C=C bond or bonds has/have lowest number.
3. The first C of the C=C bond (for C=C bond to have lowest number) identifies the positional location of the double bond.
4. Name the attached functional groups.
5. Combine the names of the attached groups and longest chain, the same as you would with alkanes.
6. For multiple double bonds, indicate the locations of all multiple bonds, use numeric prefixes indicating number of double bonds (-diene, -triene).
7. In a ring, the double bond is assumed to be between carbon 1 and carbon 2.

IUPAC and New IUPAC

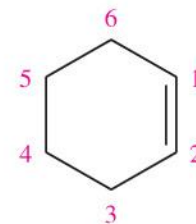
old IUPAC names:
new IUPAC names:



1-butene
but-1-ene

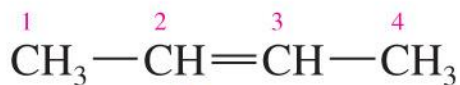


1-pentene
pent-1-ene



cyclohexene

old IUPAC names:
new IUPAC names:



2-butene
but-2-ene

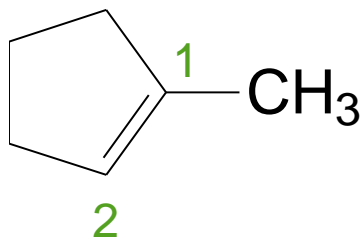


2-pentene
pent-2-ene

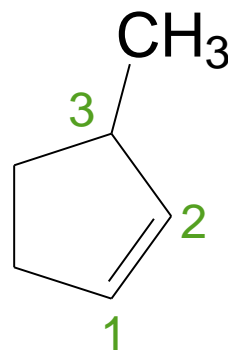
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Ring Nomenclature

In a ring, the double bond is assumed to be between carbon 1 and carbon 2.



1-methylcyclopentene



3-methylcyclopentene

Multiple Double Bonds

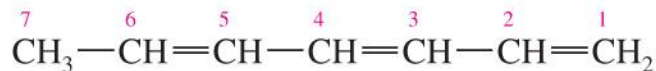
old IUPAC names:

new IUPAC names:



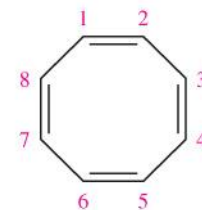
1,3-butadiene

buta-1,3-diene



1,3,5-heptatriene

hepta-1,3,5-triene



1,3,5,7-cyclooctatetraene

cycloocta-1,3,5,7-tetraene

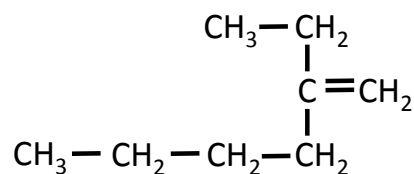
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- ▶ Give the double bonds the lowest numbers possible.
- ▶ Use *di-*, *tri-*, *tetra-* before the ending *-ene* to specify how many double bonds are present.

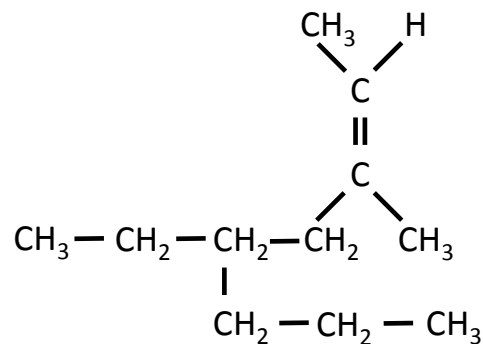
Naming Alkenes



2-pentene

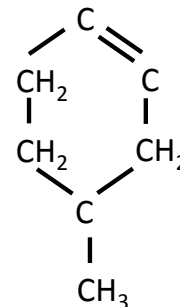


2-ethyl-1-hexene

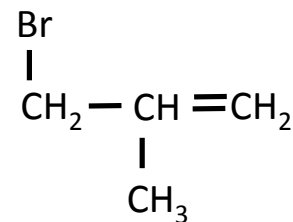


5-ethyl-3-methyl-2-octene

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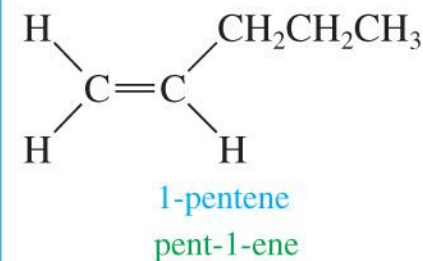
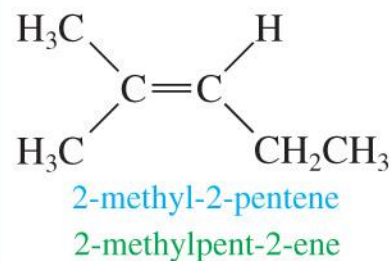
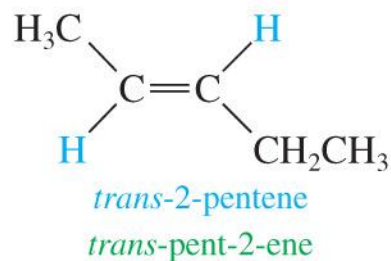
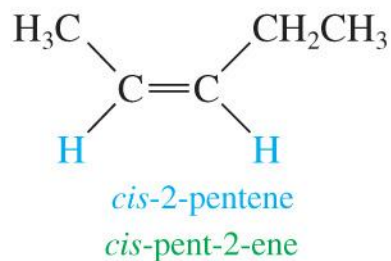


4-methylcyclohexene



3-bromo-2-methyl-1-propene

Cis-Trans Isomers



(neither *cis* nor *trans*)

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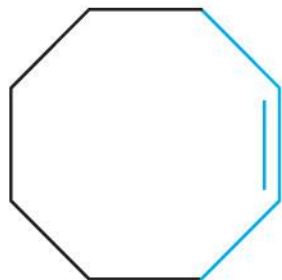
- ▶ Also called *geometric isomerism*.
- ▶ Similar groups on same side of double bond, alkene is *cis*.
- ▶ Similar groups on opposite sides of double bond, alkene is *trans*.
- ▶ Not all alkenes show *cis-trans* isomerism.

Cyclic Compounds

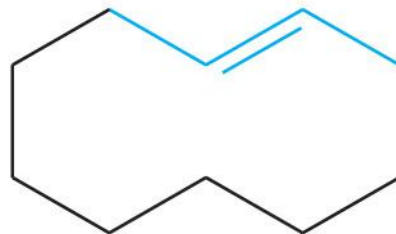


cyclohexene

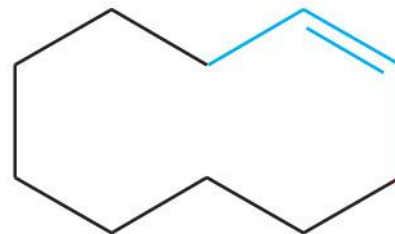
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cyclooctene



trans-cyclodecene



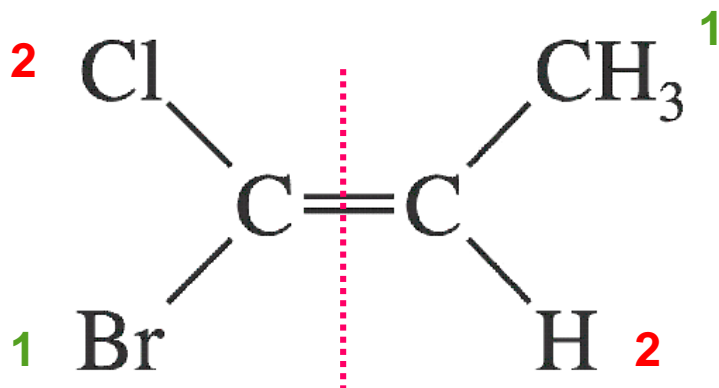
cis-cyclodecene

- ▶ Trans cycloalkenes are not stable unless the ring has at least eight carbons.
- ▶ All cycloalkenes are assumed to be cis unless otherwise specifically named trans.

E-Z Nomenclature

- ▶ The E- and Z- style is more reliable than cis/trans, and particularly suited to highly substituted alkenes, especially when the substituents are not alkyl groups.
- ▶ Use the Cahn-Ingold-Prelog rules to assign priorities to groups attached to each carbon in the double bond.
- ▶ If high-priority groups are on the *same side*, the name is **Z** (for *zusammen*).
- ▶ If high-priority groups are on **opposite sides**, the name is **E** (for *entgegen*).

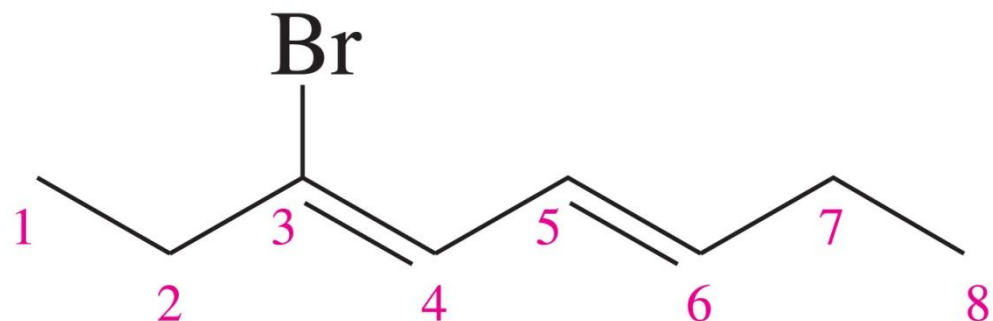
Example



***E*-1-bromo-1-chloropropene**

- ▶ Assign priority to the substituents according to their atomic number (1 is highest priority).
- ▶ If the highest priority groups are on opposite sides, the isomer is *E*.
- ▶ If the highest priority groups are on the same side, the isomer is *Z*.

Stereochemistry in Dienes

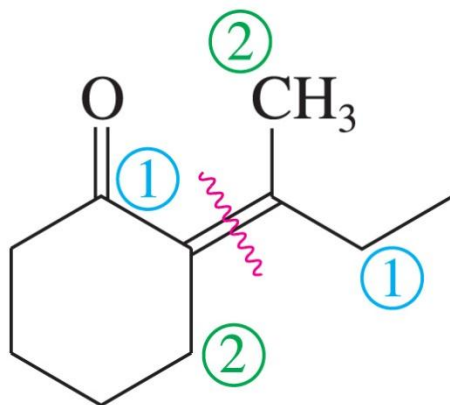


(3Z,5E)-3-bromoocta-3,5-diene

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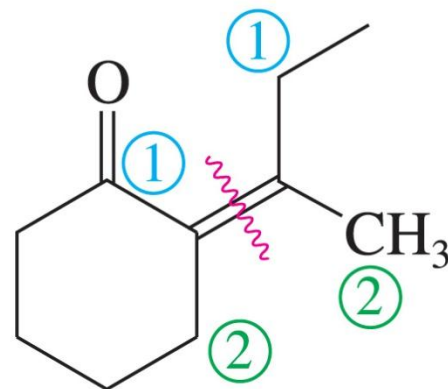
- ▶ If there is more than one double bond in the molecule, the stereochemistry of all the double bonds should be specified.

Cyclic Stereoisomers



(*E*) isomer

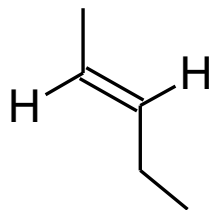
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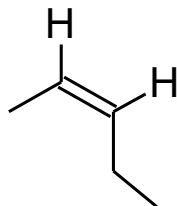
(*Z*) isomer

- ▶ Double bonds outside the ring can show stereoisomerism.

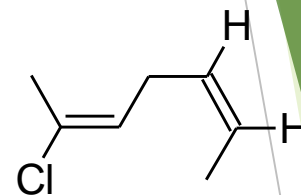
E-Z Nomenclature/Poly-enes



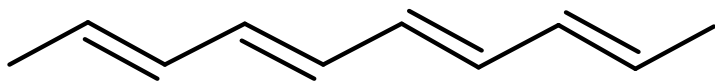
2E-penta-2-ene



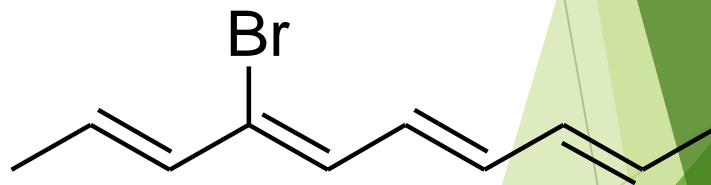
2Z-penta-2-ene



(2E,5Z)-2-chlorohepta-2,5-diene

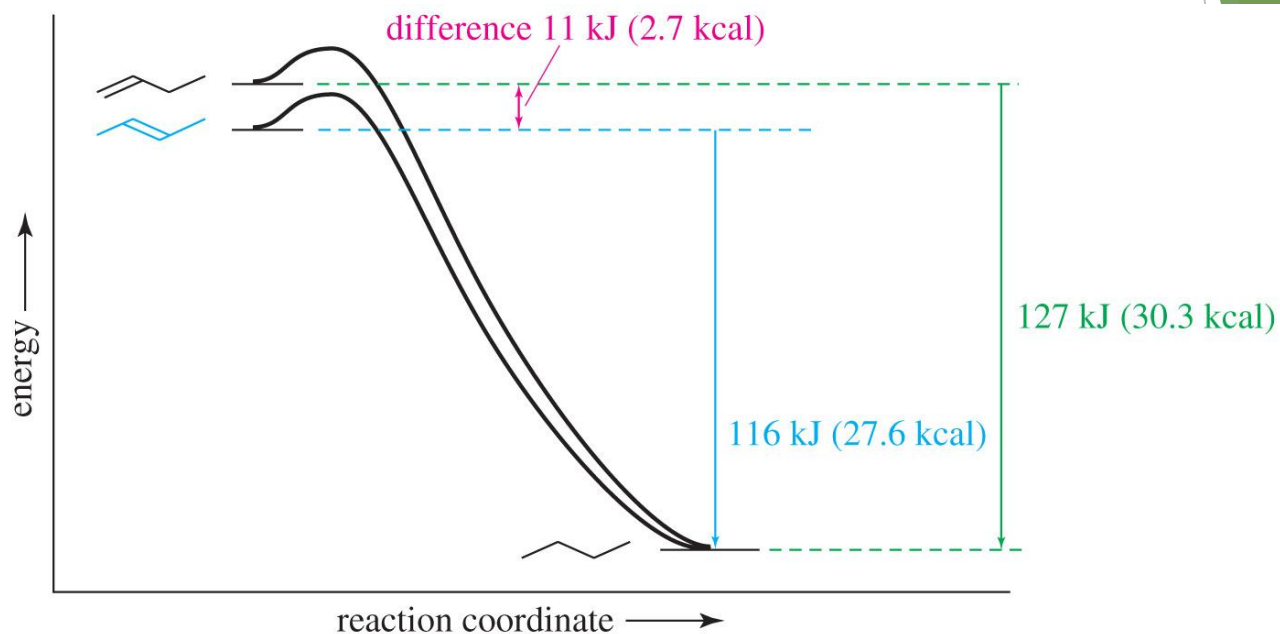


(2E,4E,6E,8E)-deca-2,4,6,8-tetraene



(2E,4Z,6E,8E)-4-bromodeca-2,4,6,8-tetraene

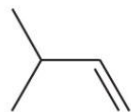
Relative Heats of Hydrogenation



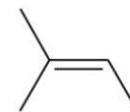
More substituted double bonds are usually more stable. Less stable alkene starts with higher potential energy, gives off more heat.

Substituent Effects

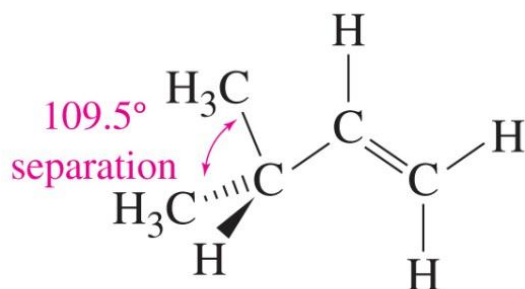
- ▶ The isomer with the more substituted double bond has a larger angular separation between the bulky alkyl groups.
- ▶ Increased angle + electron donating effects of methyl groups improve stability.



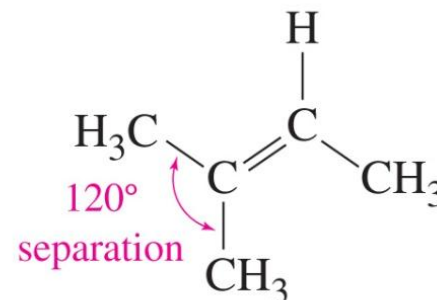
less substituted



more substituted



closer groups



wider separation

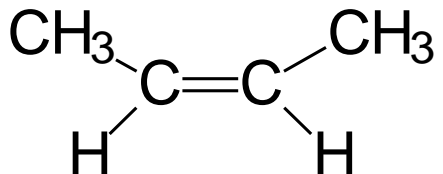
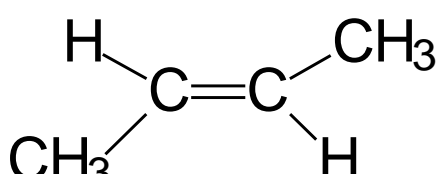
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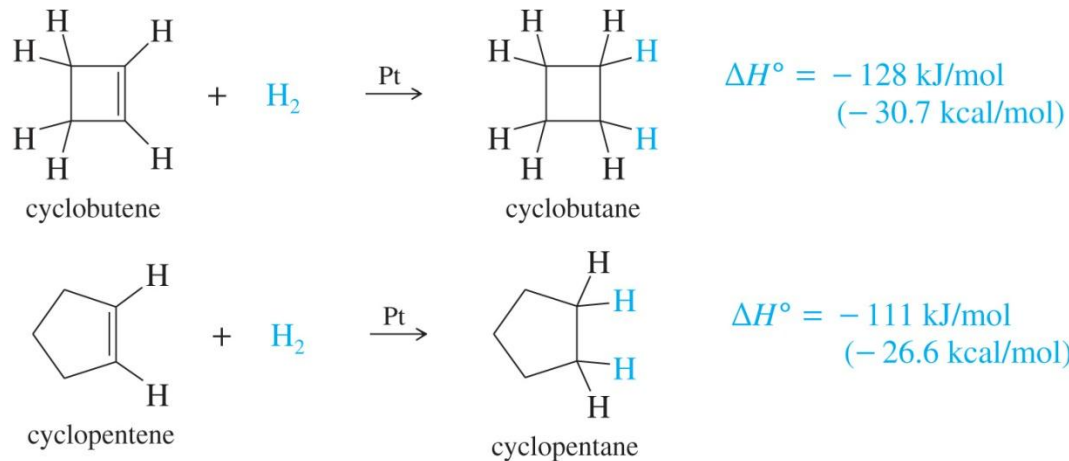
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Disubstituted Isomers

- ▶ Stability: cis < geminal < trans isomer
- ▶ The less stable isomer has a higher exothermic heat of hydrogenation.

<i>cis</i> -2-butene		-120 kJ
<i>iso</i> -butene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-117 kJ
<i>trans</i> -2-butene		-116 kJ

Cycloalkenes

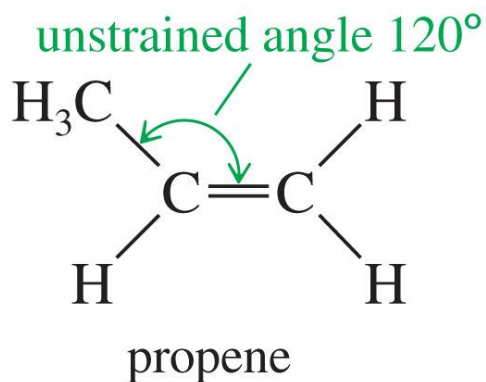


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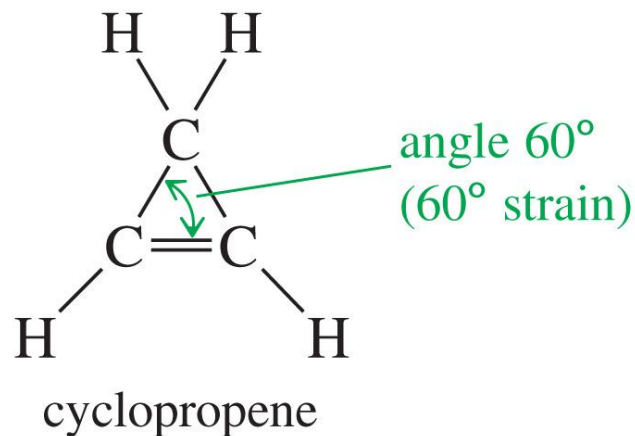
- ▶ A ring makes a major difference only if there is ring strain, either because of a small ring or because of a trans double bond.
- ▶ Rings that are five-membered or larger can easily accommodate double bonds, and these cycloalkenes react much like straight-chain alkenes.

Cyclopropene

- ▶ Cyclopropene has bond angles of about 60° , compressing the bond angles of the carbon-carbon double bond to half their usual value of 120° .
- ▶ The double bond in cyclopropene is highly strained.

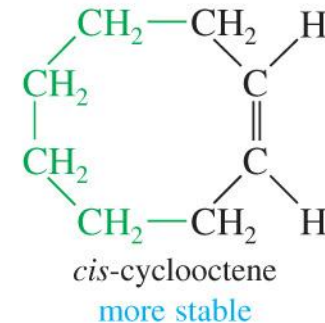
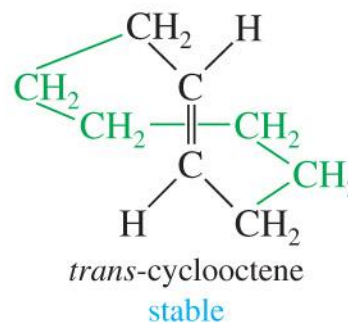
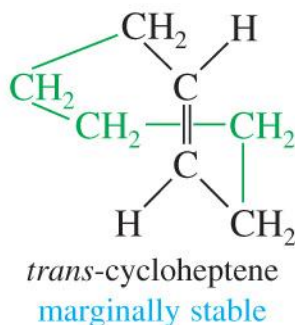
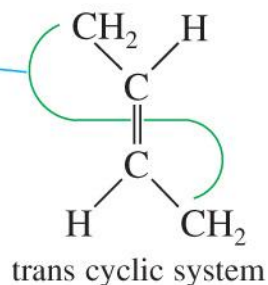


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Stability of Cycloalkenes

ring connects
behind the double bond

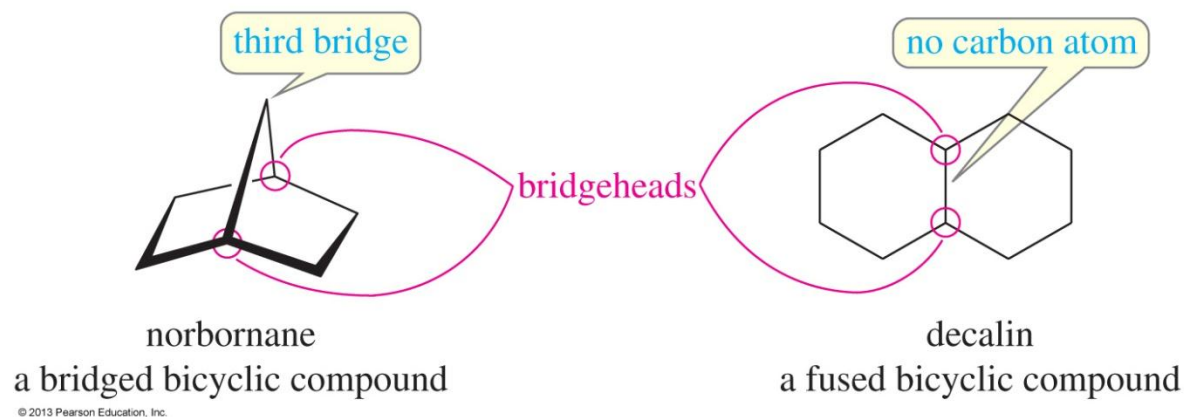


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- ▶ More difficult to make ring with trans isomer.
- ▶ Cis isomer is more stable than trans in small cycloalkenes.
- ▶ Small rings have additional ring strain.
- ▶ Must have at least eight carbons to form a stable trans double bond.
- ▶ For cyclodecene (and larger), the trans double bond is almost as stable as the cis.

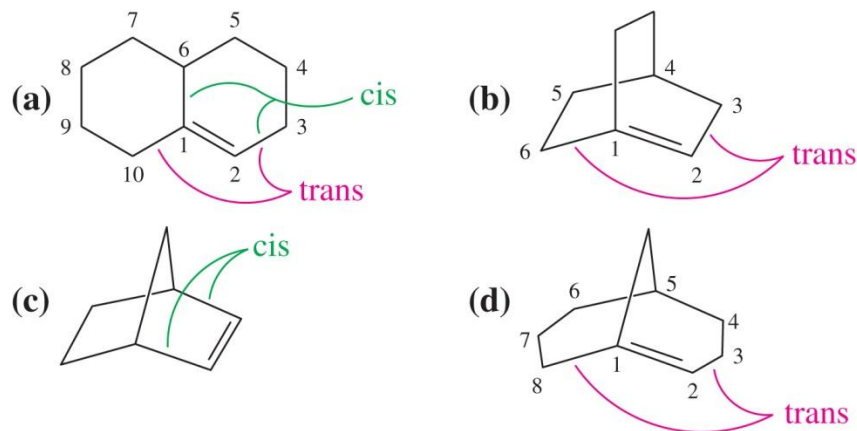
Bredt's Rule

- ▶ A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms.



Solved Problem 1

Which of the following alkenes are stable?



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Solution

Compound (a) is stable. Although the double bond is at a bridgehead, it is not a bridged bicyclic system. The trans double bond is in a ten-membered ring. Compound (b) is a Bredt's rule violation and is not stable. The largest ring contains six carbon atoms, and the trans double bond cannot be stable in this bridgehead position.

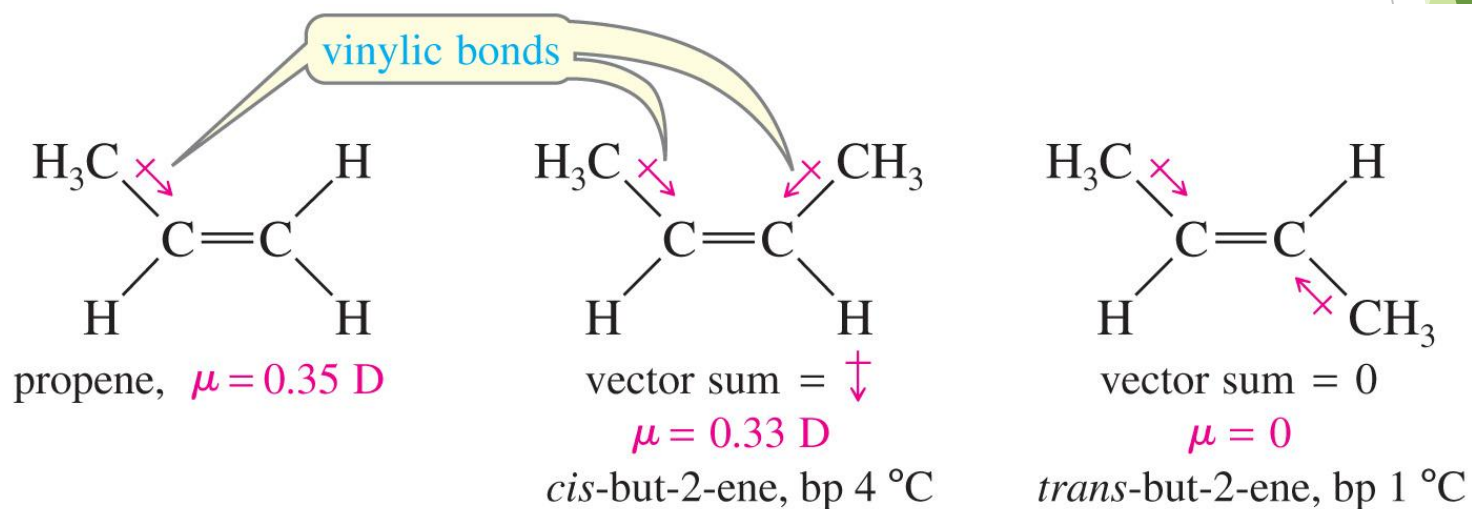
Compound (c) (norbornene) is stable. The (cis) double bond is not at a bridgehead carbon. Compound (d) is stable. Although the double bond is at the bridgehead of a bridged bicyclic system, there is an eight-membered ring to accommodate the trans double bond.

Physical Properties of Alkenes

- ▶ Low boiling points, increasing with mass.
- ▶ Branched alkenes have lower boiling points.
- ▶ Less dense than water.
- ▶ Slightly polar:
 - ▶ Pi bond is polarizable, so instantaneous dipole-dipole interactions occur.
 - ▶ Alkyl groups are electron-donating toward the pi bond, so may have a small dipole moment.

Polarity and Dipole Moments of Alkenes

- ▶ Cis alkenes have a greater dipole moment than trans alkenes, so they will be slightly polar.
- ▶ The boiling point of cis alkenes will be higher than the trans alkenes.



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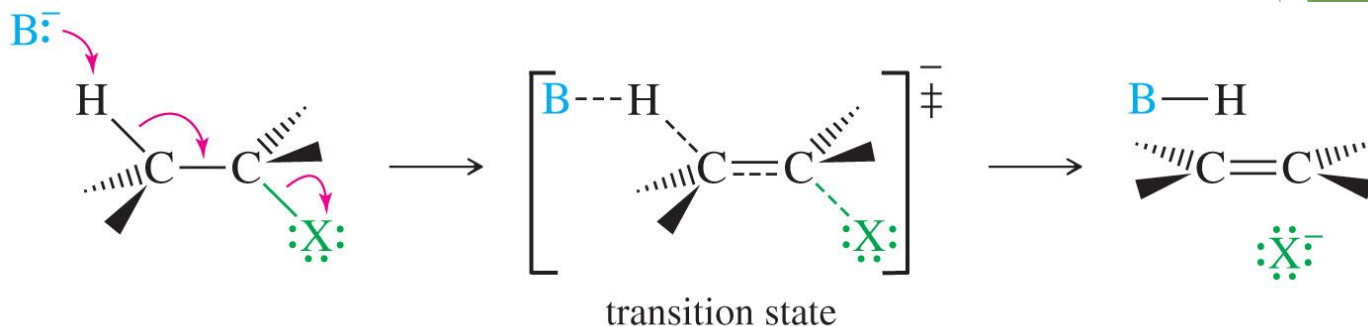
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Alkene Synthesis Overview

- ▶ E2 dehydrohalogenation (-HX)
- ▶ E1 dehydrohalogenation (-HX)
- ▶ Dehalogenation of vicinal dibromides (-X₂)
- ▶ Dehydration of alcohols (-H₂O)

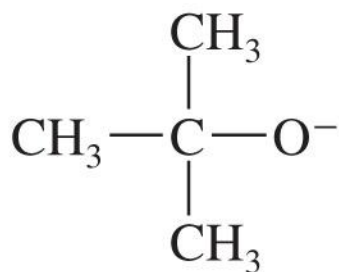
Dehydrohalogenation by the E2 Mechanism



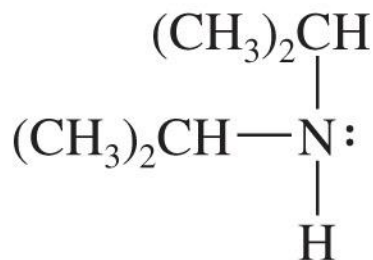
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- ▶ Strong base abstracts H^+ as double bond forms and X^- leaves from the adjacent carbon.
- ▶ Tertiary and hindered secondary alkyl halides give alkenes in good yields (S_N2 more difficult).
- ▶ Tertiary halides are the best E2 substrates because they are prone to elimination and cannot undergo S_N2 substitution.

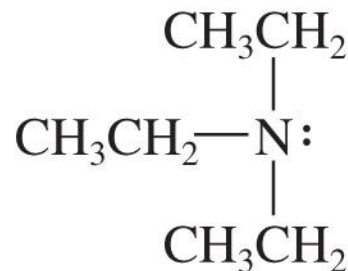
Bulky Bases Better for E2 Reactions



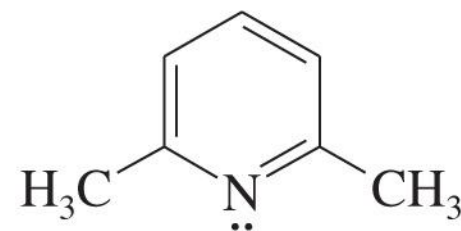
tert-butoxide



diisopropylamine



triethylamine



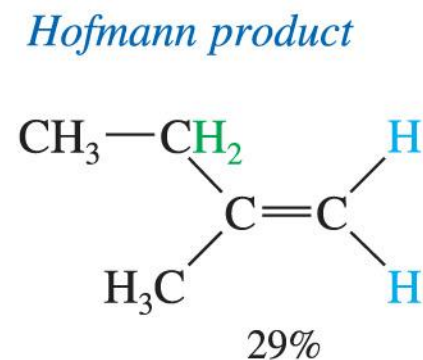
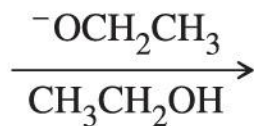
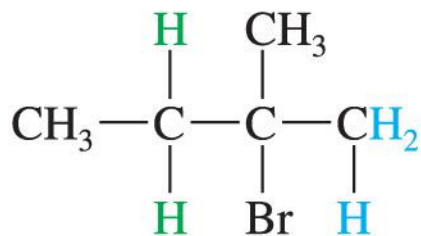
2,6-dimethylpyridine

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- ▶ If the substrate is prone to substitution, a bulky base can minimize the amount of substitution.
- ▶ Large alkyl groups on a bulky base hinder its approach to attack a carbon atom (substitution), yet it can easily abstract a proton (elimination).

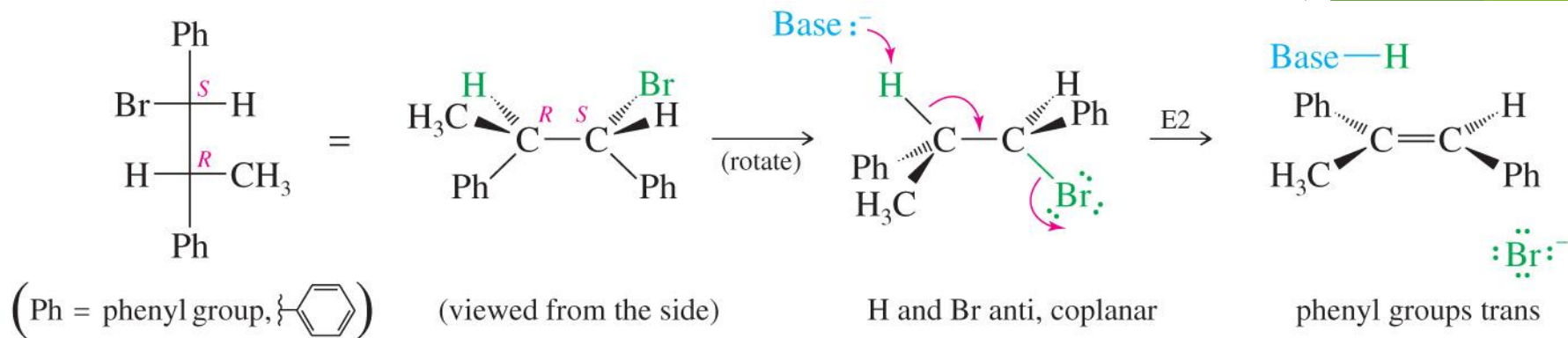
Hofmann Product

Bulky bases, such as potassium tert-butoxide, abstract the least hindered H⁺, giving the less substituted alkene as the major product (Hofmann product).



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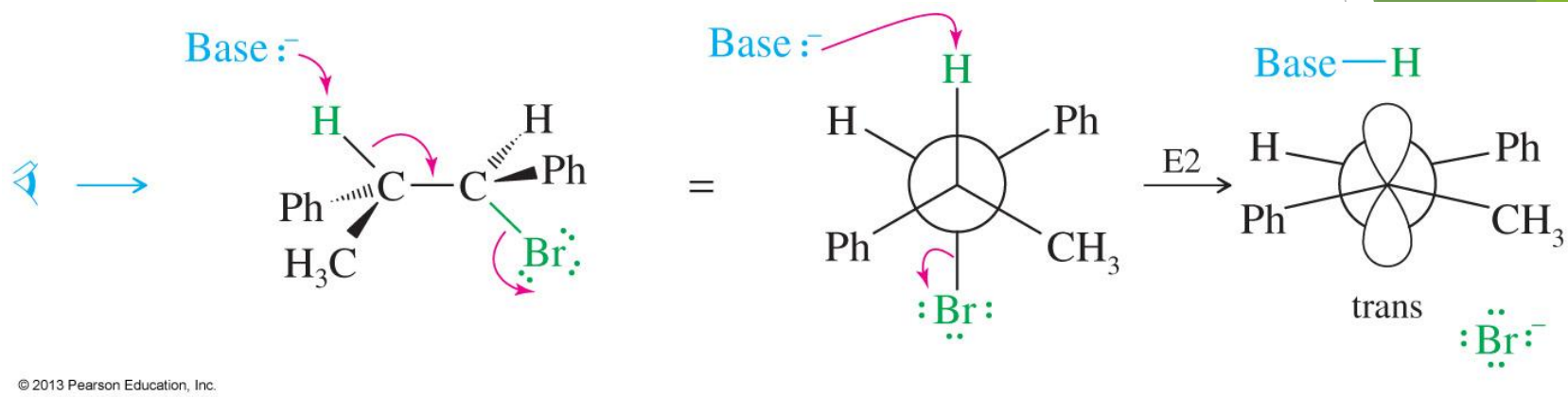
E2 Reactions Are Stereospecific



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- ▶ Depending on the stereochemistry of the alkyl halide, the E2 elimination may produce only the cis or only the trans isomer.
- ▶ The geometry of the product will depend on the anti-coplanar relationship between the proton and the leaving group.

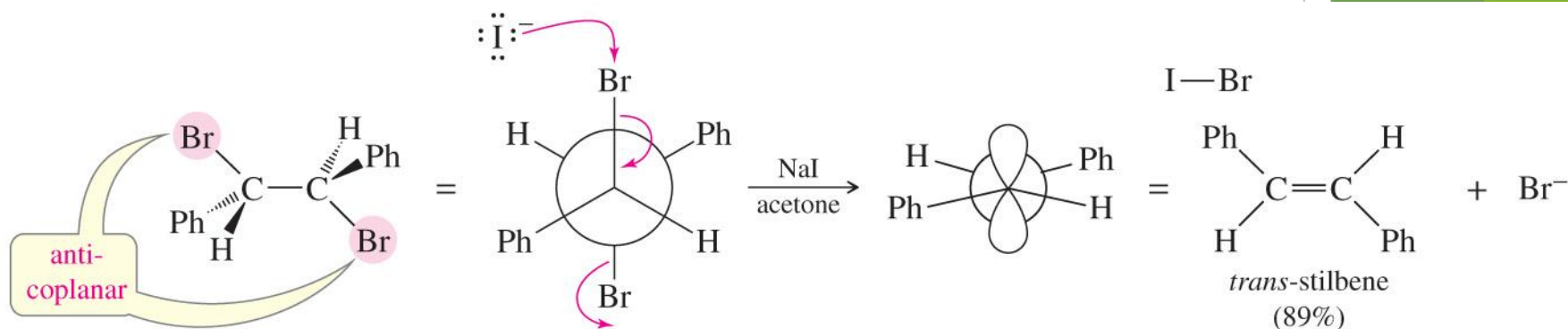
Stereochemistry of E2 Elimination



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- ▶ Most E2 reactions go through an anti-coplanar transition state.
- ▶ This geometry is most apparent if we view the reaction with the alkyl halide in a Newman projection.

E2 Debromination of a Vicinal Dibromide



meso-1,2-dibromo-1,2-diphenylethane

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- ▶ E2 debromination takes place by a concerted, stereospecific mechanism.
- ▶ Iodide ion removes one bromine atom, and the other bromine leaves as bromide ion.

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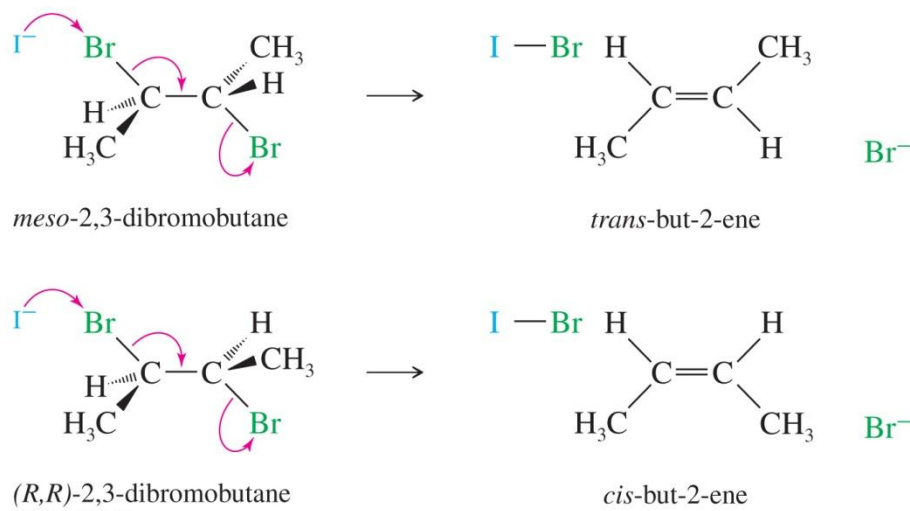
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Solved Problem 2

Show that the dehalogenation of 2,3-dibromobutane by iodide ion is stereospecific by showing that the two diastereomers of the starting material give different diastereomers of the product.

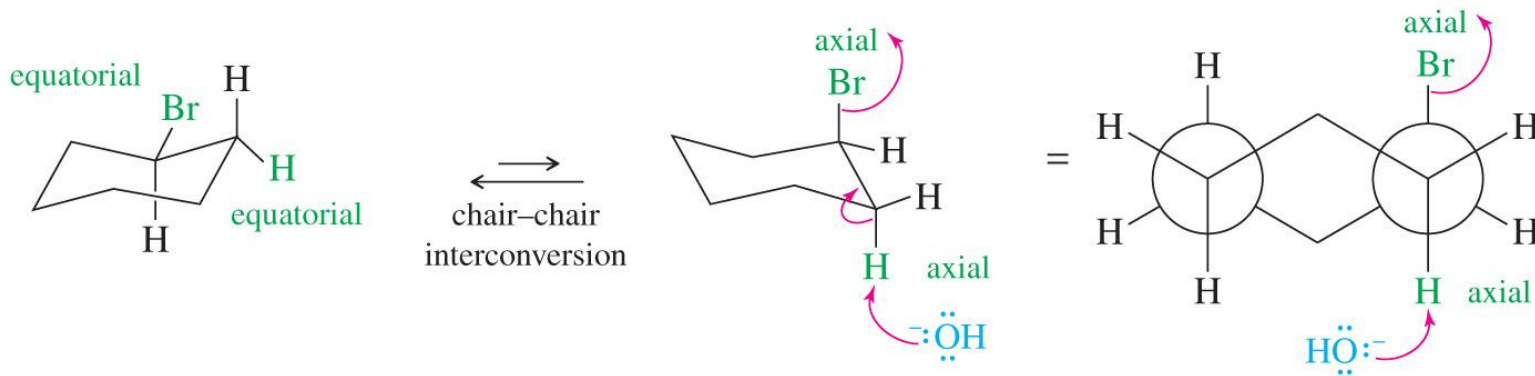
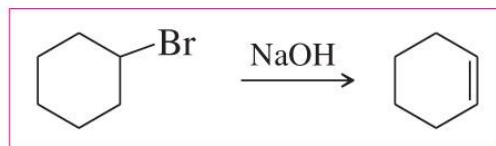
Solution

Rotating *meso*-2,3-dibromobutane into a conformation where the bromine atoms are anti and coplanar, we find that the product will be *trans*-2-butene. A similar conformation of either enantiomer of the (\pm) diastereomer shows that the product will be *cis*-2-butene. (*Hint*: Your models will be helpful.)



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E2 Reactions on Cyclohexanes

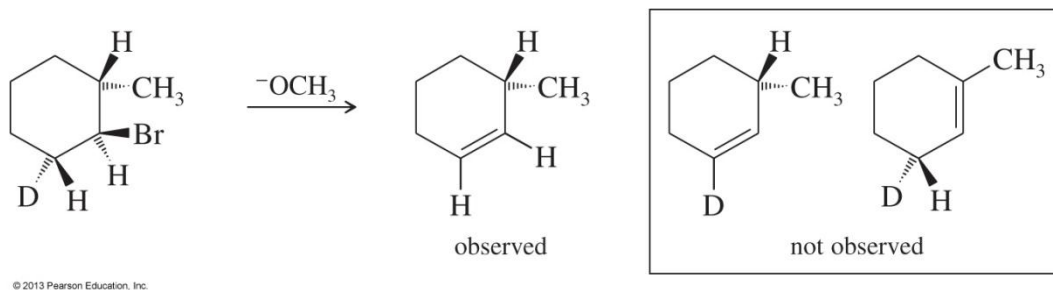


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- ▶ An anti-coplanar conformation (180°) can only be achieved when both the hydrogen and the halogen occupy axial positions.
- ▶ The chair must flip to the conformation with the axial halide in order for the elimination to take place.

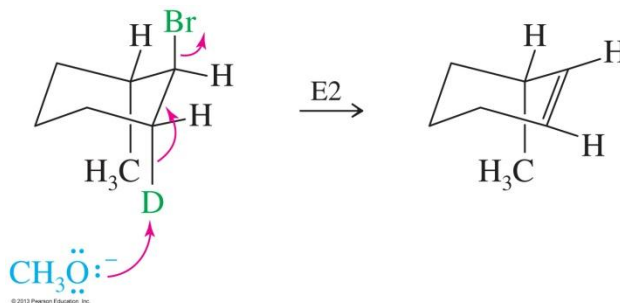
Solved Problem 3

Explain why the following deuterated 1-bromo-2-methylcyclohexane undergoes dehydrohalogenation by the E2 mechanism, to give only the indicated product. Two other alkenes are not observed.



Solution

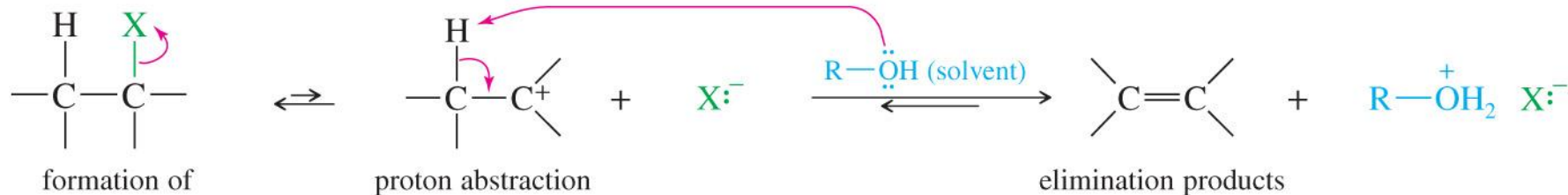
In an E2 elimination, the hydrogen atom and the leaving group must have a trans-diaxial relationship. In this compound, only one hydrogen atom—the deuterium—is trans to the bromine atom. When the bromine atom is axial, the adjacent deuterium is also axial, providing a trans-diaxial arrangement.



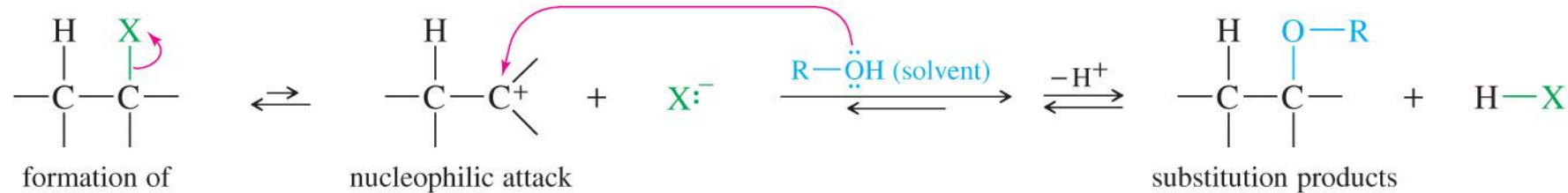
E1 Elimination Mechanism

- ▶ Better with tertiary and secondary alkyl halides:
 $3^\circ > 2^\circ$
- ▶ Carbocation intermediate.
- ▶ Rearrangements are possible.
- ▶ Works with weak nucleophiles such as water or alcohols.
- ▶ Usually have S_N1 products, too, since the solvent can attack the carbocation directly.

E1 and S_N1 Mechanisms

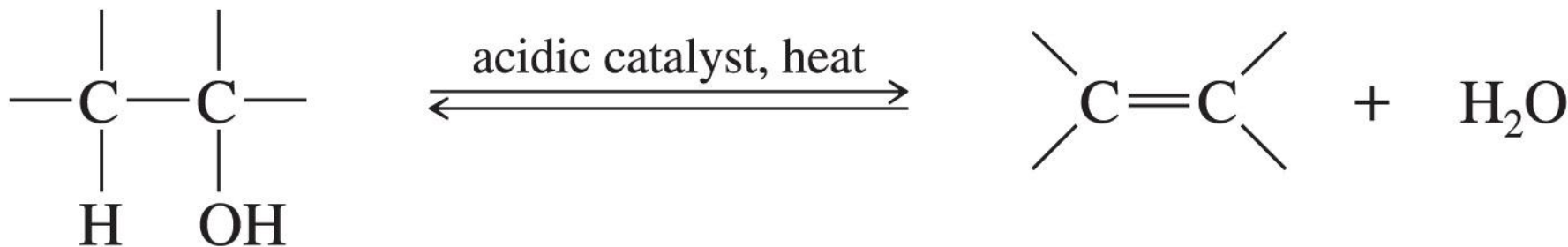


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Dehydration of Alcohols (3 step reaction)

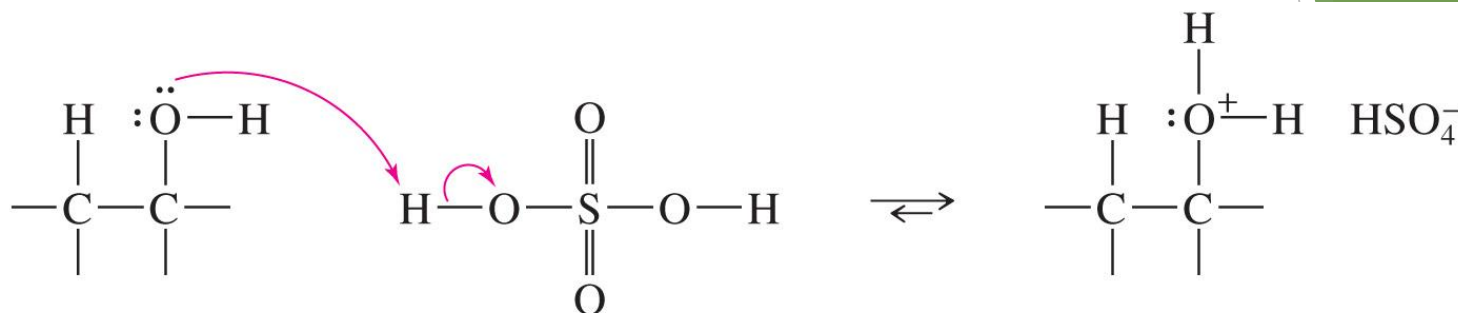


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- ▶ Use concentrated H_2SO_4 or H_3PO_4 and remove low-boiling alkene as it forms to shift the equilibrium and increase the yield of the reaction.
- ▶ E1 mechanism.
- ▶ Rearrangements are common.
- ▶ Reaction obeys Zaitsev's rule.

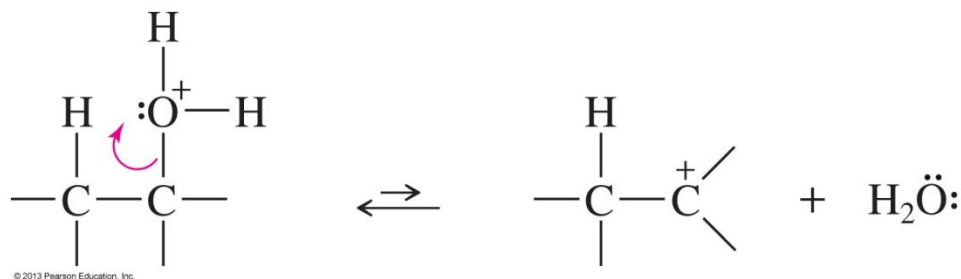
Dehydration Mechanism: E1

Step 1: Protonation of the hydroxyl group (fast equilibrium).



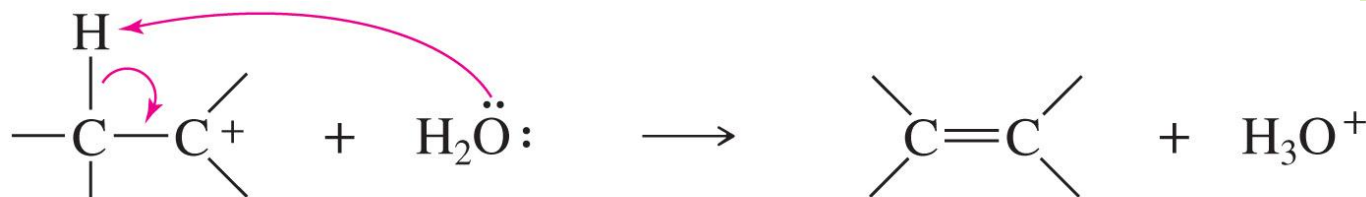
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Step 2: Ionization to a carbocation (slow; rate limiting).



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Step 3: Deprotonation to give the alkene (fast).



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HINT

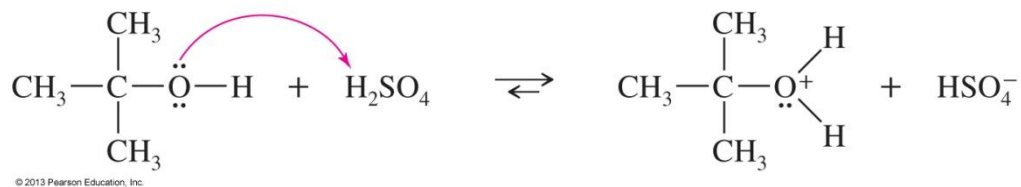
In acid-catalyzed mechanisms, the first step is often addition of H^+ , and the last step is often loss of H^+ .

Solved Problem 4

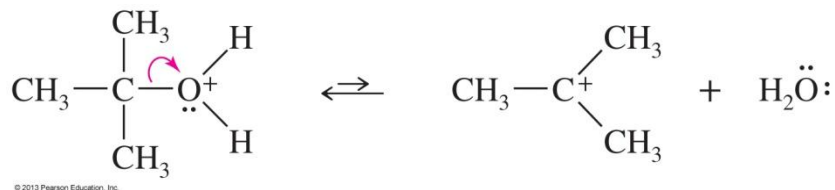
Propose a mechanism for the sulfuric acid-catalyzed dehydration of *t*-butyl alcohol.

Solution

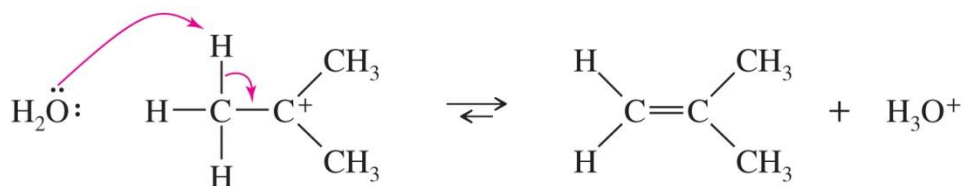
The first step is protonation of the hydroxyl group, which converts it to a good leaving group.



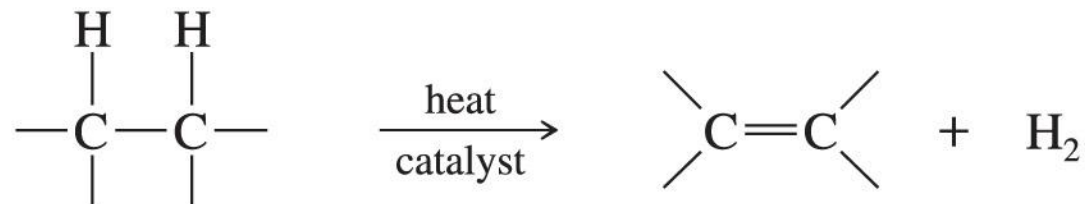
The second step is ionization of the protonated alcohol to give a carbocation.



Abstraction of a proton completes the mechanism.



Dehydrogenation of Alkanes



$$\Delta H^\circ = +80 \text{ to } +120 \text{ kJ/mol } (+20 \text{ to } +30 \text{ kcal/mol}) \quad \Delta S^\circ = +125 \text{ J/kelvin-mol}$$

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- ▶ Dehydrogenation is the removal of H₂ from a molecule, forming an alkene (the reverse of hydrogenation).
- ▶ This reaction has an unfavorable enthalpy change but a favorable entropy change.