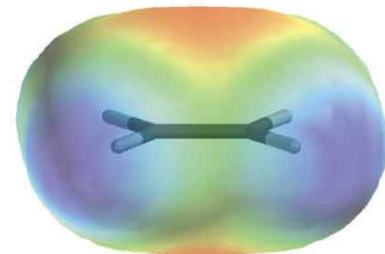


*Organic Chemistry*, 7<sup>th</sup> Edition  
L. G. Wade, Jr.



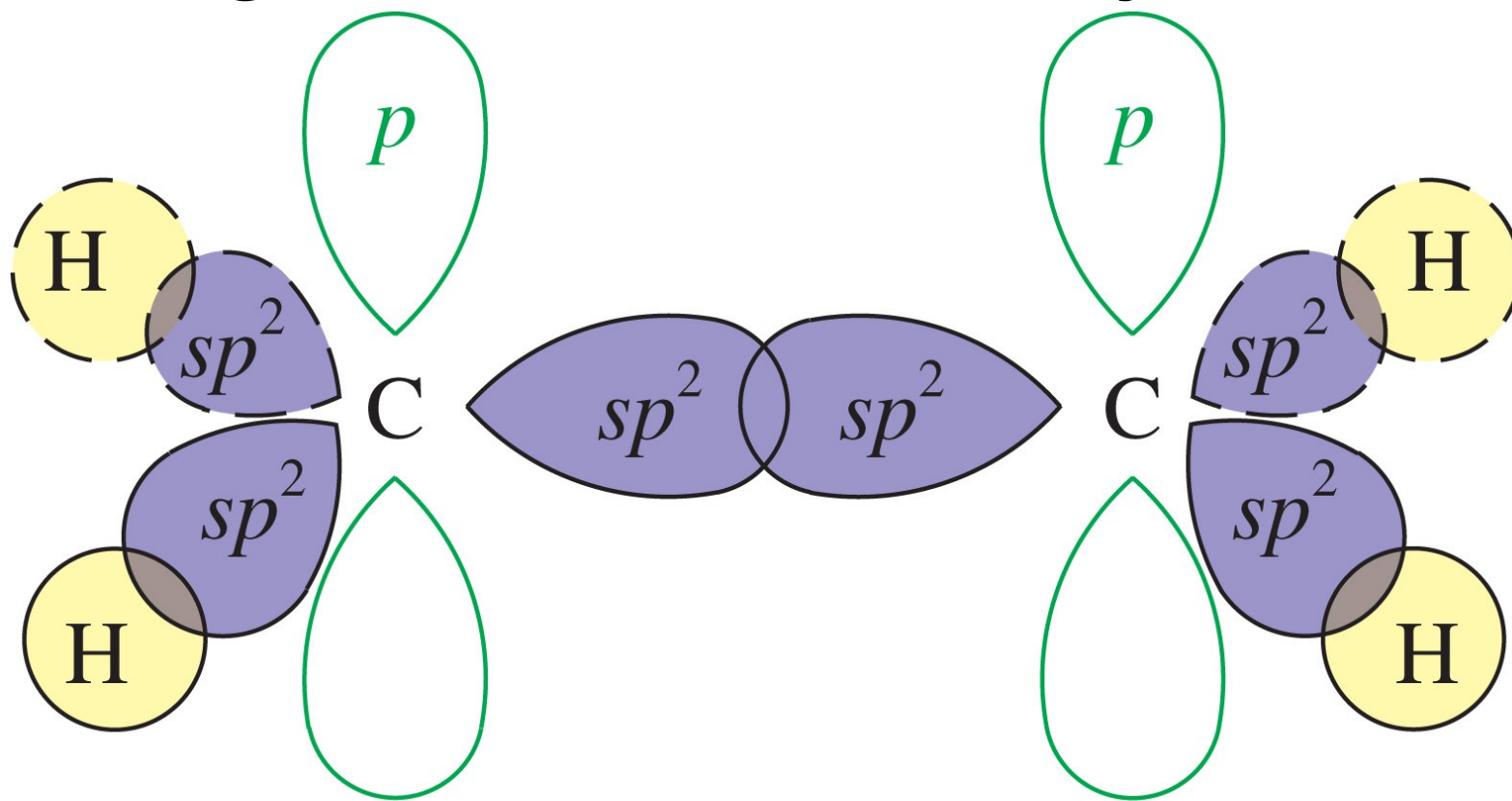
# Chapter 7

## Structure and Synthesis of Alkenes

# Introduction

- Alkenes are hydrocarbon with carbon-carbon double bonds.
- Alkenes are also called olefins, meaning “oil-forming gas”.
- The functional group of alkenes is the carbon-carbon double bond, which is reactive.

# Sigma Bonds of Ethylene



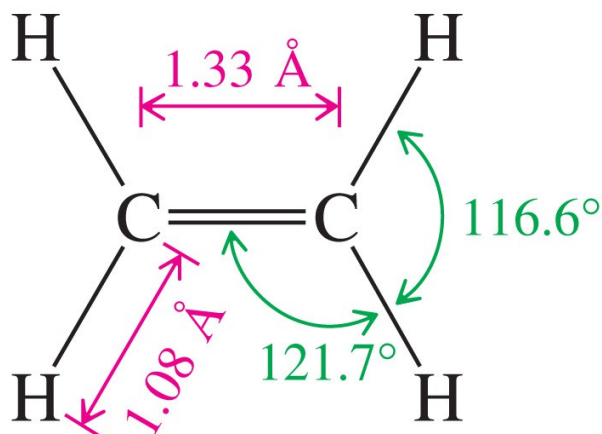
sigma bonding orbitals of ethylene

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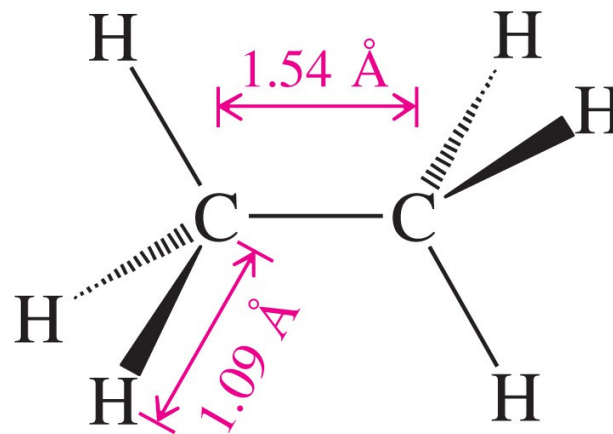
# Orbital Description

- Sigma bonds around the double-bonded carbon are  $sp^2$  hybridized.
- Angles are approximately  $120^\circ$  and the molecular geometry is trigonal planar.
- Unhybridized  $p$  orbitals with one electron will overlap forming the double bond (pi bond) .

# Bond Lengths and Angles



ethylene

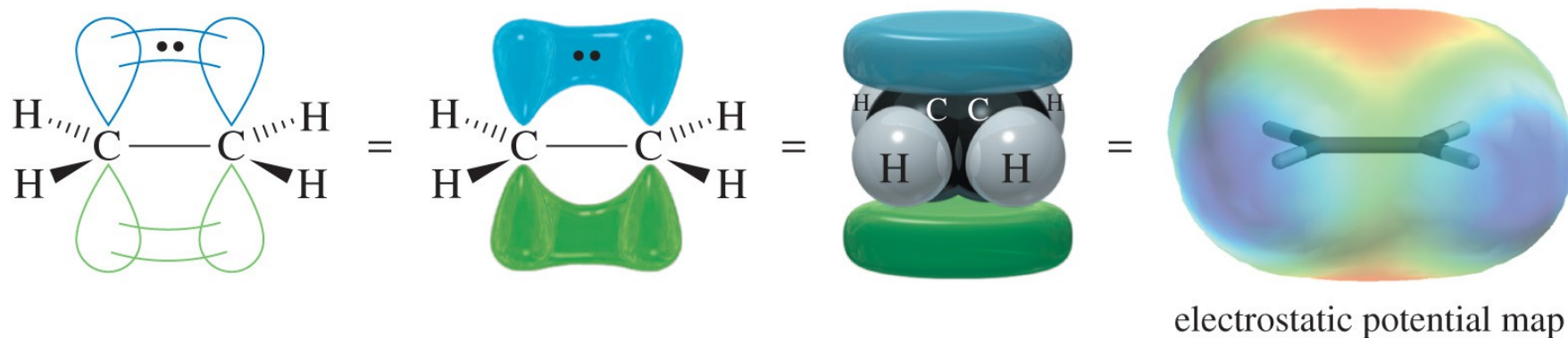


ethane

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- $sp^2$  hybrid orbitals have more s character than the  $sp^3$  hybrid orbitals.
- Pi overlap brings carbon atoms closer shortening the C—C bond from 1.54 Å in alkanes down to 1.33 Å in alkenes.

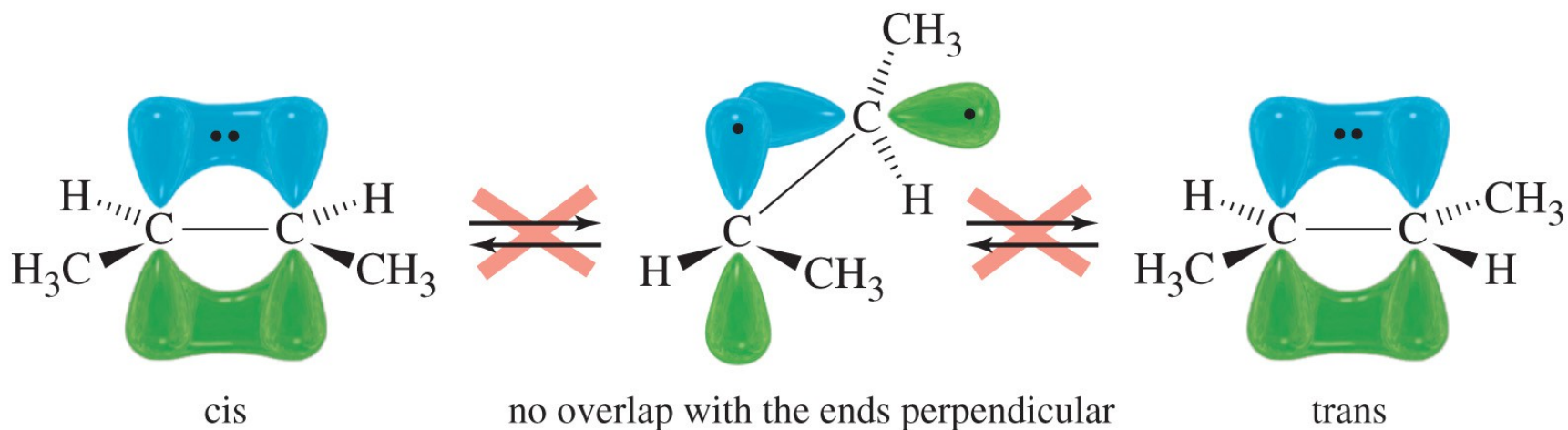
# Pi Bonding in Ethylene



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- The pi bond in ethylene is formed by overlap of the unhybridized  $p$  orbitals of the  $sp^2$  hybrid carbon atoms.
- Each carbon has one unpaired electron in the  $p$  orbital.
- This overlap requires the two ends of the molecule to be coplanar.

# Cis-Trans Interconversion



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- Cis and trans isomers cannot be interconverted.
- No rotation around the carbon—carbon bond is possible without breaking the pi bond (264 kJ/mole).

# Elements of Unsaturation

- *Unsaturation*: A structural element that decreases the number of hydrogens in the molecule by two.
- Double bonds and rings are elements of unsaturation.
- To calculate: Find number of hydrogens if they were saturated, subtract the actual number of hydrogens, then divide by 2.



# Example: Calculate the Unsaturation for a Compound with Formula C<sub>5</sub>H<sub>8</sub>.

- First calculate the number of hydrogen atoms for a saturated compound with five carbons:

$$\begin{aligned} & (2 \times C) + 2 \\ & (2 \times 5) + 2 = 12 \end{aligned}$$

- 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, or one double bond and one ring.

# Elements of Unsaturation: Heteroatoms

- Halogens replace hydrogen atoms in hydrocarbons, so when calculating unsaturations, count halides as hydrogen atoms.
- 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.

# Example: Calculate the Unsaturation for a Compound with Formula $C_4H_7Br$ .

- First calculate the number of hydrogens for a saturated compound with four carbons:

$$\begin{aligned}(2 \times C) + 2 + N \\ (2 \times 4) + 2 = 10\end{aligned}$$

- 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 Unsaturation for a Compound with Formula $C_6H_7N$ .

- 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 Nomenclature

- Find the longest continuous carbon chain that includes the double-bonded carbons.
- *-ane* changes to *-ene*.
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between Carbon 1 and Carbon 2.

# IUPAC and New IUPAC

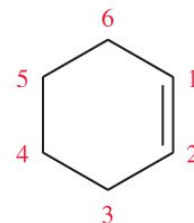
IUPAC names:  
new IUPAC names:



1-butene  
but-1-ene

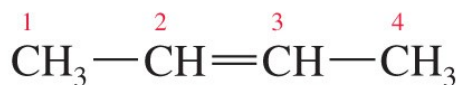


1-pentene  
pent-1-ene



cyclohexene

IUPAC names:  
new IUPAC names:



2-butene  
but-2-ene

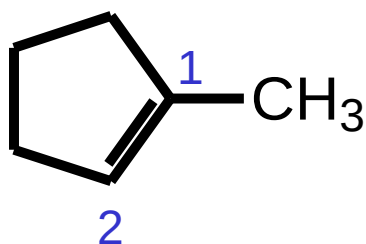


2-pentene  
pent-2-ene

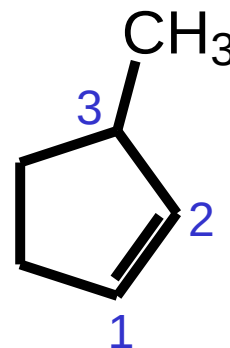
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# Ring Nomenclature

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



1-methylcyclopentene



3-methylcyclopentene

# Multiple Double Bonds



IUPAC names:

1,3-butadiene

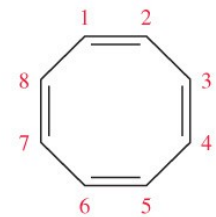
new IUPAC names:

buta-1,3-diene



1,3,5-heptatriene

hepta-1,3,5-triene



1,3,5,7-cyclooctatetraene

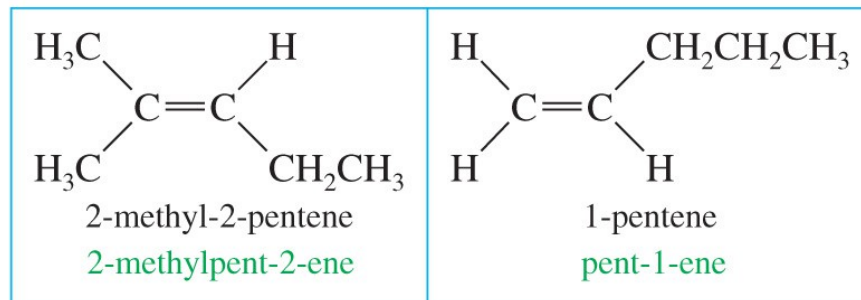
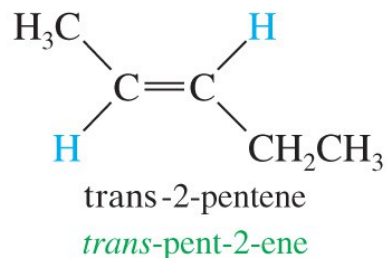
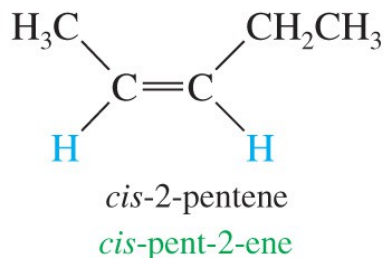
cycloocta-1,3,5,7-tetraene

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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.



# Cis-Trans Isomers



(neither *cis* nor *trans*)

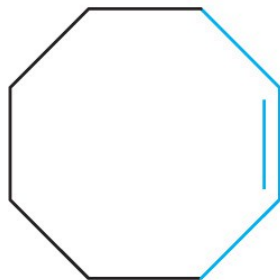
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- Similar groups on same side of double bond, alkene is *cis*.
- Similar groups on opposite sides of double bond, alkene is *trans*.
- Not all alkenes show cis-trans isomerism.

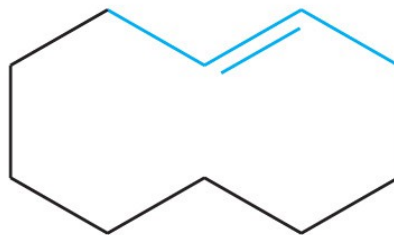
# Cyclic Compounds



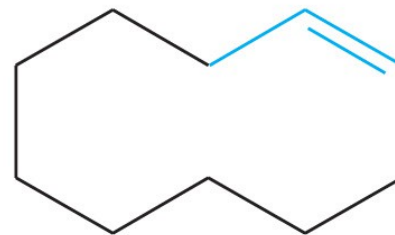
cyclohexene



cyclooctene



*trans*-cyclodecene



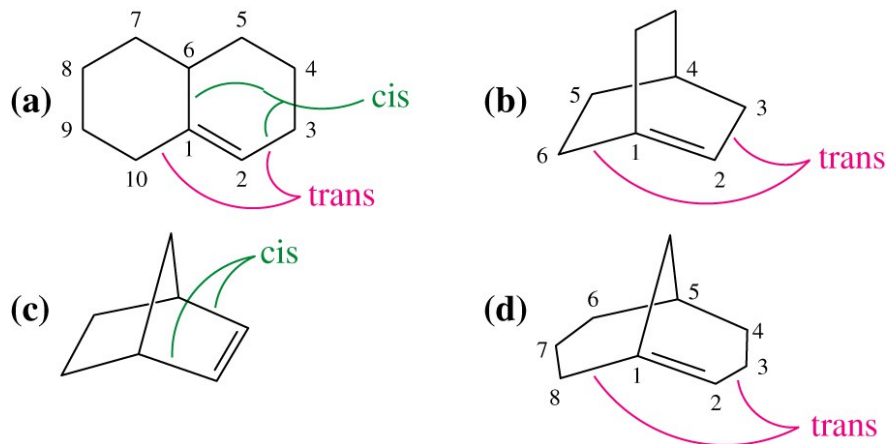
*cis*-cyclodecene

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

# Solved Problem 1

Which of the following alkenes are stable?



## Solution

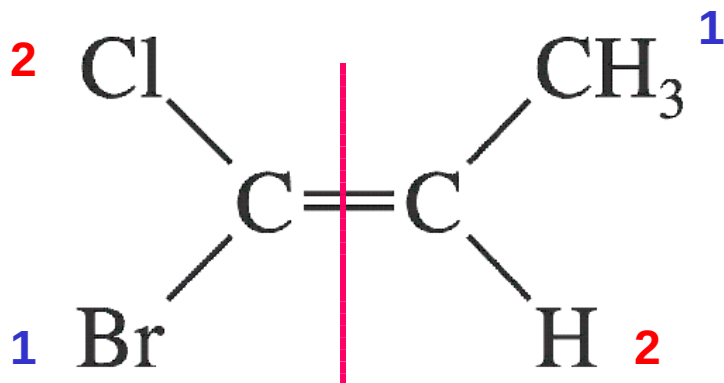
Compound (a) is stable. Although the double bond is at a bridgehead, it is not a bridged bicyclic system. The trans double bond is in a ten membered ring. Compound (b) is a Bredt's rule violation and is not stable. The largest ring contains six carbon atoms, and the trans double bond cannot be stable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

# *E-Z* Nomenclature

- 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*).

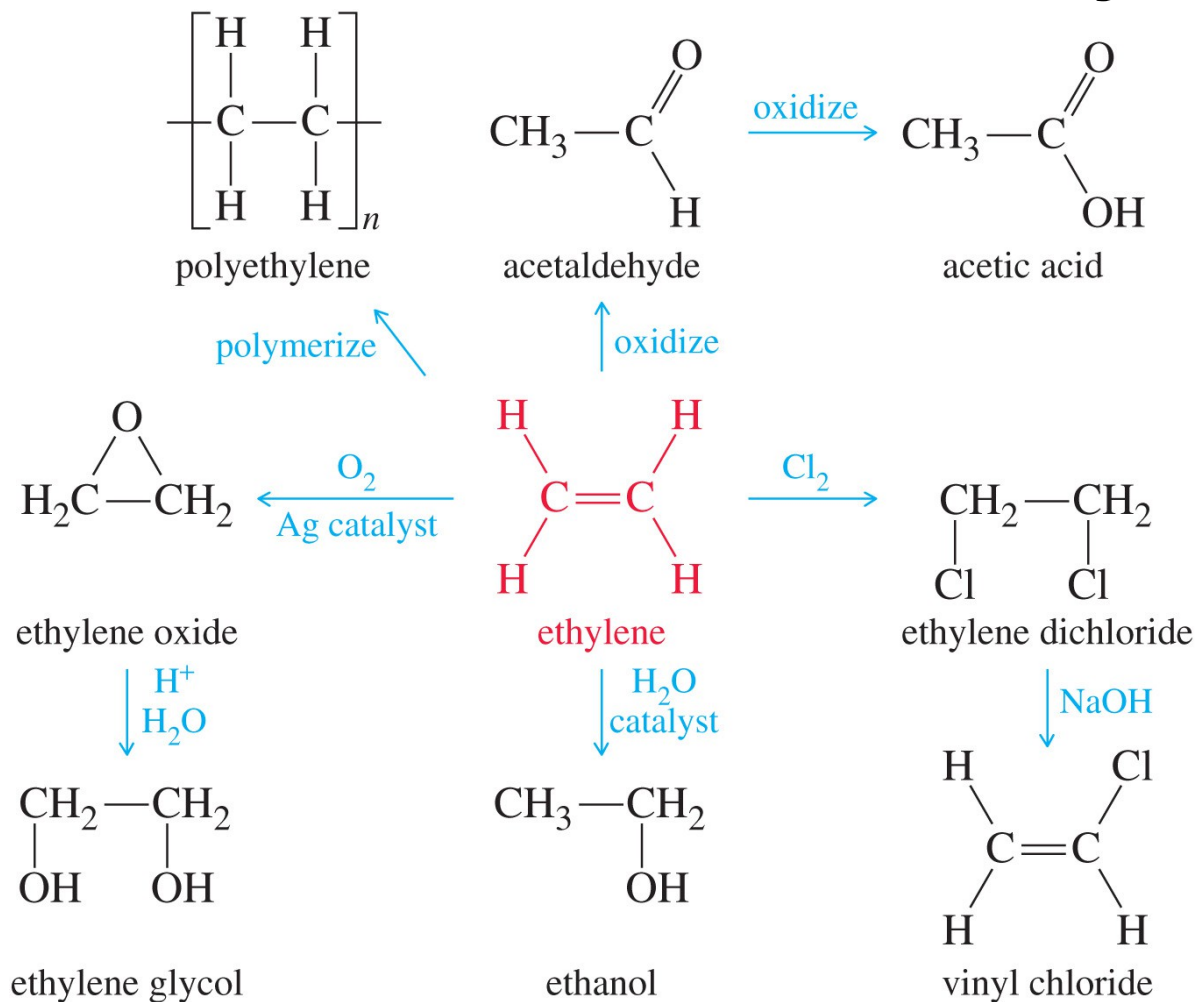
# Example



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

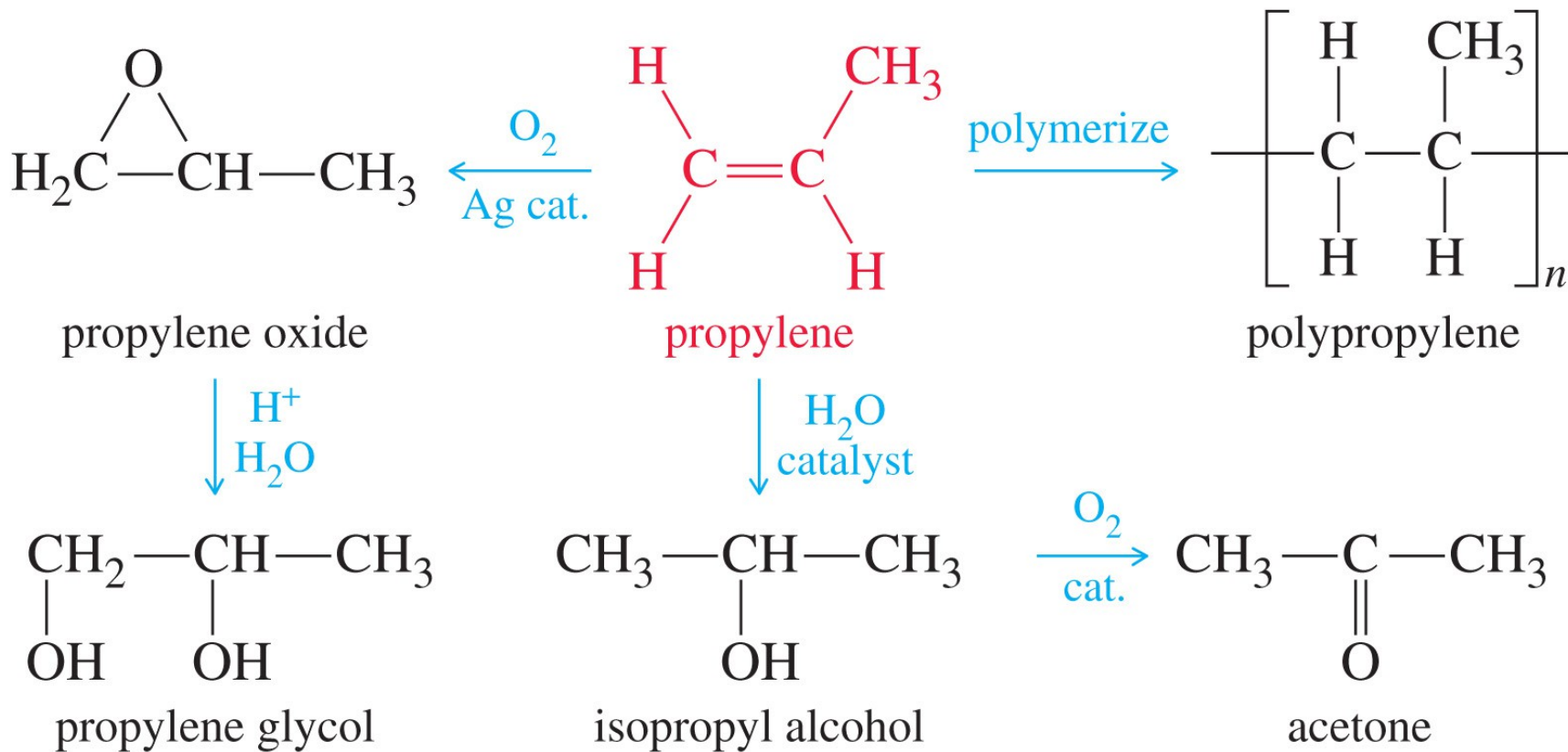
- Assign priority to the substituents according to their atomic number (1 is highest priority).
- If the highest priority groups are on opposite sides, the isomer is *E*.
- If the highest priority groups are on the same side, the isomer is *Z*.

# Commercial Uses of Ethylene



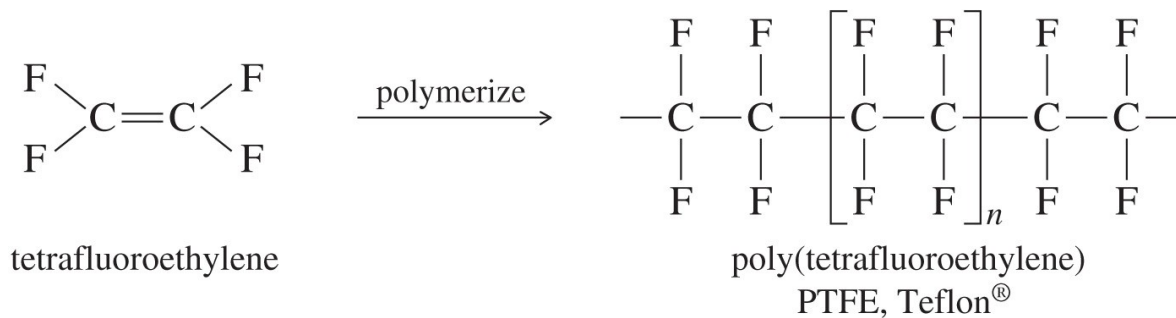
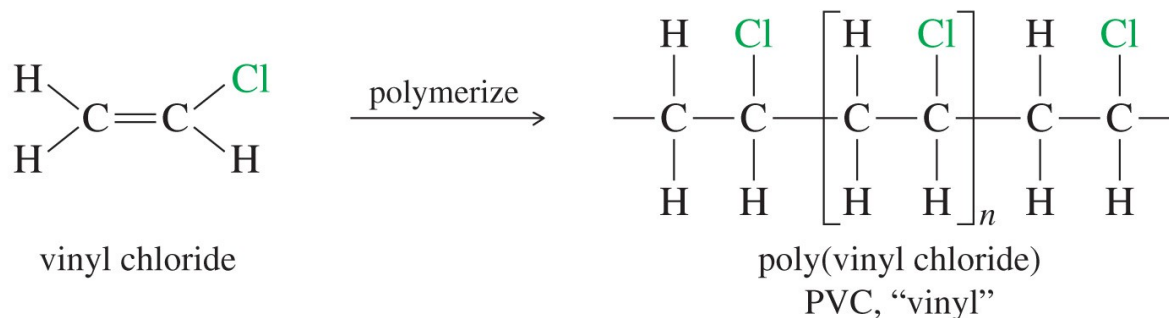
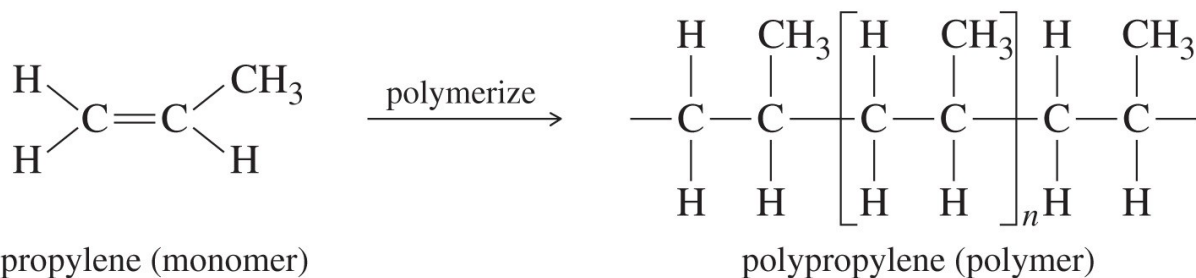
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# Commercial Uses of Propylene



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# Addition Polymers

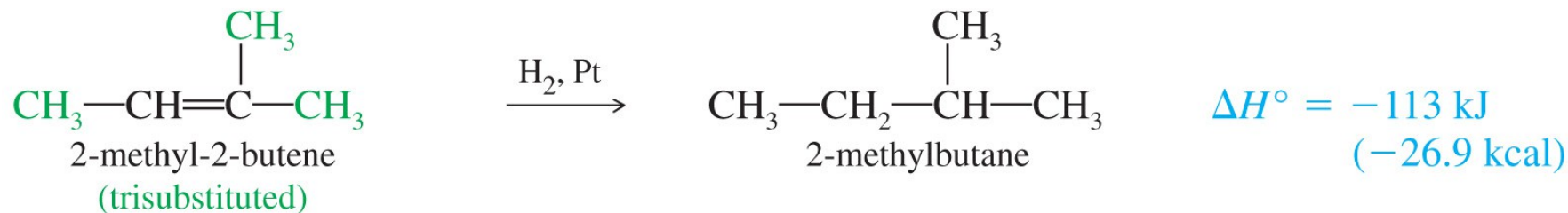
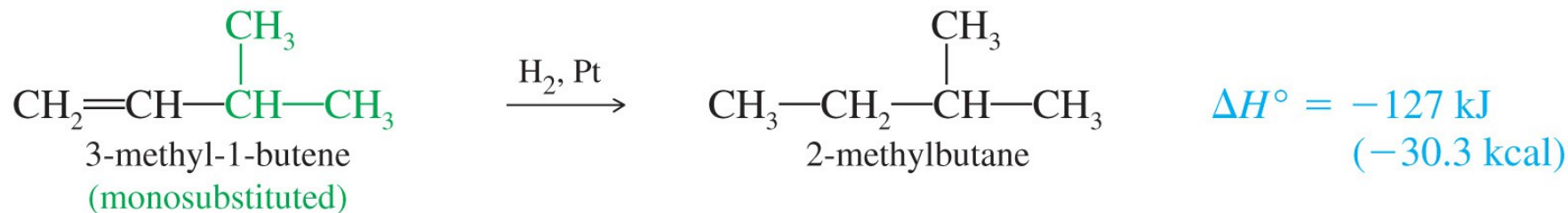


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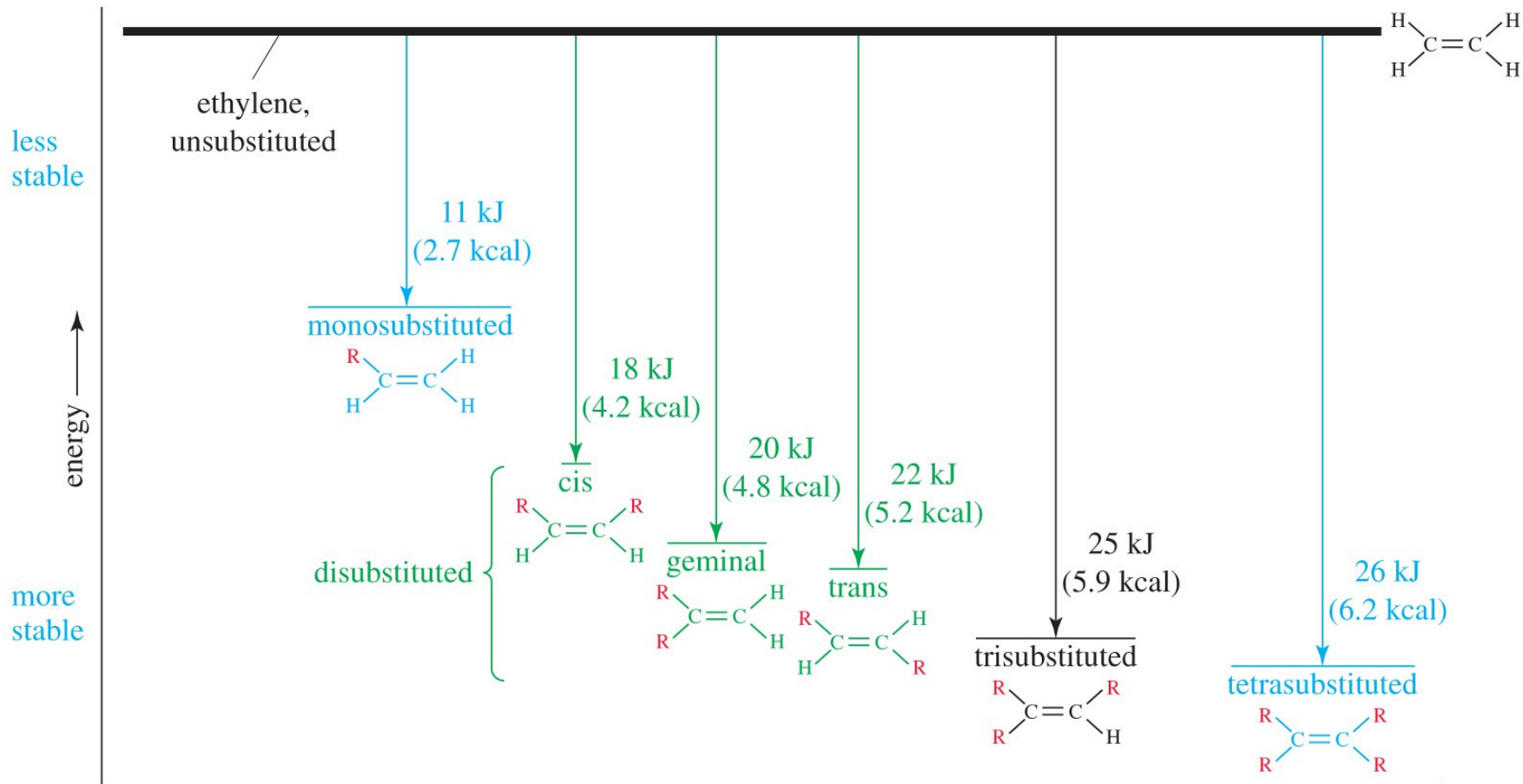
# Heat of Hydrogenation

- Combustion of an alkene and hydrogenation of an alkene can provide valuable data as to the stability of the double bond.
- The more substituted the double bond, the lower its heat of hydrogenation.



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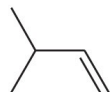
# Relative Stabilities



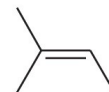
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# Substituent Effects

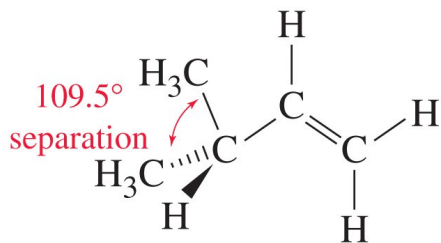
- Among constitutional isomers, more substituted double bonds are usually more stable.
- Wider separation between the groups means less steric interaction and increased stability.



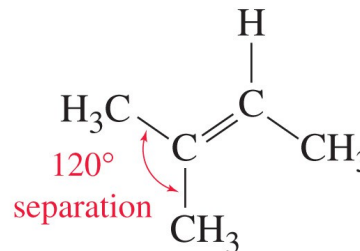
less substituted



more substituted



closer groups

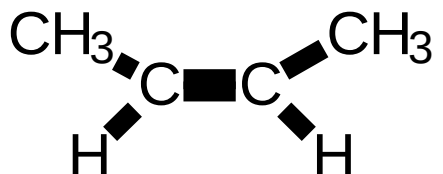
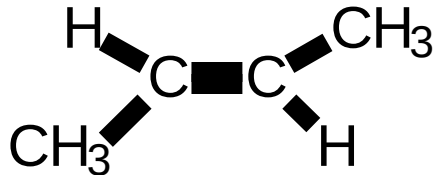


wider separation

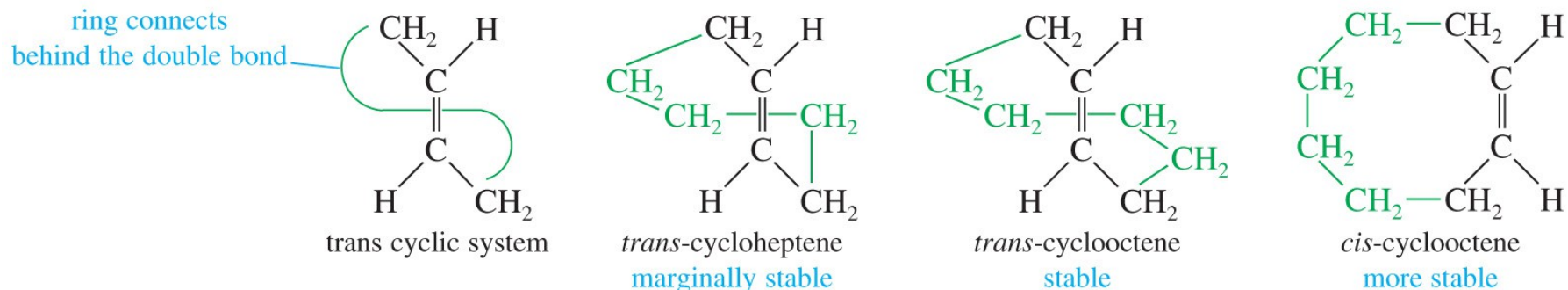
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# Disubstituted Isomers

- 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

# Stability of Cycloalkene

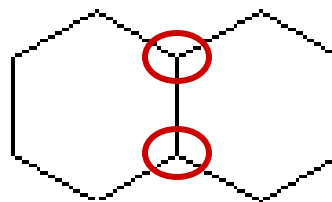
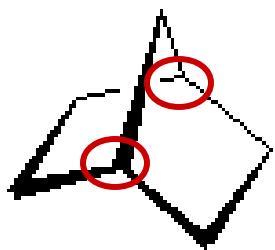


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- Cis isomer more stable than trans in small cycloalkenes.
- Small rings have additional ring strain.
- Must have at least eight carbons to form a stable trans double bond.
- For cyclodecene (and larger), the trans double bond is almost as stable as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

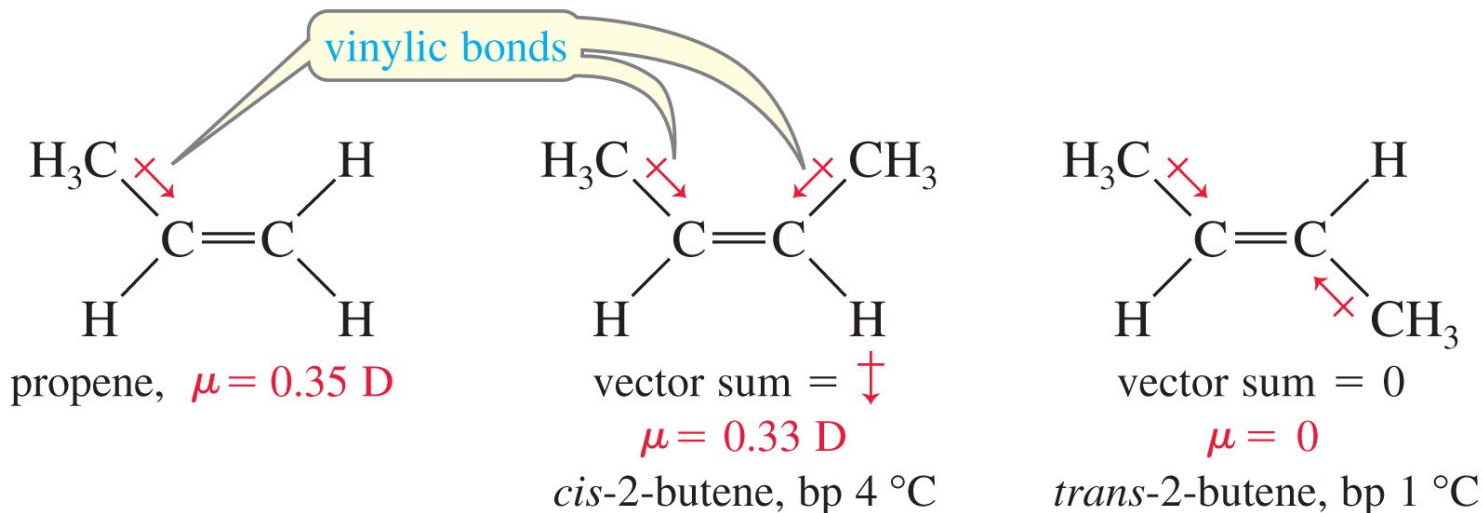


# Physical Properties of Alkenes

- 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.



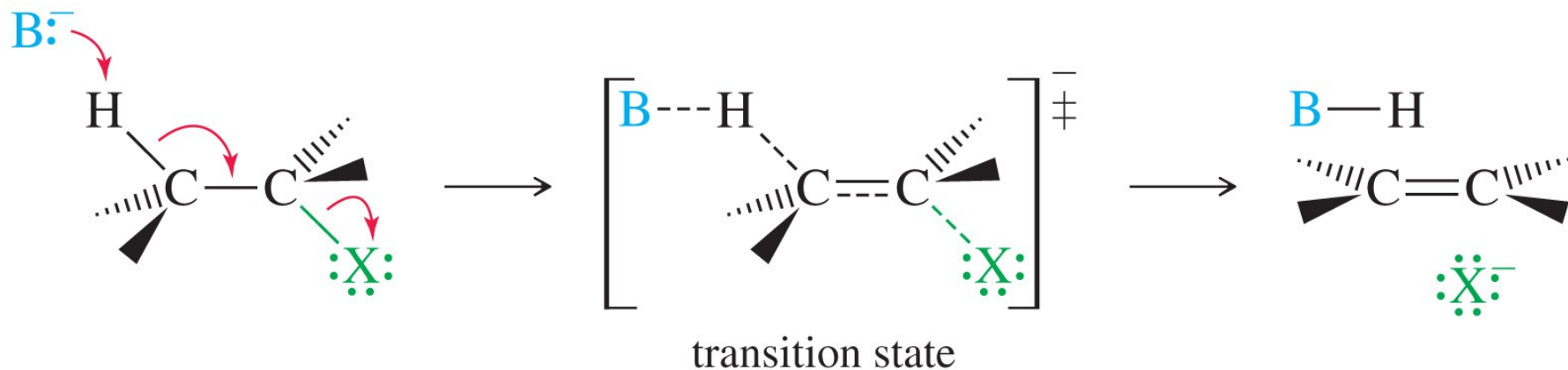
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# Alkene Synthesis Overview

- E2 dehydrohalogenation (-HX)
- E1 dehydrohalogenation (-HX)
- Dehalogenation of vicinal dibromides (-X<sub>2</sub>)
- Dehydration of alcohols (-H<sub>2</sub>O)

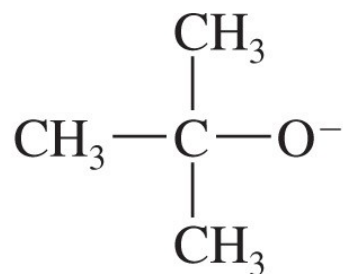
# Dehydrohalogenation by the E2 Mechanism



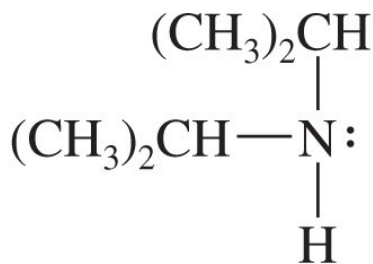
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- Strong base abstracts  $\text{H}^+$  as double bond forms and  $\text{X}^-$  leaves from the adjacent carbon.
- Tertiary and hindered secondary alkyl halides give good yields.

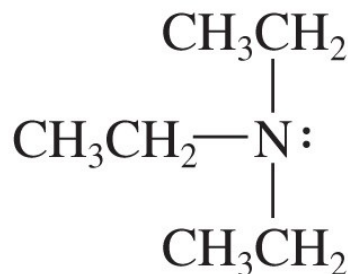
# Bulky Bases for E2 Reactions



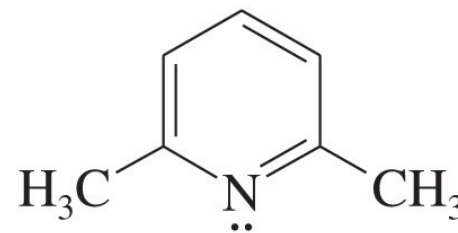
*tert*-butoxide



diisopropylamine



triethylamine



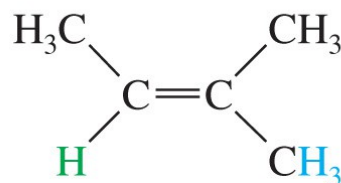
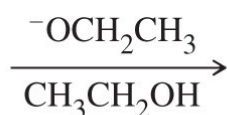
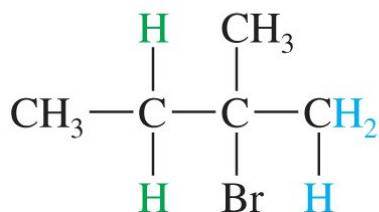
2,6-dimethylpyridine

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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 Products

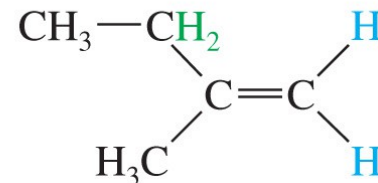
Bulky bases, such as potassium tert-butoxide, abstract the least hindered H<sup>+</sup> giving the less substituted alkene as the major product (Hofmann product).



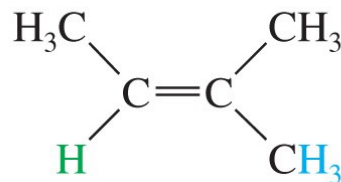
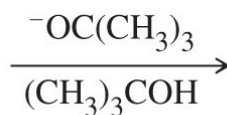
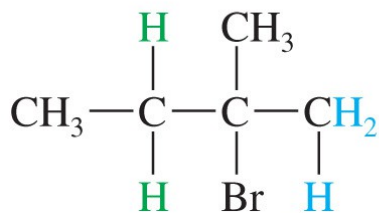
71%

*Zaitsev product*

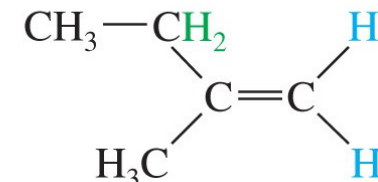
*Hofmann product*



29%



28%

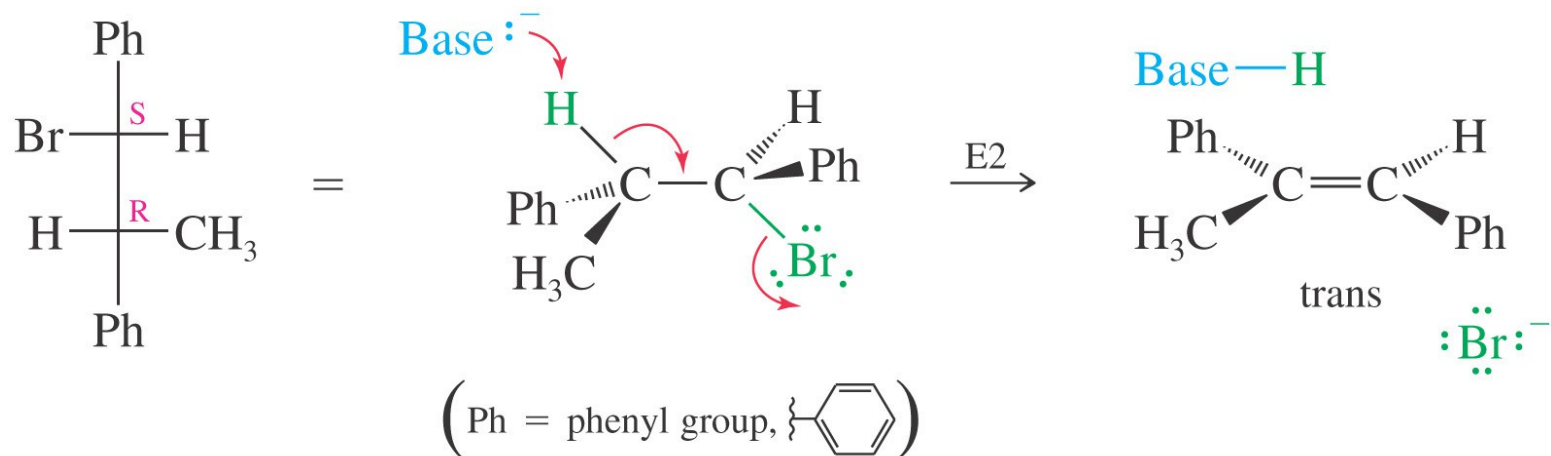


72%

less hindered

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# Stereochemistry of E2 Elimination



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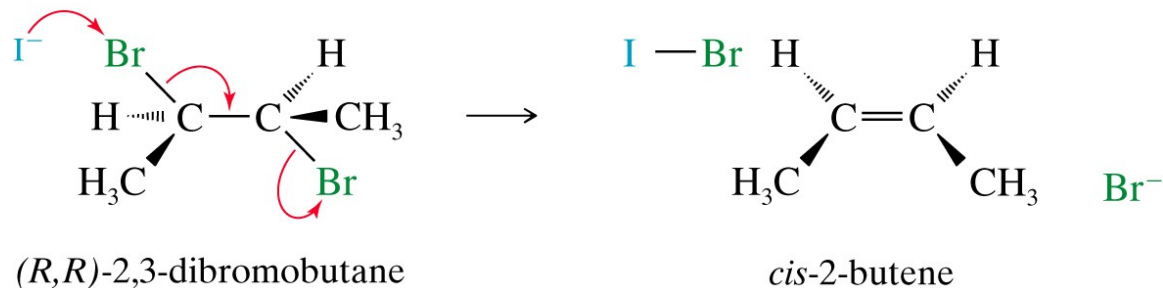
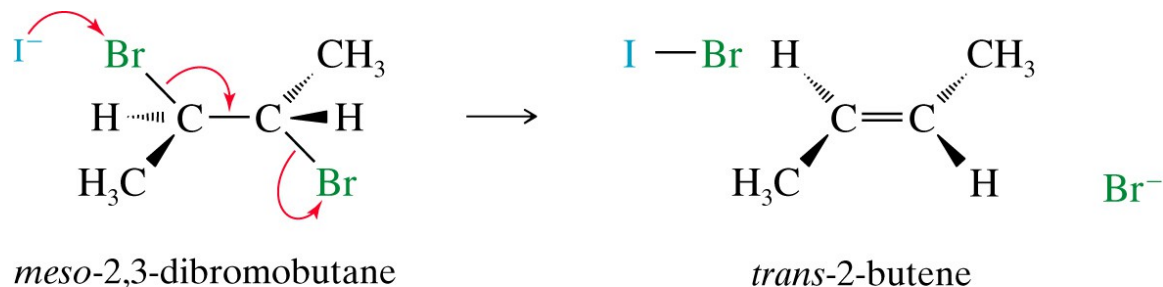
- Depending on the stereochemistry of the alkyl halide, the E2 elimination may produce only the cis or only the trans isomer.
- The geometry of the product will depend on the anti-coplanar relationship between the proton and the leaving group.

# Solved Problem 2

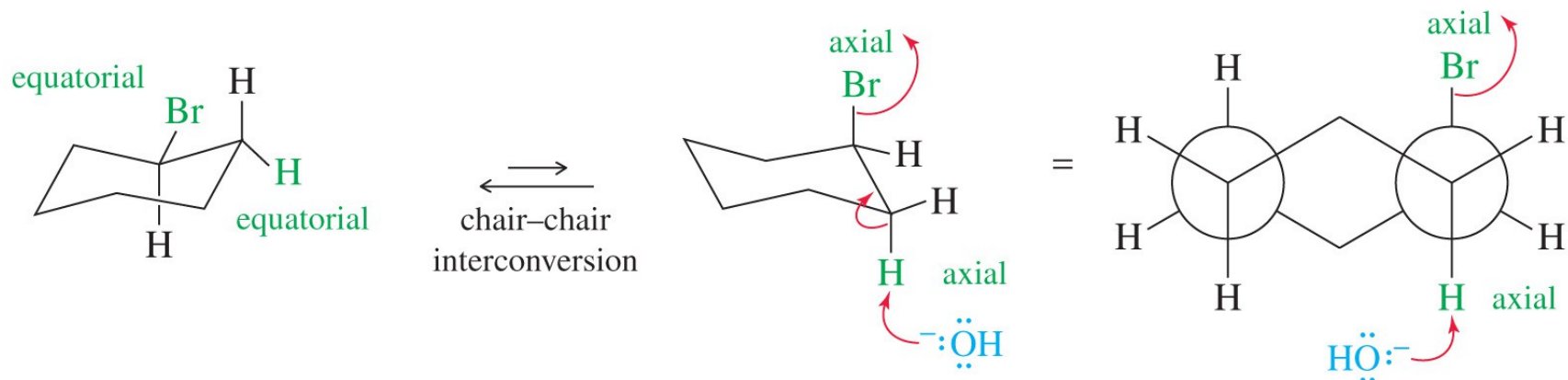
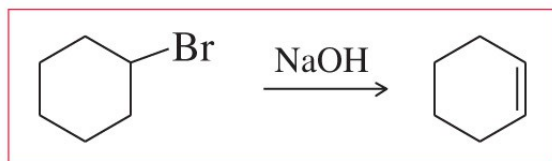
Show that the dehalogenation of 2,3-dibromobutane by iodide ion is stereospecific by showing that the two diastereomers of the starting material give different diastereomers of the product.

## 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.)



# E2 Reactions on Cyclohexanes

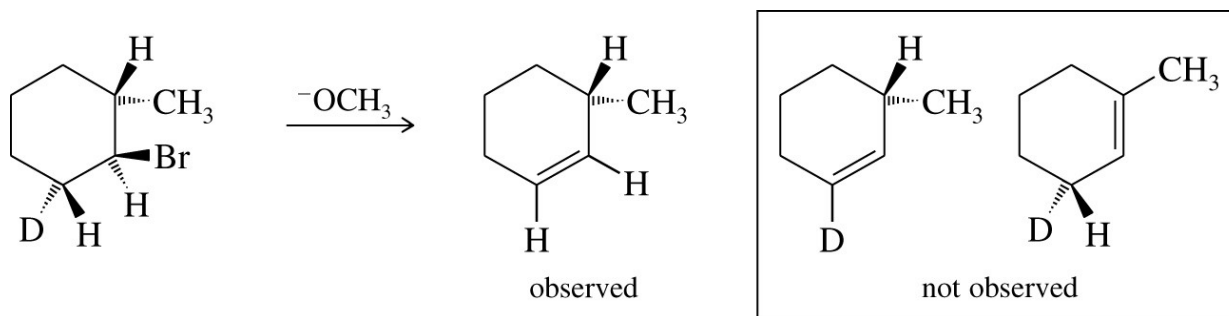


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- An anti-coplanar conformation ( $180^\circ$ ) can only be achieved when both the hydrogen and the halogen occupy axial positions.
- The chair must flip to the conformation with the axial halide in order for the elimination to take place.

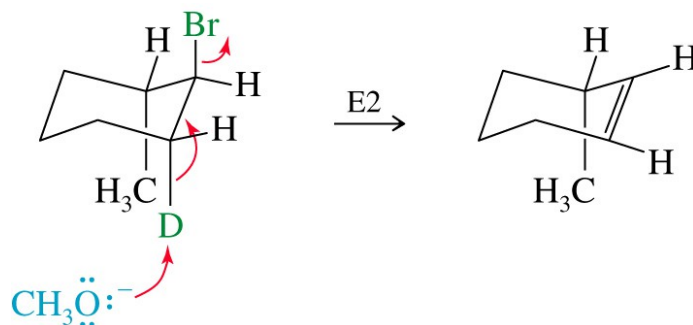
# Solved Problem 3

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.



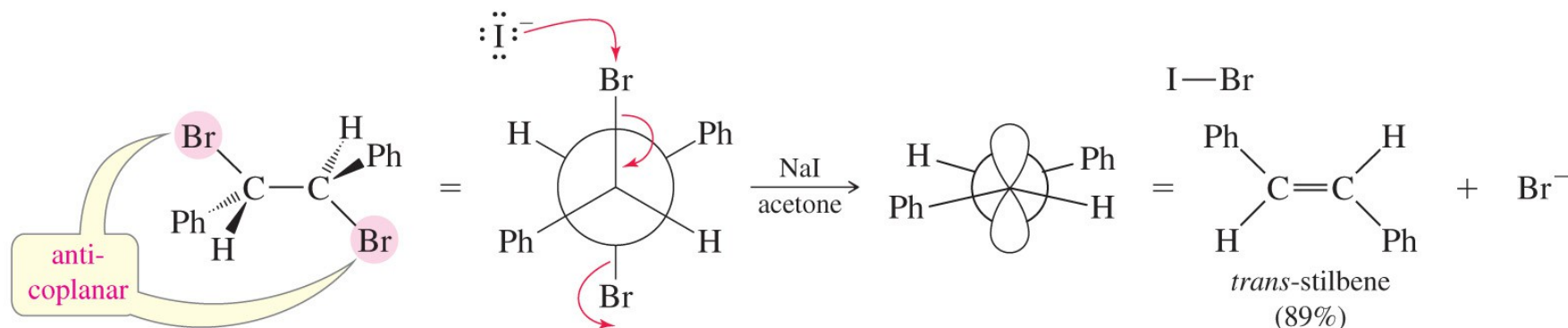
## Solution

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.





# Dehalogenation of Vicinal Dibromides



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

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- Remove  $\text{Br}_2$  from adjacent carbons.
- Bromines must be anti-coplanar (E2).
- Use NaI in acetone, or Zn in acetic acid.

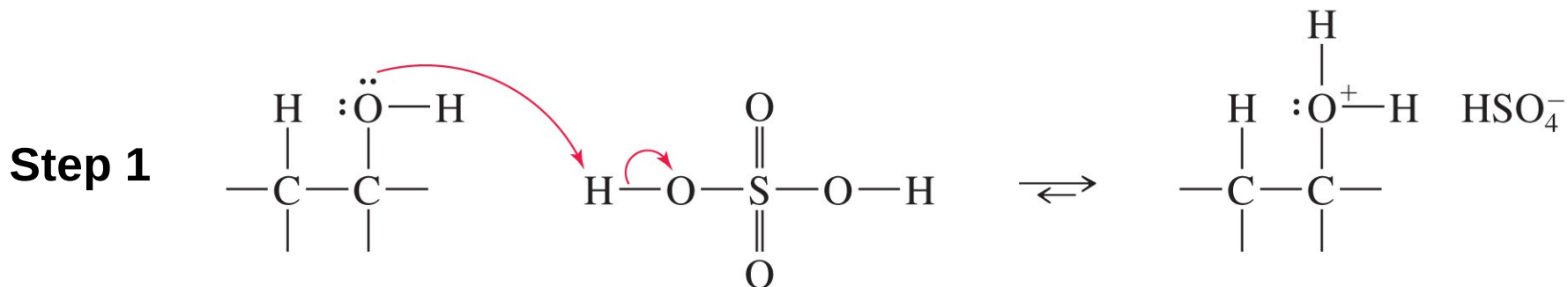
# E1 Elimination Mechanism

- Tertiary and secondary alkyl halides:  
 $3^\circ > 2^\circ$
- A carbocation is the intermediate.
- Rearrangements are possible.
- Weak nucleophiles such as water or alcohols.
- Usually have substitution products too.

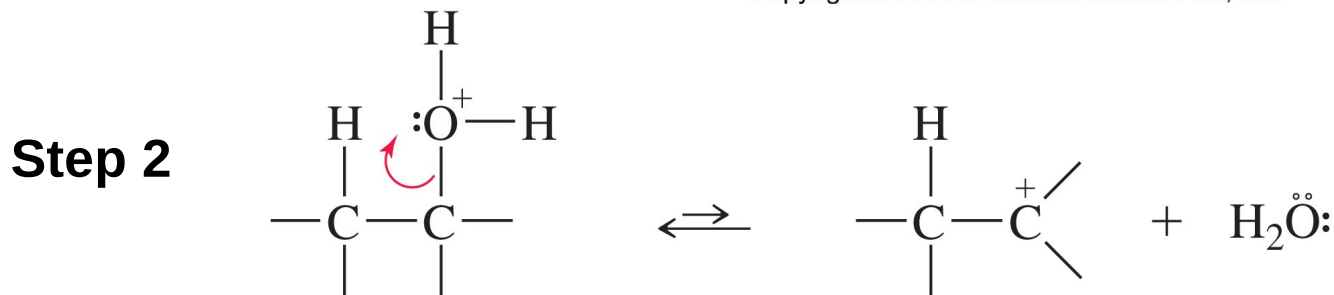
# Dehydration of Alcohols

- Use concentrated sulfuric or phosphoric acid, remove low-boiling alkene as it forms to shift the equilibrium, and increase the yield of the reaction.
- Carbocation intermediate: 3° alcohols react faster than 2°. Primary alcohols are the least reactive.
- Rearrangements are common.
- Reaction obeys Zaitsev's rule.

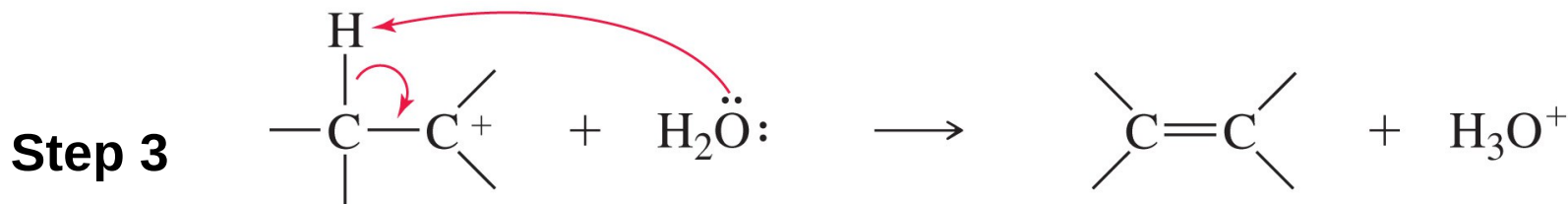
# Dehydration Mechanism: E1



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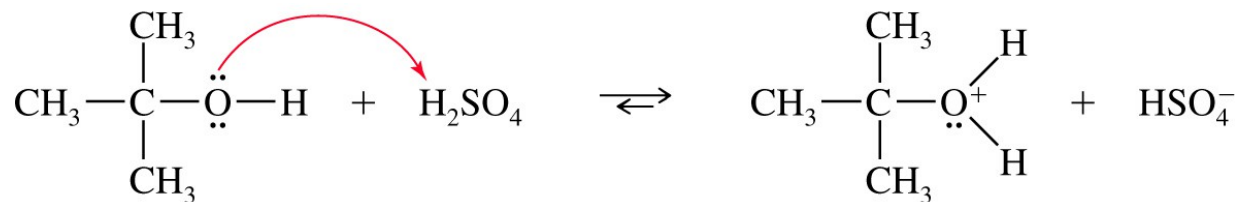
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# Solved Problem 4

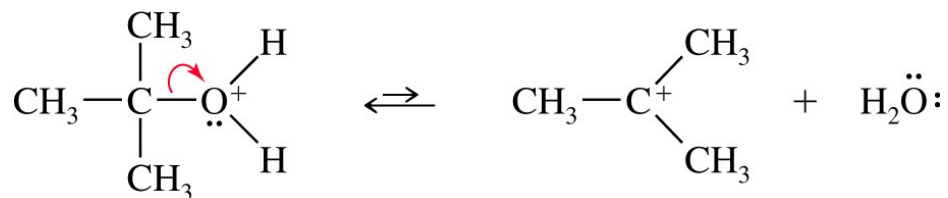
Propose a mechanism for the sulfuric acid-catalyzed dehydration of *t*-butyl alcohol.

## Solution

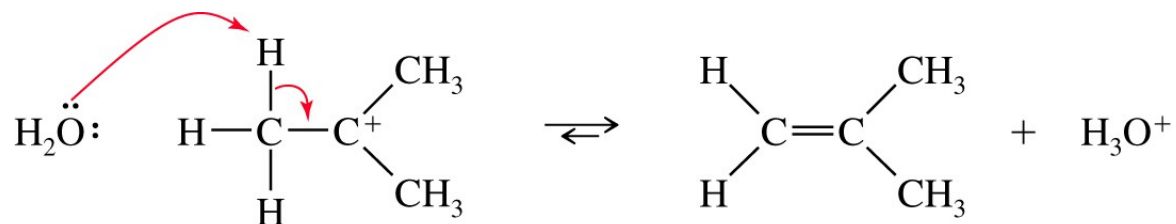
The first step is protonation of the hydroxyl group, which converts it to a good leaving group.



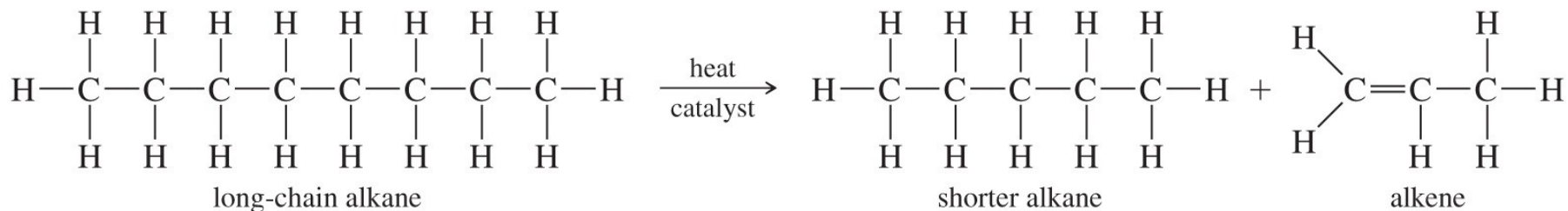
The second step is ionization of the protonated alcohol to give a carbocation.



Abstraction of a proton completes the mechanism.



# Catalytic Cracking of Alkanes



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- Long-chain alkane is heated with a catalyst to produce an alkene and shorter alkane.
- Complex mixtures are produced.