Organic Chemistry

Alkenes

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Expected Outcomes

In the end of this chapter, student will have the ability to:

- Describe characteristics and physical properties of alkene
- Draw and name alkene using IUPAC nomenclature
- Write alkene reaction mechanism

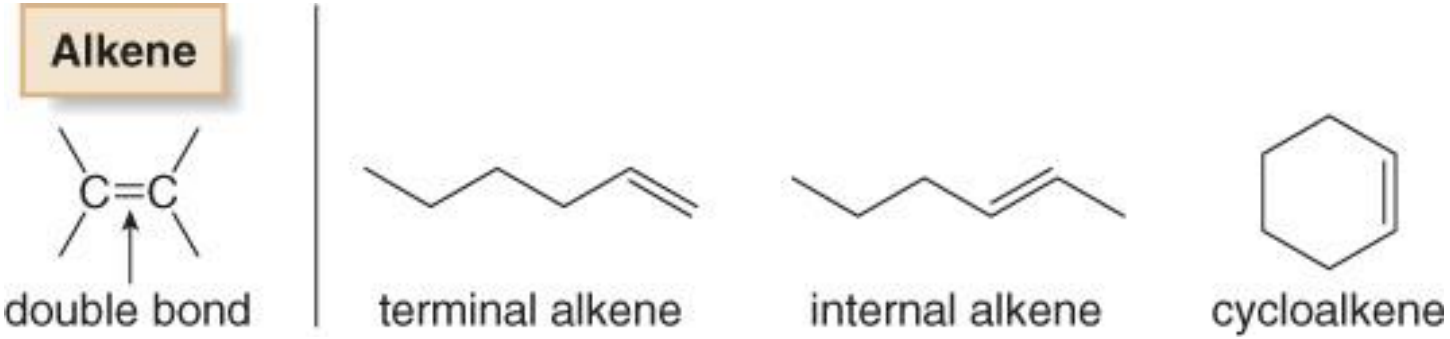
Contents

- Alkenes
- Physical properties
- Nomenclature
- Alkene reaction mechanisms

Alkenes

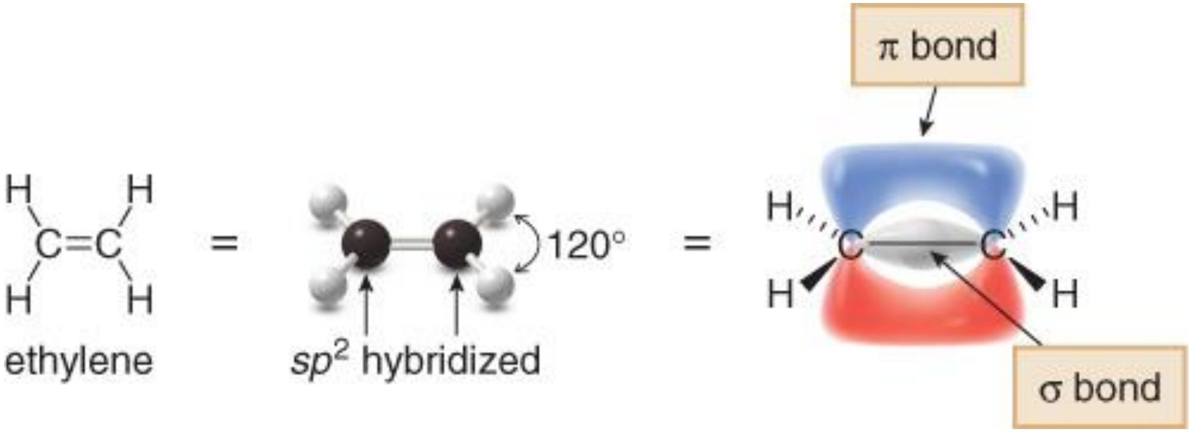
Introduction—Structure and Bonding

- **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.**



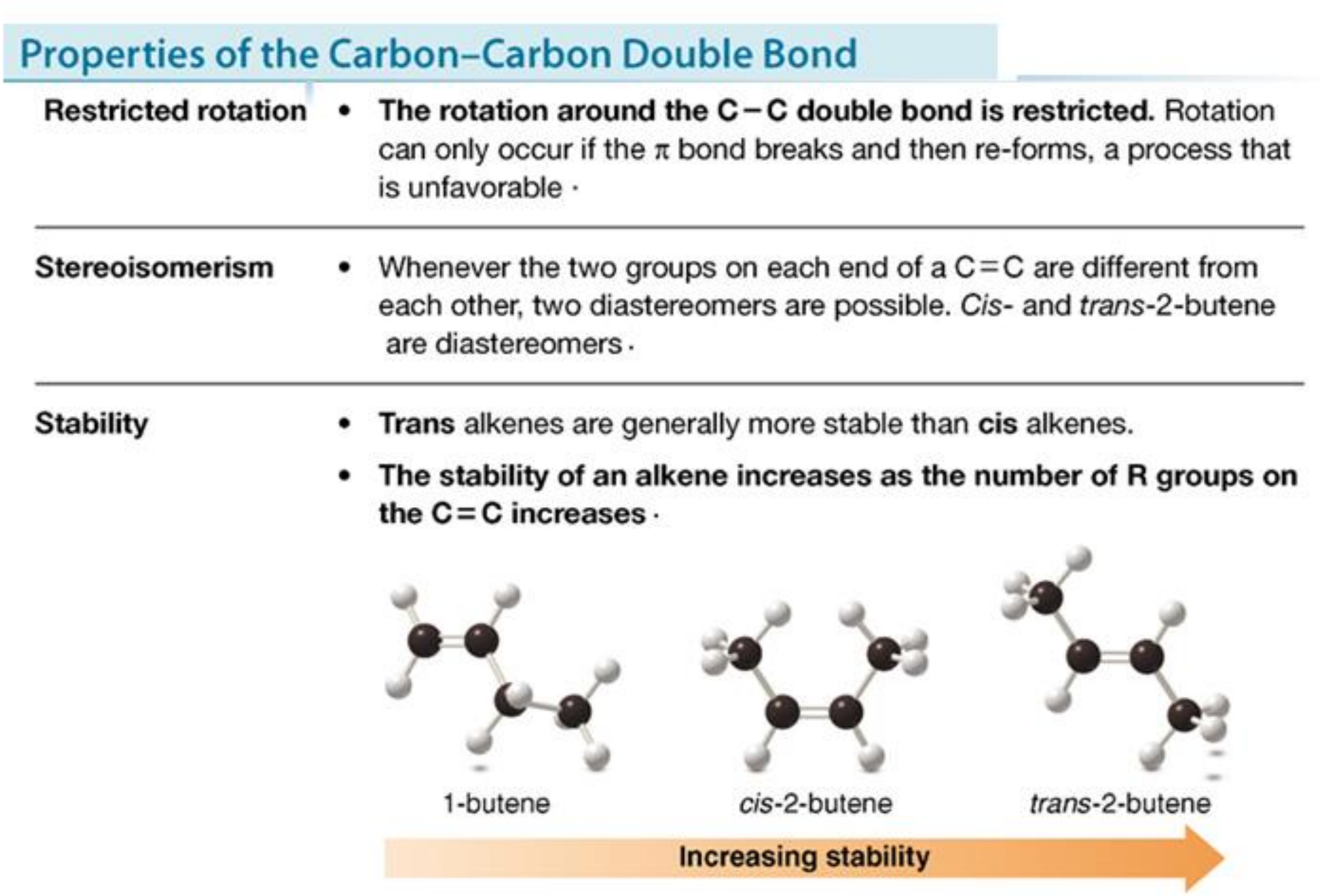
Introduction—Structure and Bonding

- 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°.



Alkenes

Introduction—Structure and Bonding



Properties of the Carbon–Carbon Double Bond

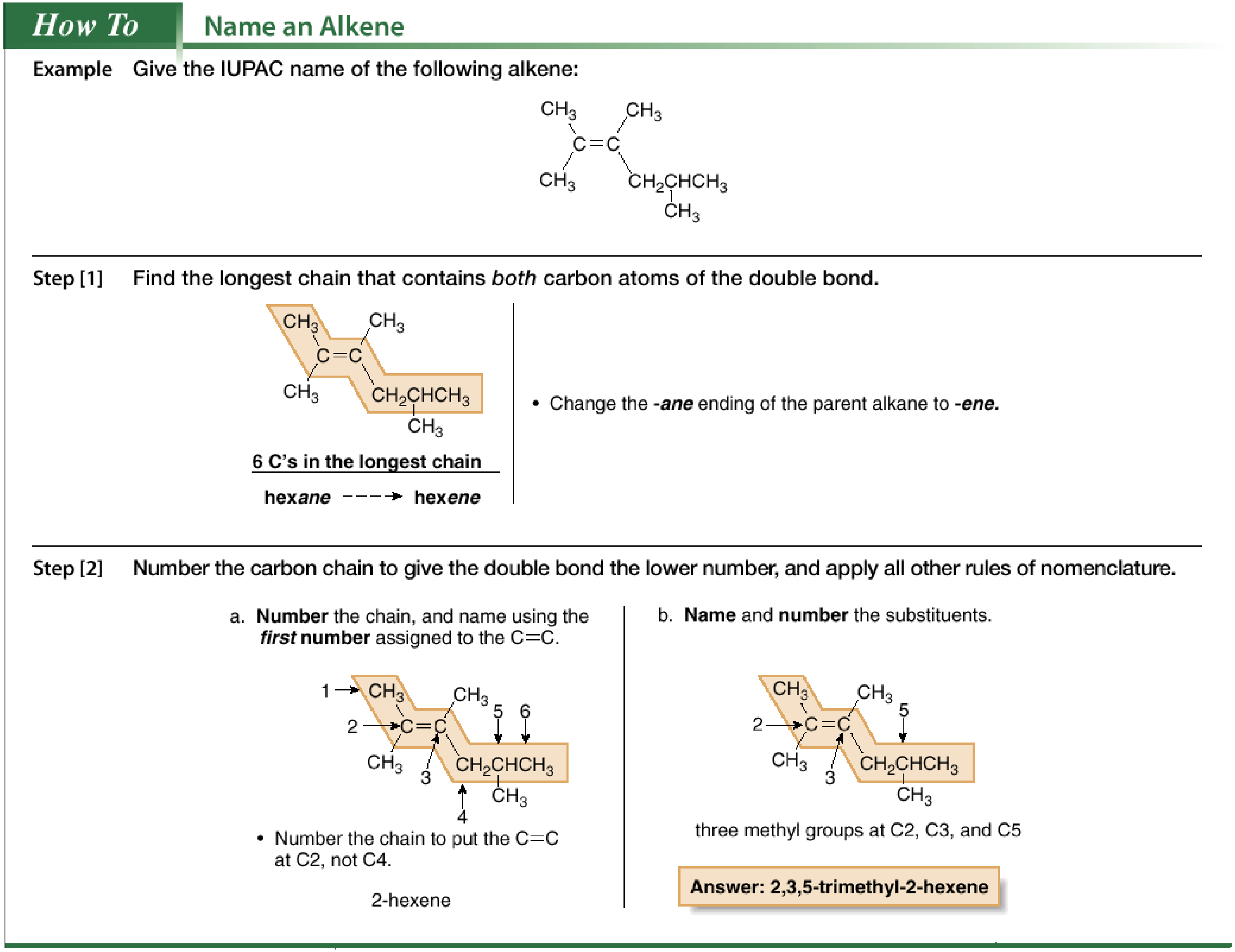
Restricted rotation	• **The rotation around the C–C double bond is restricted.** Rotation can only occur if the π bond breaks and then re-forms, a process that is unfavorable .
Stereoisomerism	• Whenever the two groups on each end of a C=C are different from each other, two diastereomers are possible. *Cis*- and *trans*-2-butene are diastereomers .
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 .**

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

Increasing stability

Alkenes

Nomenclature 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.

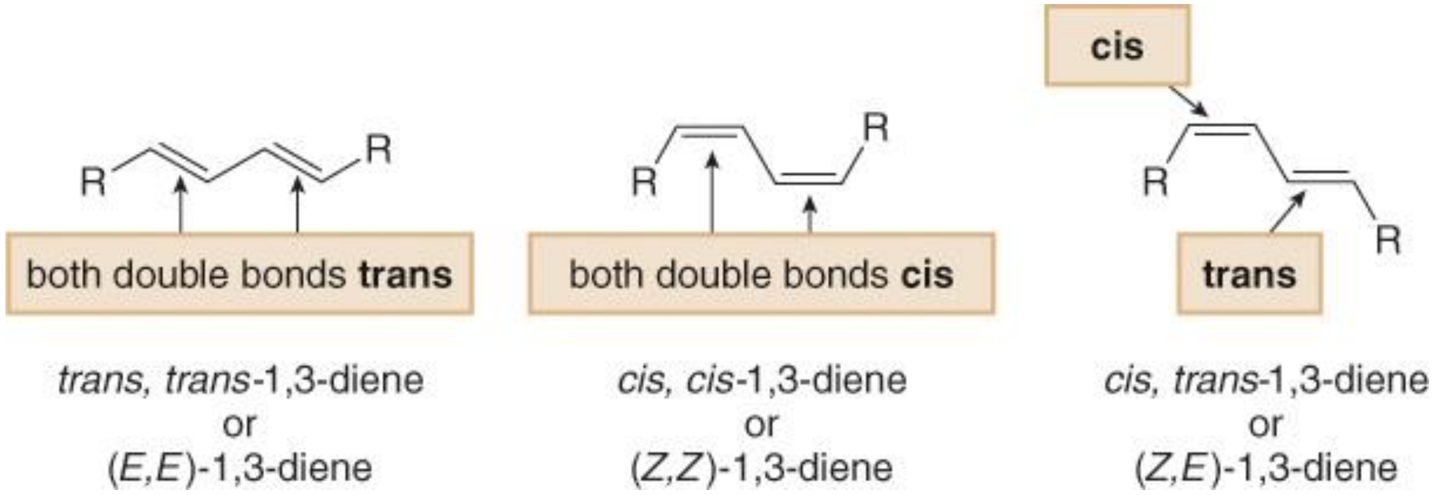
three methyl groups at C2, C3, and C5

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

Conjugated Dienes

- Conjugated dienes are compounds having two double bonds joined by one σ bond.
- Conjugated dienes are also called 1,3-dienes.
- 1,3-Butadiene ($CH_2=CH-CH=CH_2$) is the simplest conjugated diene.

- Different stereoisomers are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



trans, trans-1,3-diene
or
(*E*,*E*)-1,3-diene

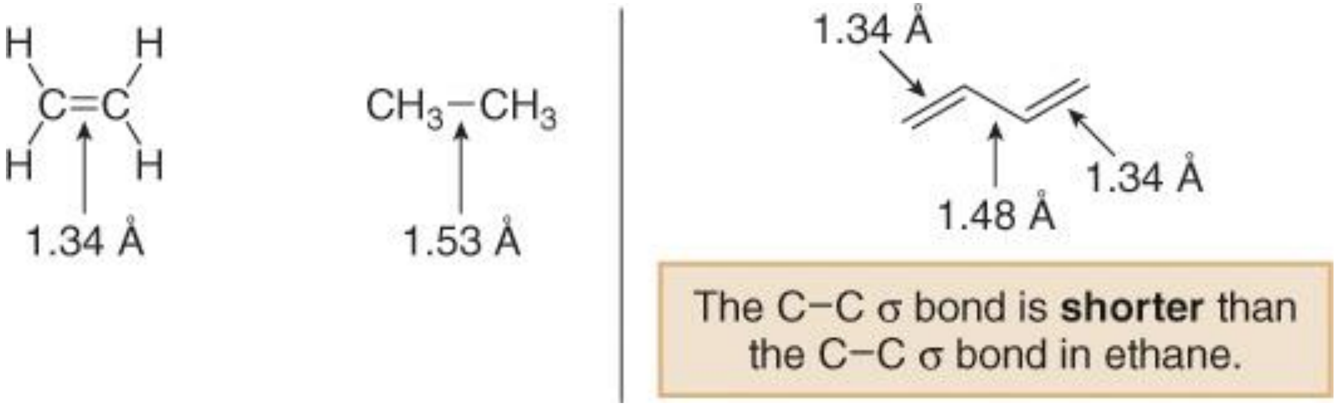
cis, cis-1,3-diene
or
(*Z*,*Z*)-1,3-diene

cis, trans-1,3-diene
or
(*Z*,*E*)-1,3-diene

The Carbon-Carbon σ Bond Length in 1,3-Butadiene

Four features distinguish conjugated dienes from isolated dienes.

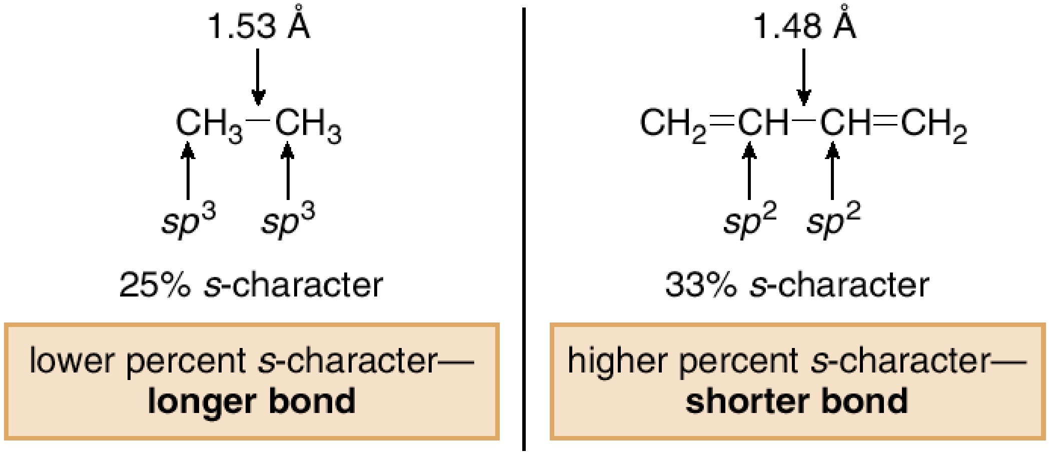
1. **The C—C single bond joining the two double bonds is unusually short.**
2. **Conjugated dienes are more stable than similar isolated dienes.**
3. **Some reactions of conjugated dienes are different than reactions of isolated double bonds.**
4. **Conjugated dienes absorb longer wavelengths of ultraviolet light.**



The C−C σ bond is **shorter** than the C−C σ bond in ethane.

The Carbon—Carbon σ Bond Length in 1,3-Butadiene

The observed bond distances can be explained by looking at hybridization.



1.53 Å

CH_3-CH_3

sp^3 sp^3

25% *s*-character

lower percent *s*-character—
longer bond

1.48 Å

$CH_2=CH-CH=CH_2$

sp^2 sp^2

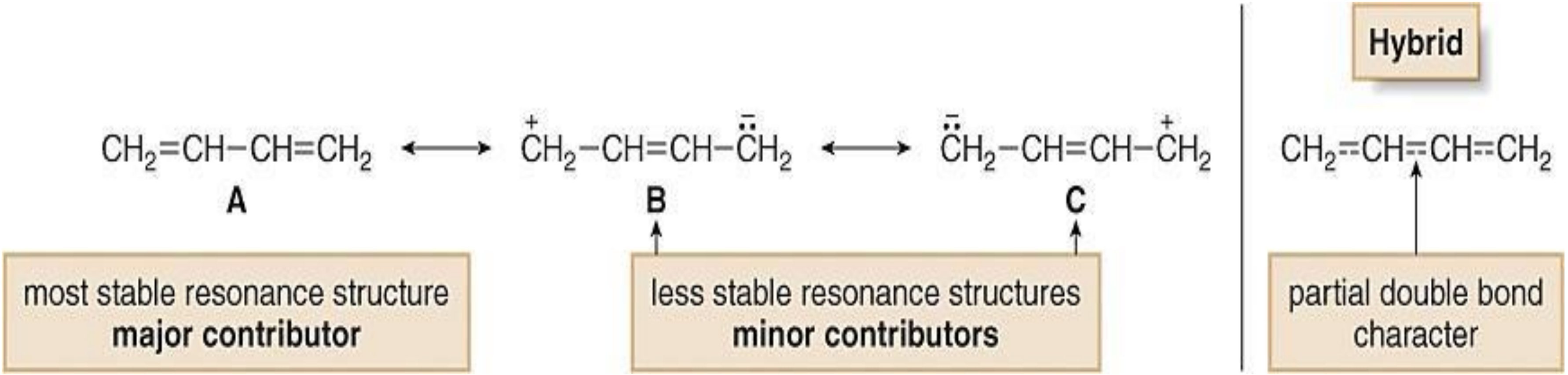
33% *s*-character

higher percent *s*-character—
shorter bond

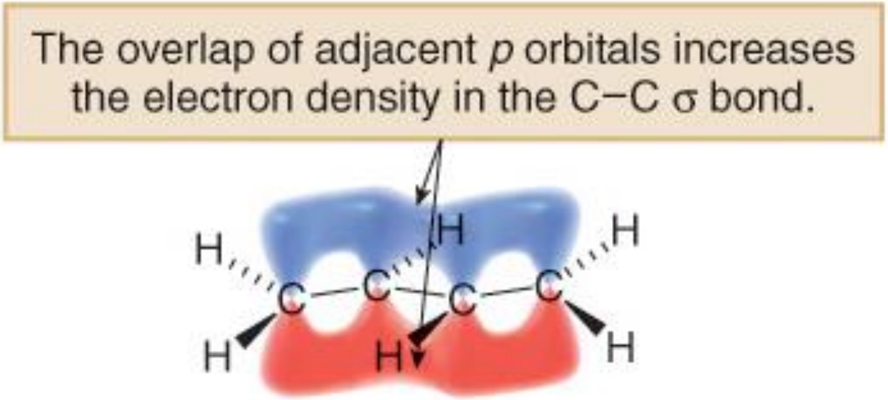
- Based on hybridization, a $C_{sp^2}-C_{sp^2}$ bond should be shorter than a $C_{sp^3}-C_{sp^3}$ bond because it is formed from orbitals having a higher percent *s*-character.

A resonance argument can also be used to explain the shorter C—C σ bond length in 1,3-butadiene.

- Based on resonance, the central C—C bond in 1,3-butadiene is shorter because it has partial double bond character (as resonance structures below show).

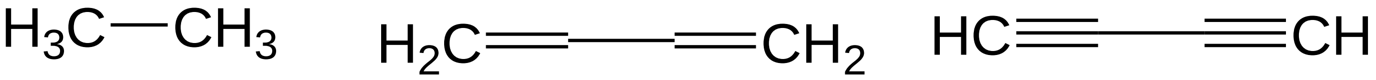


- Finally, 1,3-butadiene is a conjugated molecule with four overlapping *p* orbitals on adjacent atoms.
- Consequently, the π electrons are not localized between the carbon atoms of the double bonds, but rather delocalized over four atoms.
- This places more electron density between the central two carbon atoms of 1,3-butadiene than would normally be present.
- This shortens the bond.



The overlap of adjacent *p* orbitals increases the electron density in the C–C σ bond.

Using hybridization, compare the C-C bonds of the following three compounds.

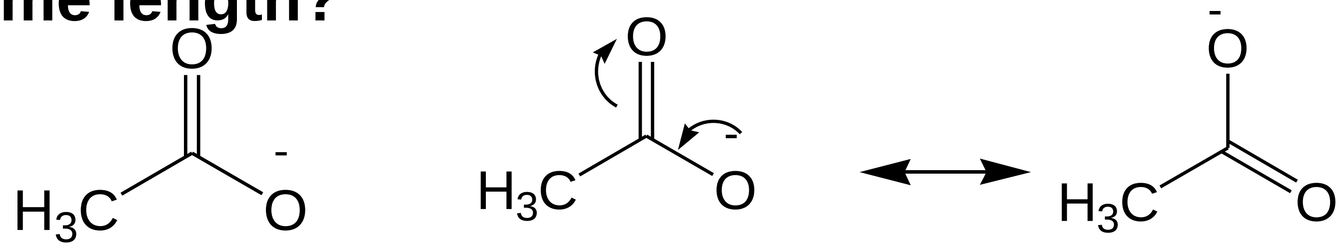


sp³ — sp^3: **25% *s* character**

*sp*² — sp^2: 33% *s* character

sp: 50% *s* character

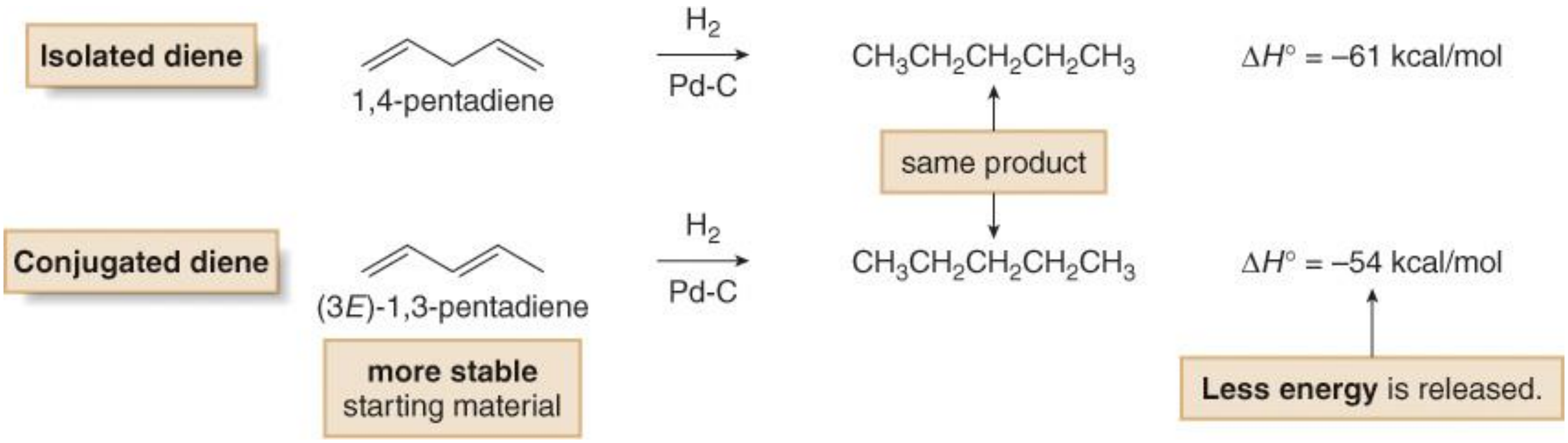
Using resonance, why are the two C—O bonds of the same length?



The two resonance structures show how the electron density is delocalized over 3 atoms.

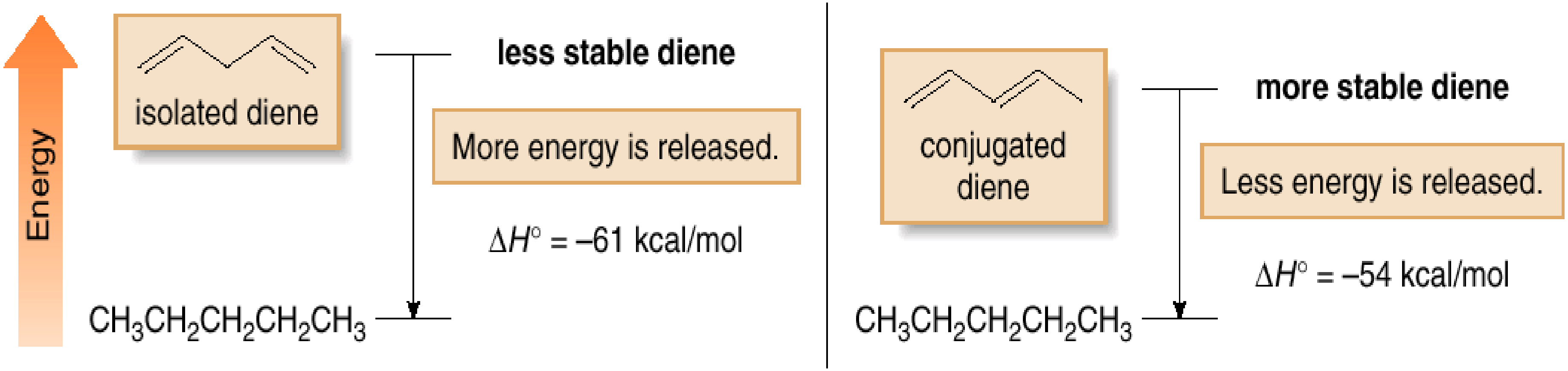
Stability of Conjugated Dienes

When hydrogenation gives the same alkane from two dienes, the more stable diene has the smaller heat of hydrogenation.



A conjugated diene has a smaller heat of hydrogenation and is more stable than a similar isolated diene.

Relative energies of an isolated and conjugated diene:



Energy

isolated diene

less stable diene

More energy is released.

$\Delta H^\circ = -61$ kcal/mol

$CH_3CH_2CH_2CH_2CH_3$

conjugated diene

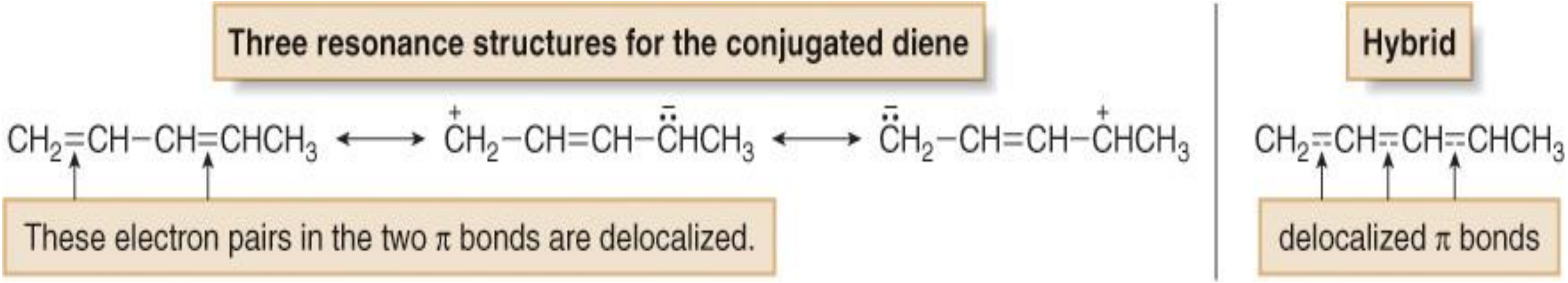
more stable diene

Less energy is released.

$\Delta H^\circ = -54$ kcal/mol

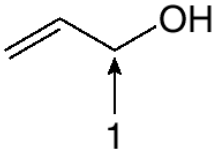
$CH_3CH_2CH_2CH_2CH_3$

- **A conjugated diene is more stable than an isolated diene because a conjugated diene has overlapping *p* orbitals on four adjacent atoms. Thus, its π electrons are delocalized over four atoms.**
- **This delocalization, which cannot occur in an isolated diene is illustrated by drawing resonance structures. For example, no resonance structures can be drawn for 1,4-pentadiene, but three can be drawn for (3*E*)-1,3-pentadiene (or any other conjugated diene).**

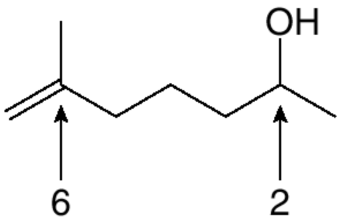


Nomenclature of Alkenes

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



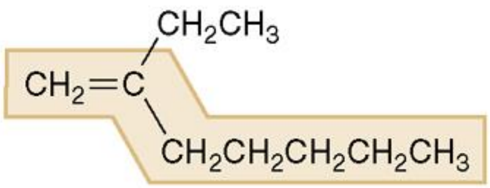
2-propen-1-ol



6-methyl-6-hepten-2-ol

Nomenclature of Alkenes

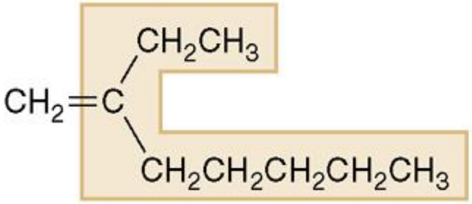
Naming an alkene in which the longest carbon chain does not contain both atoms of the double bond



7 C's ----→ heptene

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

Correct: **2-ethyl-1-heptene**

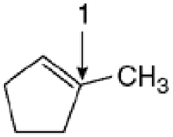


8 C's

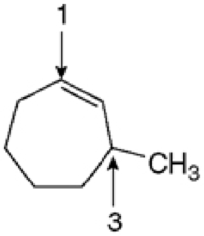
Both C's of the C=C are NOT contained in this long chain.

Incorrect

Examples of cycloalkene nomenclature

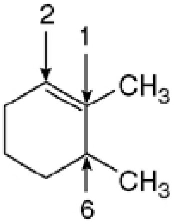


1-methylcyclopentene



3-methylcycloheptene

Number clockwise beginning at the C=C and place the CH_3 at C3.



1,6-dimethylcyclohexene

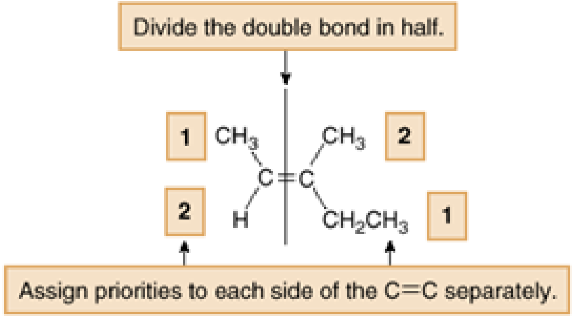
Number counterclockwise beginning at the C=C and place the first CH_3 at C1.

Nomenclature of Alkenes

How To Assign the Prefixes *E* and *Z* to an Alkene

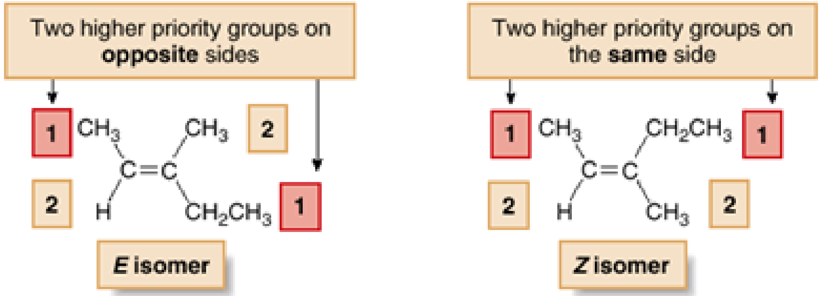
Step [1] Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R*,*S* nomenclature ·

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


Divide the double bond in half.

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

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


Two higher priority groups on **opposite** sides

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

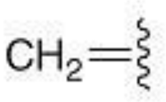
(*E*)-3-methyl-2-pentene

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

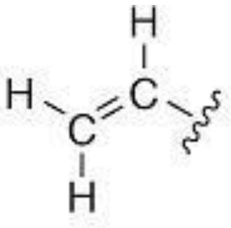
- The ***E*** isomer has the two higher priority groups on the **opposite sides.**
- The ***Z*** isomer has the two higher priority groups on the **same side.**

Nomenclature of Alkenes

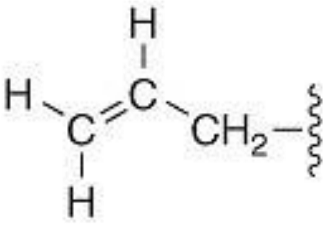
- **Some alkene or alkenyl substituents have common names.**
- **The simplest alkene, $CH_2{=}CH_2$, named in the IUPAC system as ethene, is often called ethylene.**



methylene group

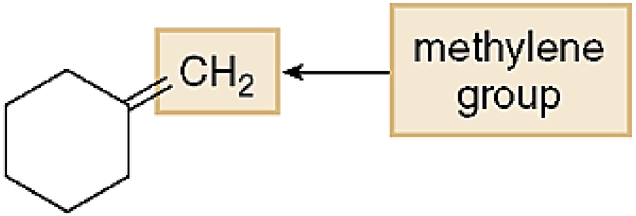


vinyl group

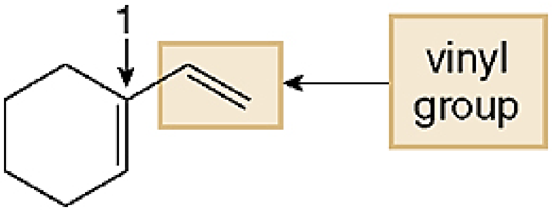


allyl group

Naming alkenes with common substituent names



methylenecyclohexane

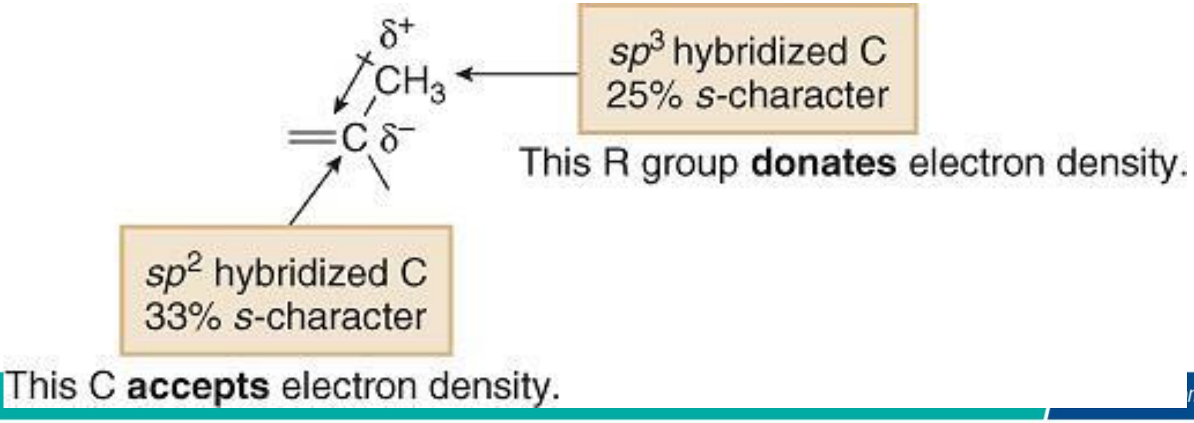


1-vinylcyclohexene

Alkenes

Physical Properties

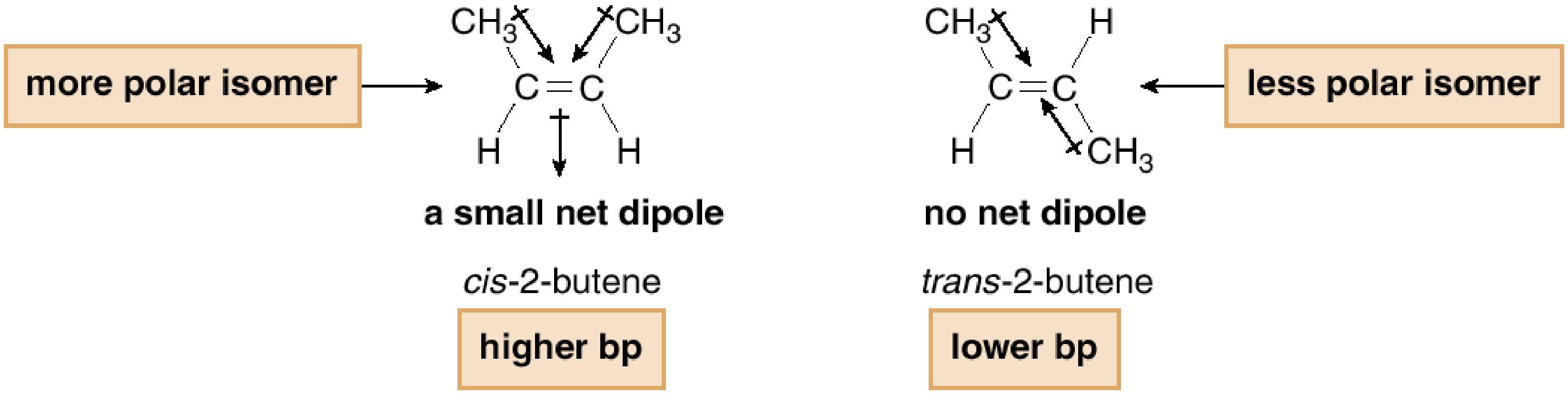
- **Most alkenes exhibit only weak van der Waals interactions, so their physical properties are similar to alkanes of comparable molecular weight.**
- **Alkenes have low melting points and boiling points.**
- **Melting and boiling points increase as the number of carbons increases because of increased surface area.**
- **Alkenes are soluble in organic solvents and insoluble in water.**
- **The C—C 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.**



Alkenes

Physical Properties

- **A consequence of this 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.**



a small net dipole

cis-2-butene

higher bp

no net dipole

trans-2-butene

lower bp

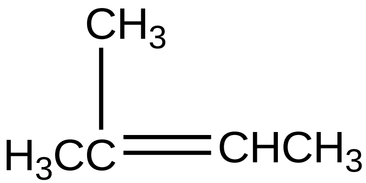
- A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point and making it more soluble in polar solvents.

Q-1 Which of these compounds exhibit cis-trans isomerism? Draw both cis-trans isomers when they exist.

a) $H_3CH_2CHC{=}CHCH_3$

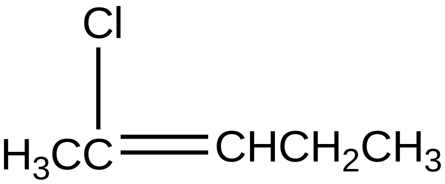
b) $H_3CH_2CHC{=}CH_2$

c)



$H_3C\overset{CH_3}{C}{=}CHCH_3$

d)

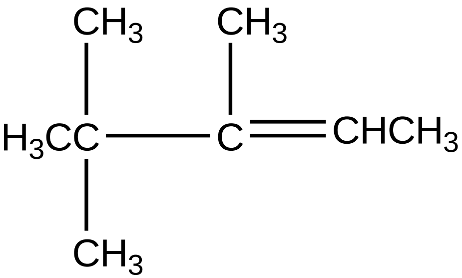


$H_3C\overset{Cl}{C}{=}CHCH_2CH_3$

Q-2 Draw the cis-trans isomers for these compounds and explain which is more stable:

a) $H_3CH_2CHC{=}CHCH_3$

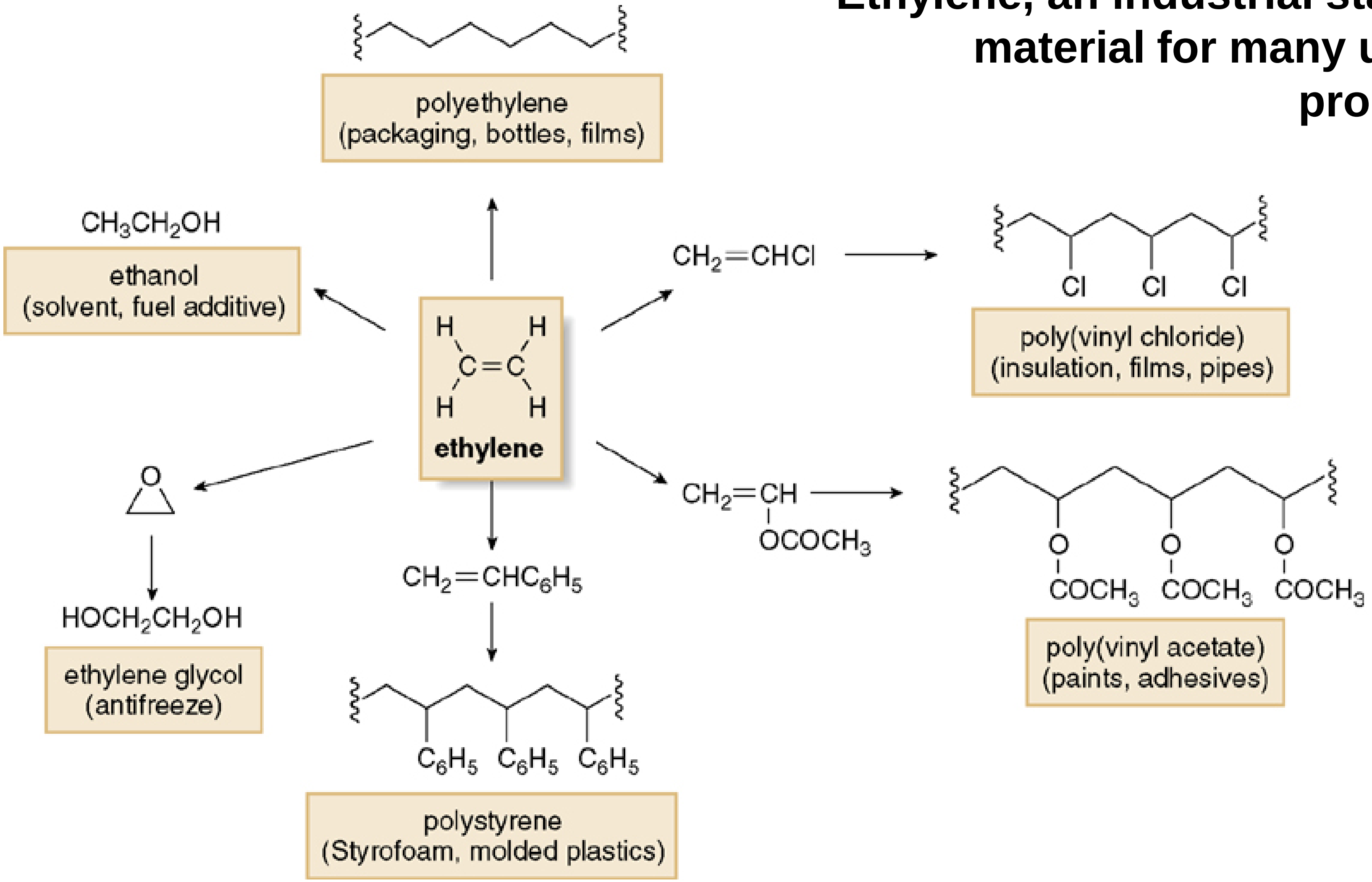
b)



$H_3C\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{C}{=}CHCH_3$

Interesting synthetic Alkenes

Ethylene, an industrial starting material for many useful products



polyethylene
(packaging, bottles, films)

CH_3CH_2OH

ethanol
(solvent, fuel additive)

ethylene

$CH_2{=}CHCl$

poly(vinyl chloride)
(insulation, films, pipes)

ethylene glycol
(antifreeze)

$HOCH_2CH_2OH$

$CH_2{=}CHC_6H_5$

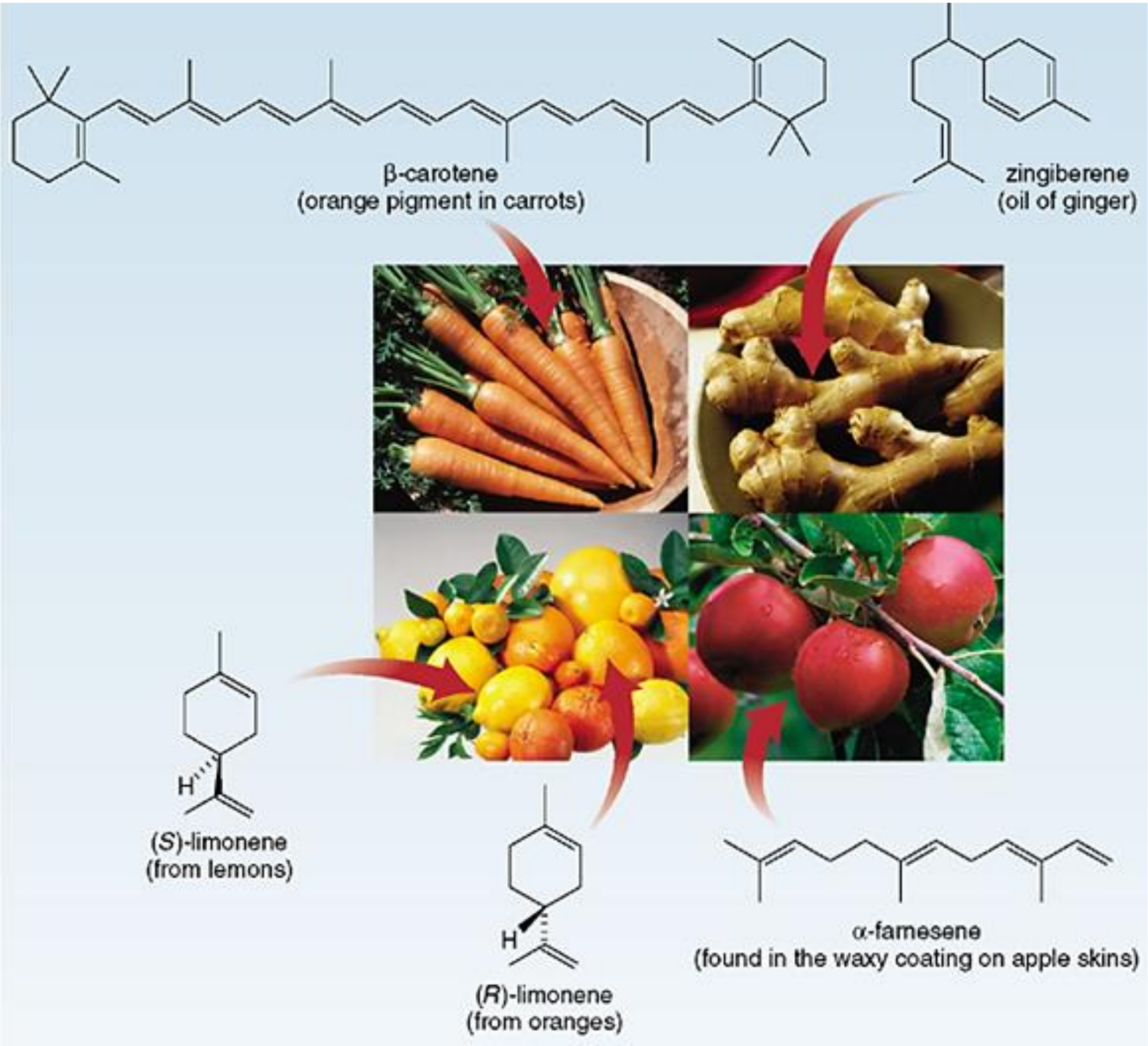
polystyrene
(Styrofoam, molded plastics)

$CH_2{=}CH(OCOCH_3)$

poly(vinyl acetate)
(paints, adhesives)

Interesting Alkenes

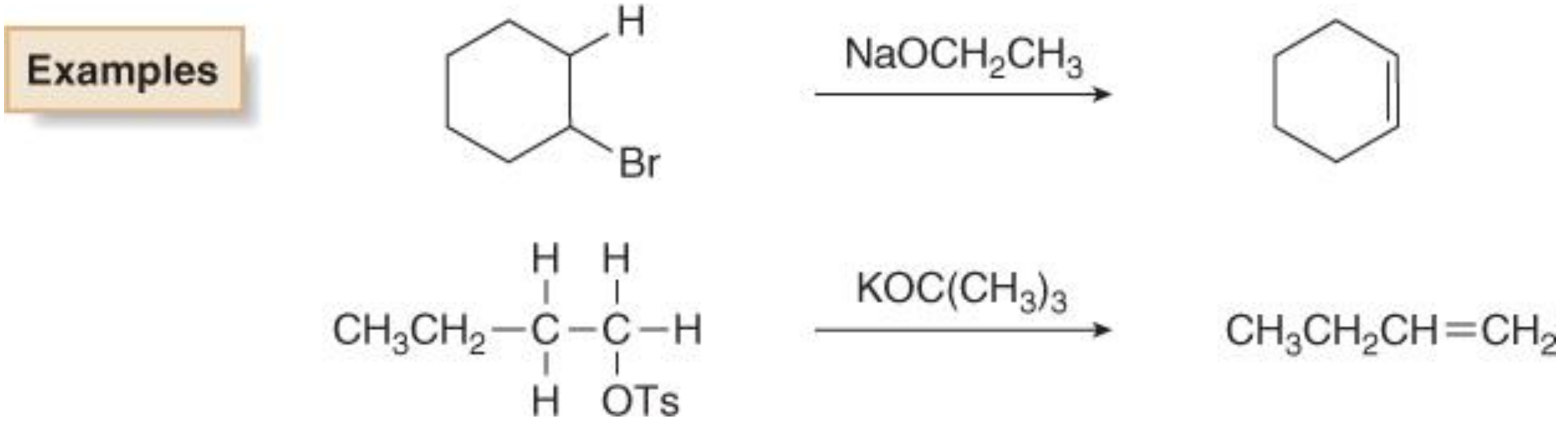
Five naturally occurring alkenes

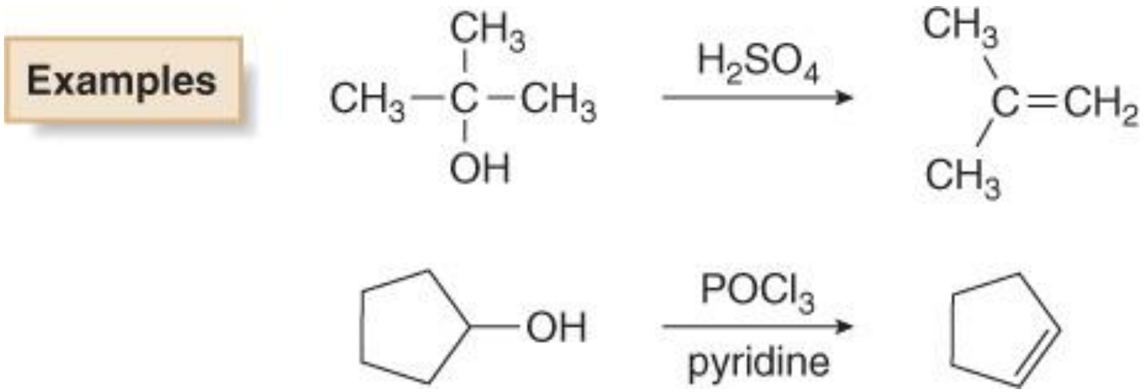


Alkenes

Preparation of Alkenes

- **Recall that alkenes can be prepared from alkyl halides and alcohols via elimination reactions.**



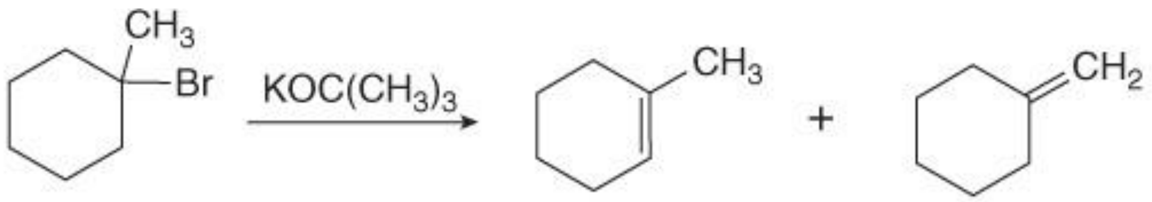


Phosphorus trichloride oxide

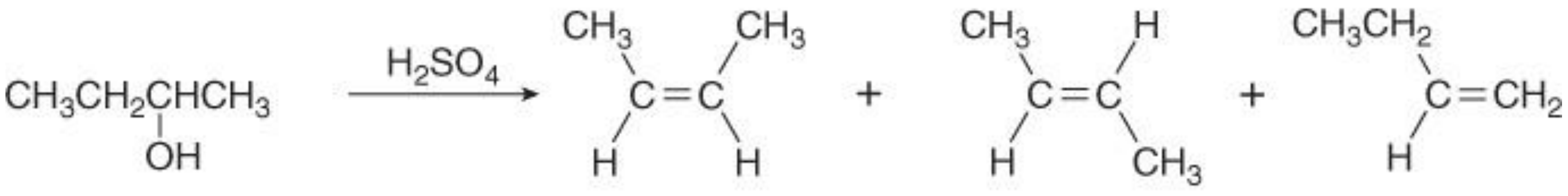
Alkenes

Preparation of Alkenes

- **Also recall that the most stable alkene is usually formed as the major product in these elimination reaction.**



major product



major product
trans disubstituted alkene