

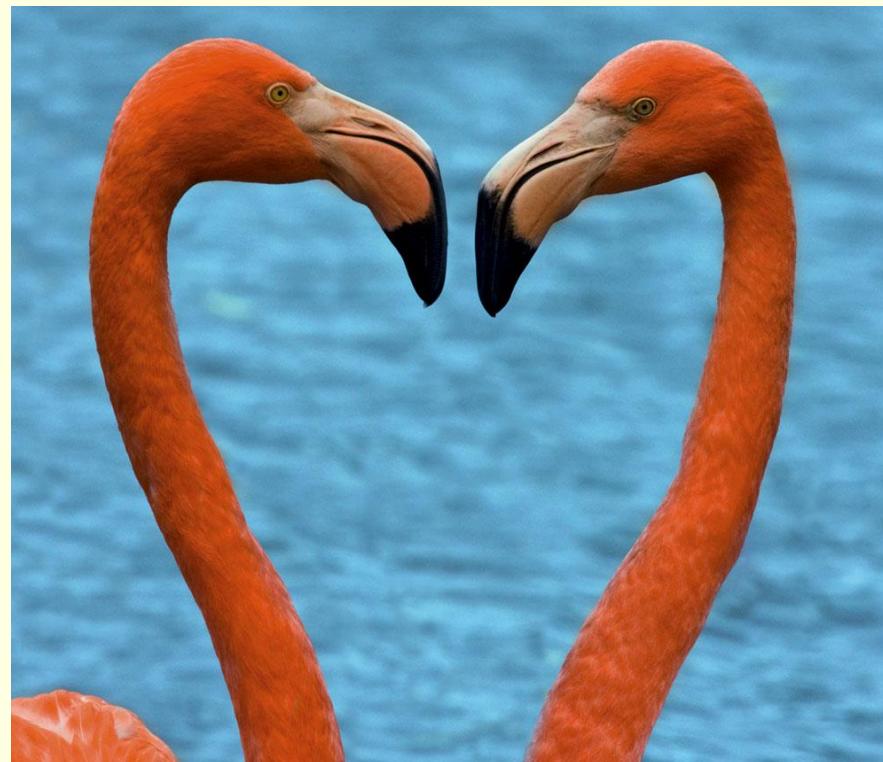


3. Alkenes and Alkynes: The Nature of Organic Reactions

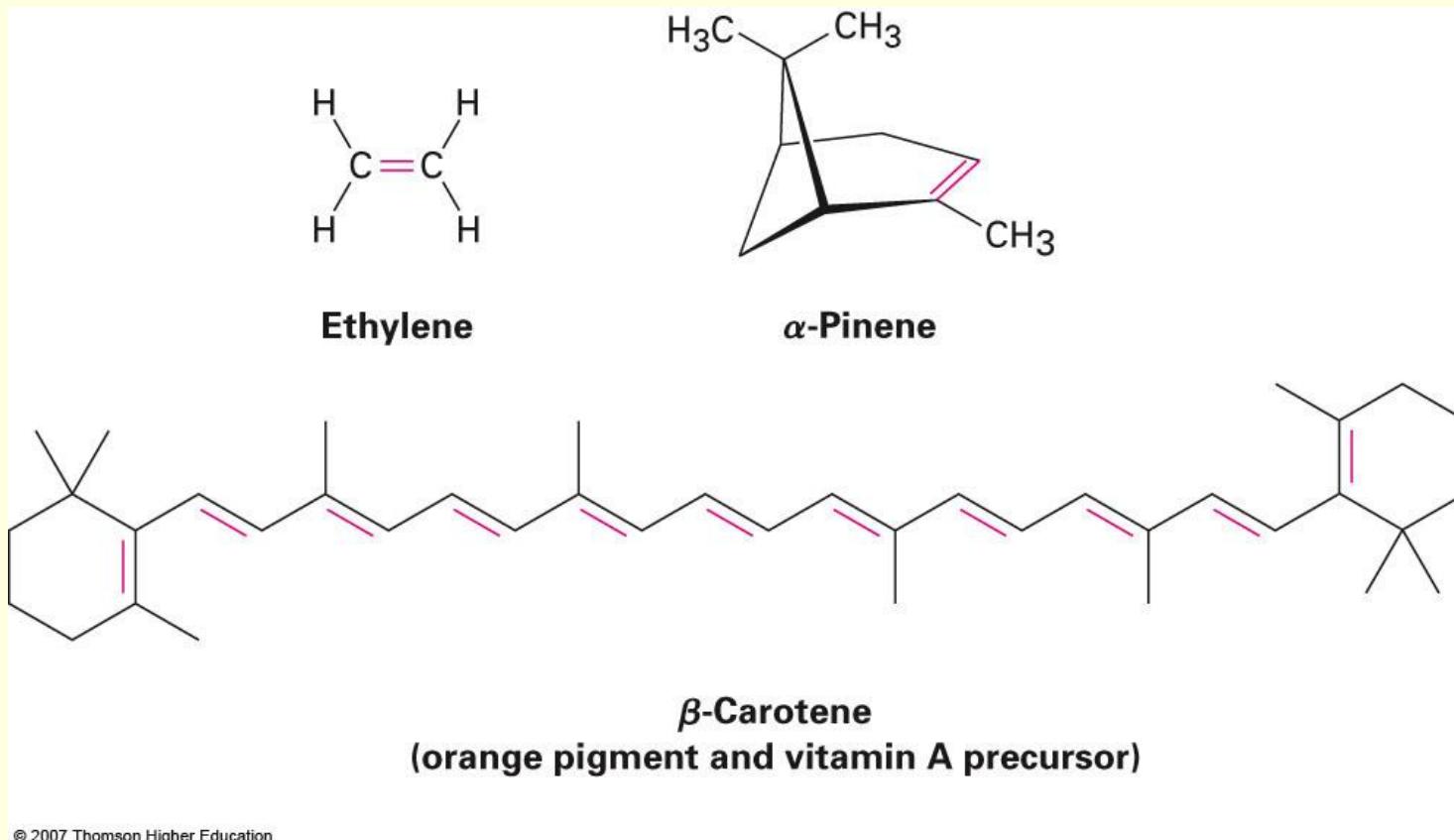
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3. Alkenes and Alkynes: The Nature of Organic Reactions



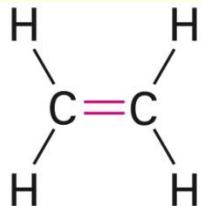
- Alkenes - Hydrocarbon with carbon-carbon **double** Bonds
- Also called an olefin but *alkene* is better
- Alkynes - Hydrocarbons that contain carbon-carbon **triple** bonds
- Includes many naturally occurring materials
 - Flavors, fragrances, vitamins



Why this Chapter?

- **C-C double bonds** are present in **most** organic and biological molecules
- To examine consequences of alkene **stereoisomerism**
- To focus on general alkene reaction: **electrophilic addition**
- We will use alkyne chemistry to begin looking at general strategies used in organic synthesis

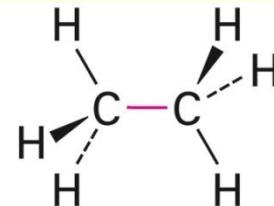
3.1 Naming of Alkenes and Alkynes



Ethylene: C_2H_4



Acetylene: C_2H_2

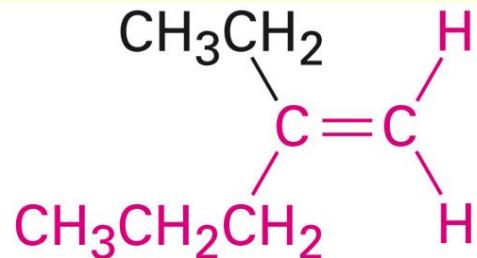


Ethane: C_2H_6

(Fewer hydrogens—*unsaturated*) (More hydrogens—*saturated*)

- Name the parent hydrocarbon
- Number carbons in chain so that double bond carbons have lowest possible numbers
- Write the full name

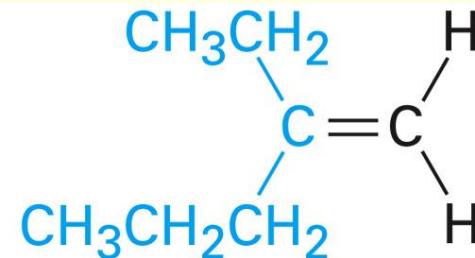
1. Name the parent hydrocarbon: suffix **-ene** instead of **-ane**



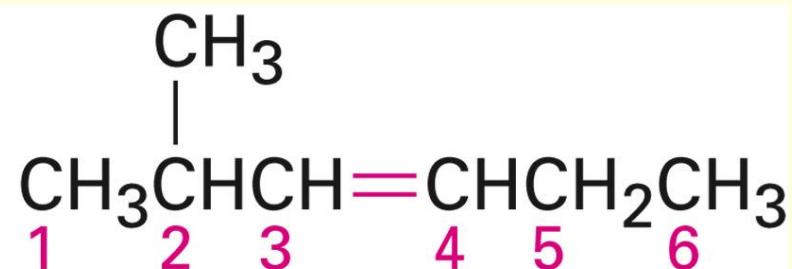
Named as a *pentene*

NOT

as a hexene, since the double bond is not contained in the six-carbon chain



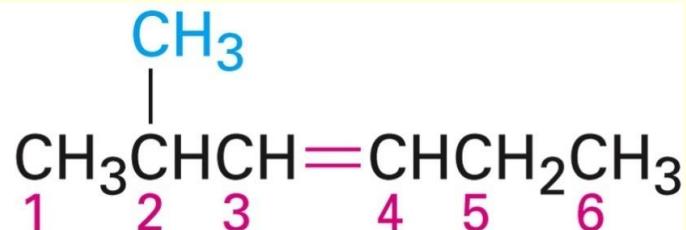
2. Number carbons in chain so that double bond carbons have **lowest possible numbers**



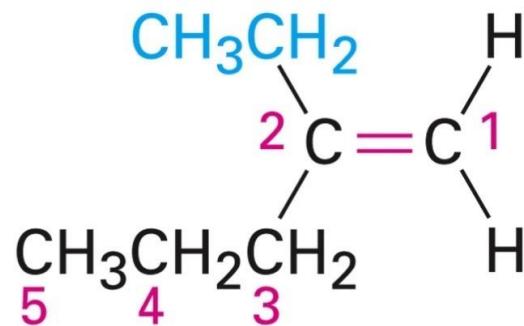
3. Write the full name



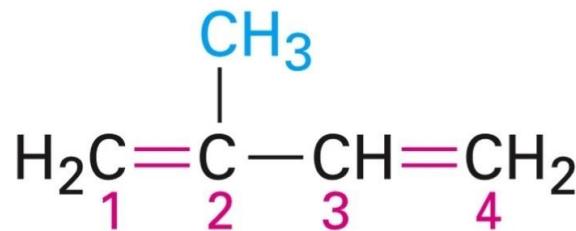
Hex-2-ene



2-Methylhex-3-ene



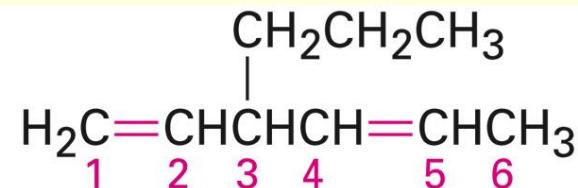
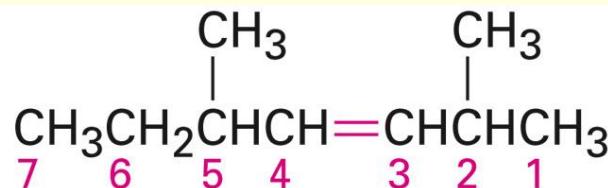
2-Ethylpent-1-ene



2-Methylbuta-1,3-diene

If more than one double bond is present, give the position of each and use the appropriate multiplier suffix *-diene*, *-triene*, *-tetraene*, and so on.

IUPAC changed its naming rules in 1993

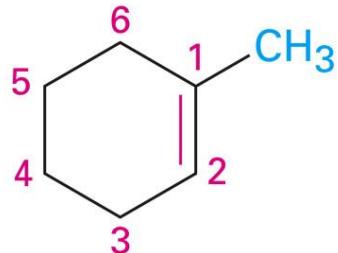


New naming system: **2,5-Dimethylhept-3-ene** 3-Propylhexa-1,4-diene

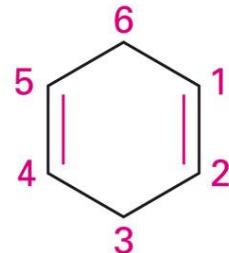
(Old naming system: **2,5-Dimethyl-3-heptene** 3-Propyl-1,4-hexadiene)

We should also note that IUPAC changed its naming rules in 1993. **Prior to that time**, the locant, or number locating the **position** of the double bond, was placed before the parent name rather than before the **-ene** suffix: **2-butene rather than but-2-ene**, for instance.

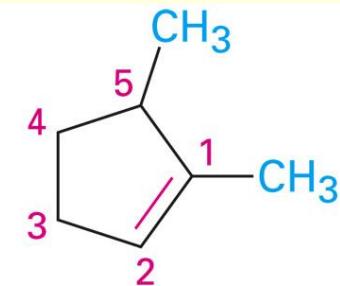
Changes always take time to be fully accepted, so the new rules have not yet been adopted universally and some texts have not yet been updated.



1-Methylcyclohexene



Cyclohexa-1,4-diene
(Old name: **1,4-Cyclohexadiene**)



1,5-Dimethylcyclopentene

Cycloalkenes are named similarly, but because there is no chain end to begin from, **we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible**. Note that it's **not necessary** to specify the position of the double bond in the name because it's always between C1 and C2.

Many Alkenes Are Known by **Common Names**

Table 3.1

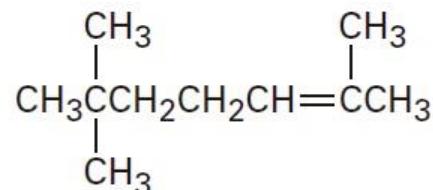
Common Names of Some Alkenes

Compound	Systematic name	Common name
$\text{H}_2\text{C}=\text{CH}_2$	Ethene	Ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	2-Methylpropene	Isobutylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	2-Methylbuta-1,3-diene	Isoprene

Worked Example 3.1

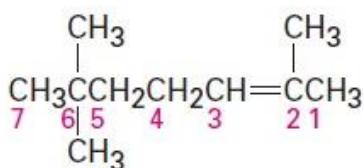
Naming an Alkene

What is the IUPAC name of the following alkene?



Strategy

First, find the longest chain containing the double bond—in this case, a heptene. Next, number the chain beginning at the end nearer the double bond, and identify the substituents at each position. In this case, there are three methyl groups, one at C2 and two at C6.

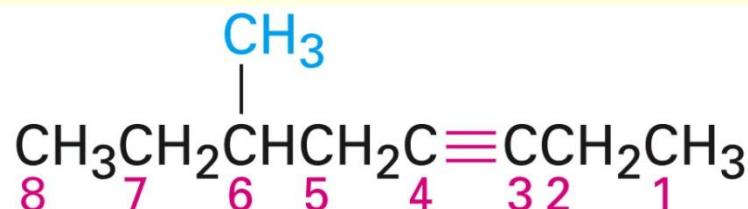


Solution

Write the full name, listing the substituents alphabetically and giving the position of each. Identify the position of the double bond by placing the number of the first alkene carbon before the *-ene* suffix: 2,6,6-trimethylhept-2-ene.

Alkynes

- General hydrocarbon rules apply with “-yne” as a suffix indicating an alkyne
- Numbering of chain with triple bond is set so that the **smallest** number possible for the first carbon of the triple bond



Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne

(Old name: **6-Methyl-3-octyne**)

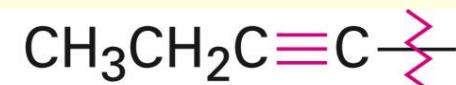
Alkenyl and alkynyl groups



Butyl
(an alkyl group)



But-1-enyl
(a vinylic group)



But-1-ynyl
(an alkynyl group)

3.2 Electronic Structure of Alkenes

- Carbon atoms in a double bond are **sp^2 -hybridized**
 - Three equivalent orbitals at 120° separation in plane
 - Fourth orbital is atomic p orbital
- Combination of electrons in two sp^2 orbitals of two atoms forms **σ bond** between them
- Additive interaction of p orbitals creates a **π bonding orbital**
- Occupied π bond prevents rotation about σ -bond
- Rotation prevented by π bond - high barrier, about 268 kJ/mole in ethylene

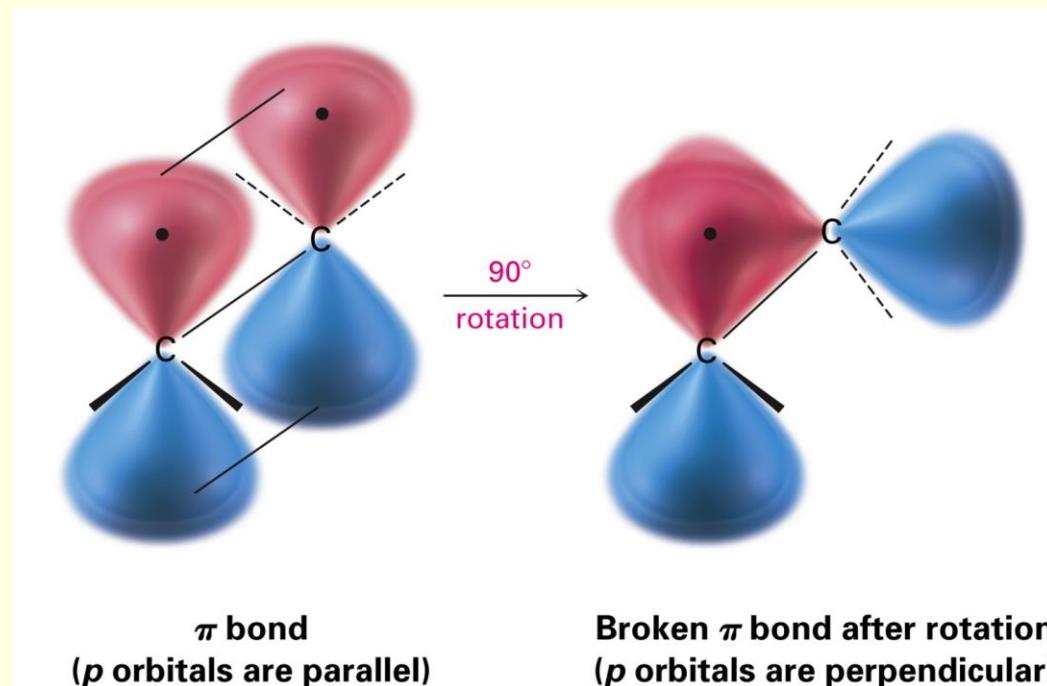
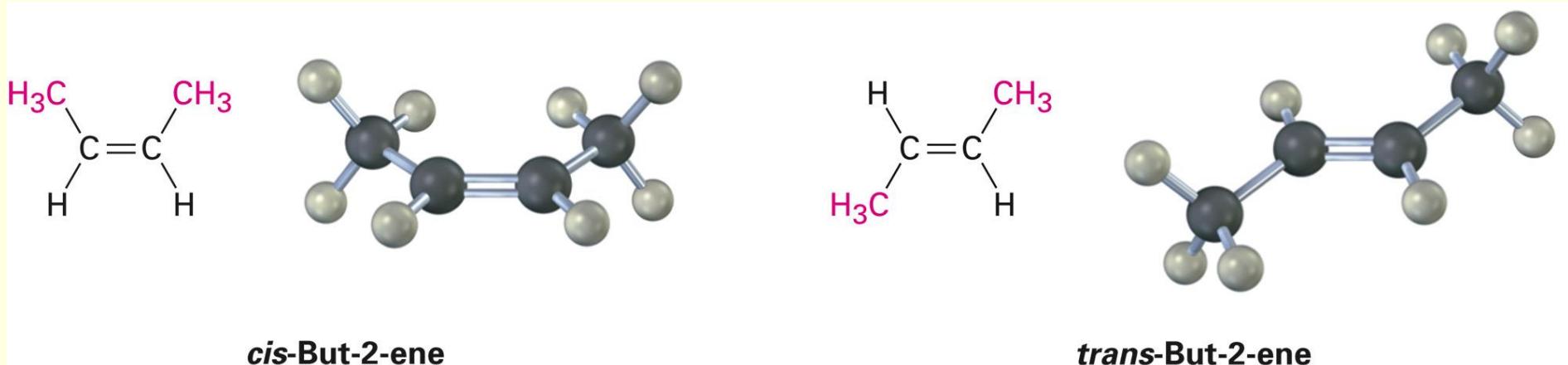


Figure 3.1 The bond must break momentarily for rotation around a carbon–carbon double bond to take place, requiring a large amount of energy.

3.3 Cis-Trans Isomers of Alkenes

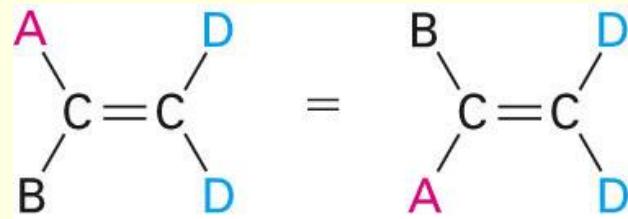
- The presence of a carbon-carbon double bond can create two possible structures
 - cis isomer** - two similar groups on **same** side of the double bond
 - trans isomer** - similar groups on **opposite** sides
- Each carbon must have two different groups for these isomers to occur



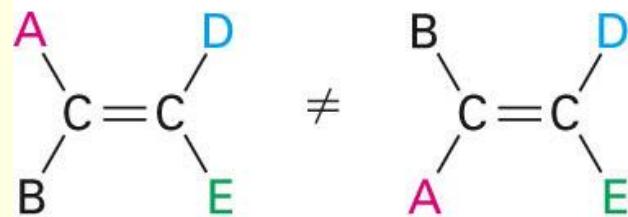
Cis, Trans Isomers Require That End Groups Must Differ in Pairs

Cis-trans isomerism is not limited to disubstituted alkenes. It occurs whenever each double-bond carbon is attached **to two different groups**.

If one of the double-bond carbons is attached to **two identical groups**, however, then cis-trans isomerism is not possible



These two compounds are identical;
they are not cis-trans isomers.



These two compounds are not identical;
they are cis-trans isomers.

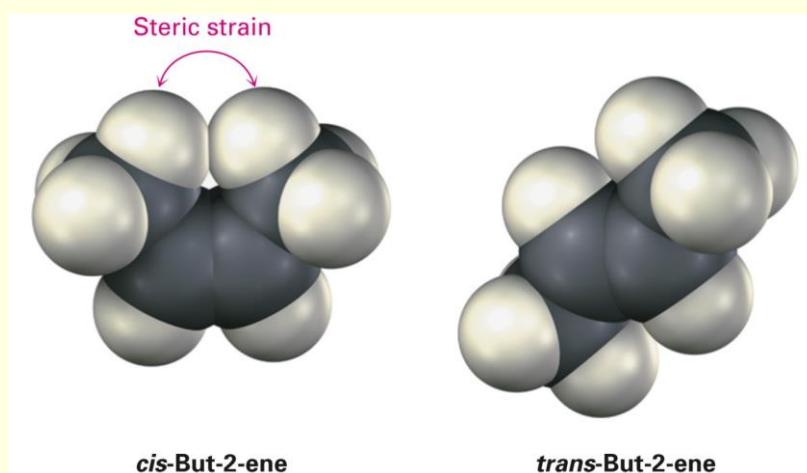
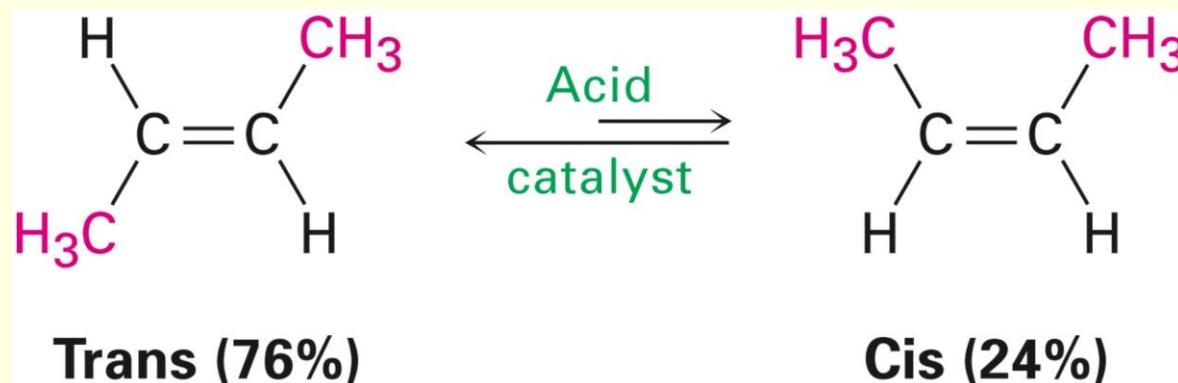
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Figure 3.3 The requirement for cis-trans isomerism in alkenes. Compounds that have one of **their carbons bonded to two identical groups can't exist as cis-trans isomers**.

Only when both carbons are bonded to two different groups are cis-trans isomers possible.

Interconversion of cis and trans alkene isomers

Although the interconversion of cis and trans alkene isomers doesn't occur spontaneously, it can be brought about by treating the alkene with a strong acid catalyst. If we do, in fact, interconvert *cis*-but-2-ene with *trans*-but-2-ene and allow them to reach equilibrium, we find that they aren't of equal stability. **The trans isomer is more favored than the cis isomer by a ratio of 76:24.**



Worked Example 3.2

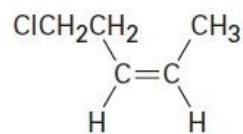
Drawing Cis and Trans Alkene Isomers

Draw the cis and trans isomers of 5-chloropent-2-ene.

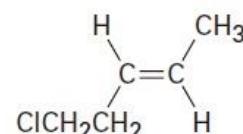
Strategy

First, draw the molecule without indicating isomers to see the overall structure: $\text{ClCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$. Then locate the two substituent groups on the same side of the double bond for the cis isomer and on opposite sides for the trans isomer.

Solution



cis-5-Chloropent-2-ene



trans-5-Chloropent-2-ene