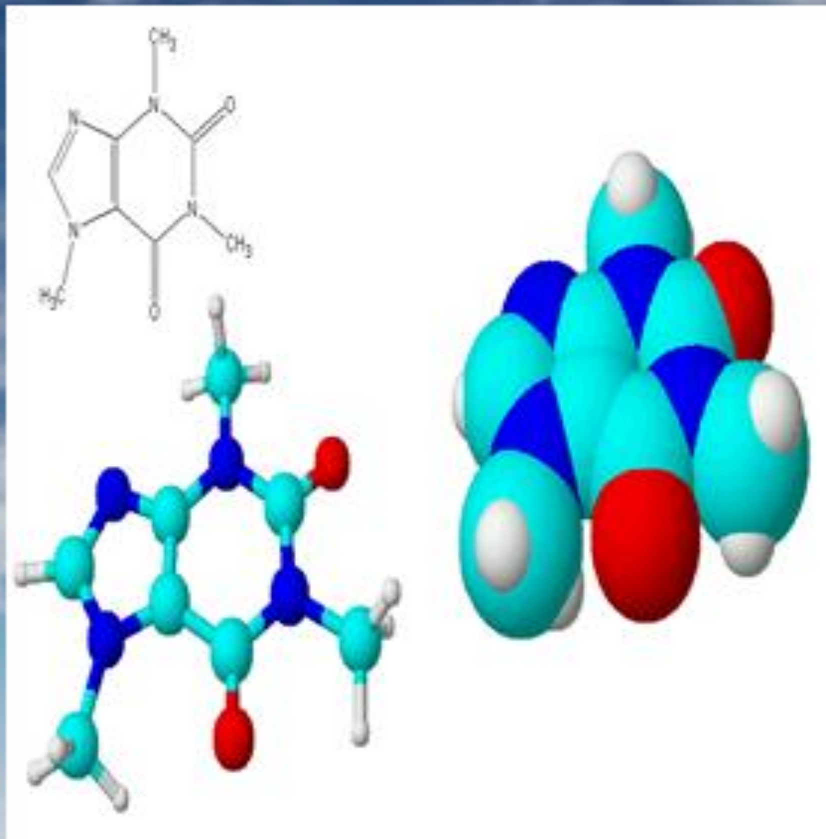
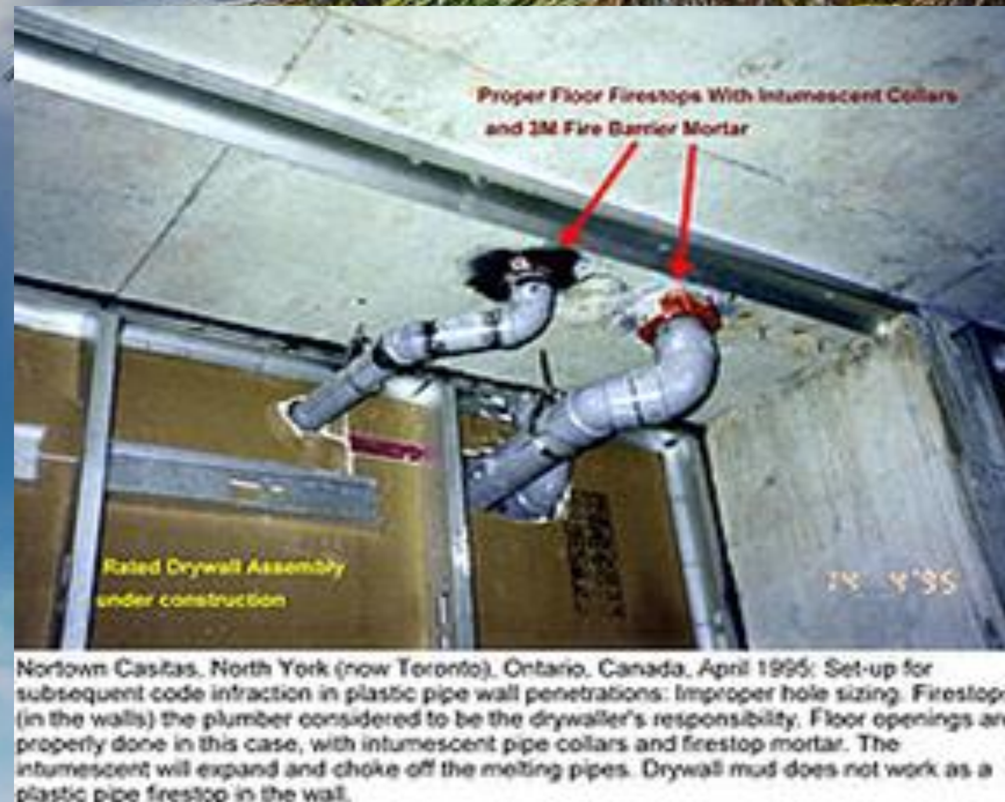
ORGANIC CHEMISTRY



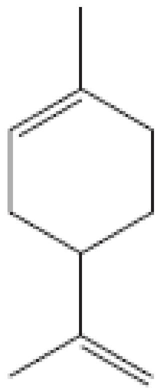


By

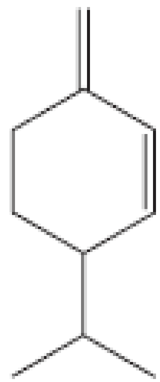
Mubarak O. AMEEN

- **Alkenes**

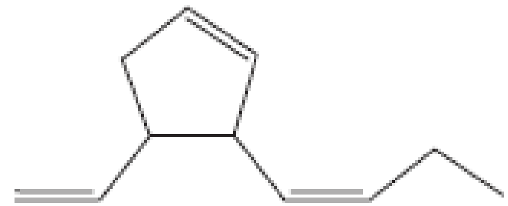
Alkenes



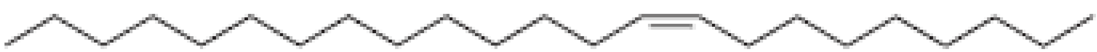
limonene
from lemon and orange oils



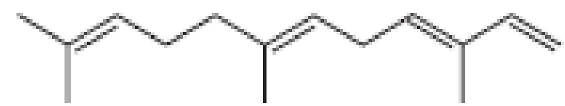
β-phellandrene
oil of eucalyptus



multifidene
sex attractant of brown algae



muscalure
sex attractant of the housefly



α-farnesene
found in the waxy coating on apple skins

Alkenes

- The general molecular formula for an *acyclic alkene* is C_nH_{2n}
- As a result of the carbon–carbon double bond, an alkene has two fewer hydrogens than an alkane with the same number of carbon atoms.
- Thus, the general molecular formula for a *cyclic alkene* is C_nH_{2n-2}
- We can, therefore, make the following statement:
  - *The general molecular formula for a hydrocarbon is* C_nH_{2n+2} *minus two hydrogens for every bond and/or ring in the molecule*.

$CH_3CH_2CH_2CH_2CH_3$

an alkane

C_5H_{12}

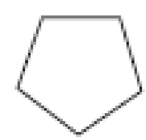
C_nH_{2n+2}

$CH_3CH_2CH_2CH{=}CH_2$

an alkene

C_5H_{10}

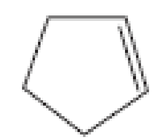
C_nH_{2n}



a cyclic alkane

C_5H_{10}

C_nH_{2n}



a cyclic alkene

C_5H_8

C_nH_{2n-2}

Alkenes

- Alkanes contain the maximum number of carbon–hydrogen bonds possible—that is, they are saturated with hydrogen—they are called **saturated hydrocarbons**.
- In contrast, alkenes are called **unsaturated hydrocarbons**, because they have fewer than the maximum number of hydrogens.
- The total number of π bonds and rings in an alkene is called its **degree of unsaturation**.

$CH_3CH_2CH_2CH_3$

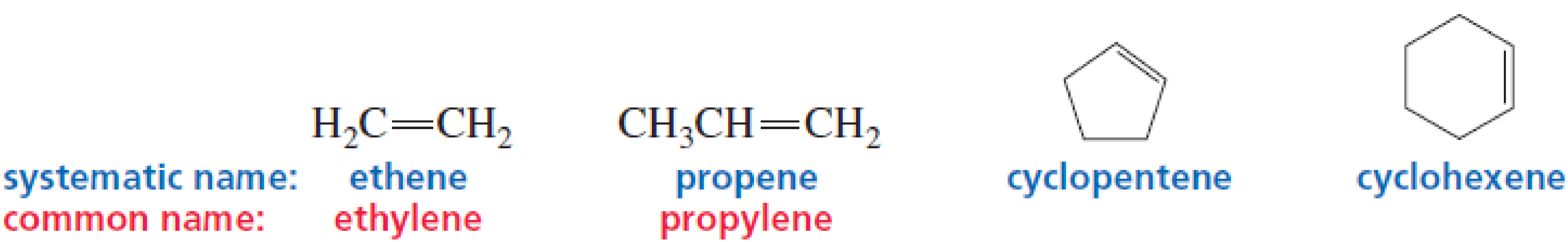
a saturated hydrocarbon

$CH_3CH{=}CHCH_3$

an unsaturated hydrocarbon

NOMENCLATURE

- The systematic (IUPAC) name of an alkene is obtained by replacing the "**<u>ane</u>**" ending of the corresponding alkane with "**<u>ene</u>**."
- For example, a two-carbon alkene is called eth**<u>ene</u>** and a three-carbon alkene is called prop**<u>ene</u>**.
- Ethene also is frequently called by its common name: ethylene



NOMENCLATURE

- Most alkene names need a number to indicate the position of the double bond.
- The IUPAC rules learned previously is applicable to alkenes as well:
- The longest continuous chain containing the functional group (in this case, the carbon–carbon double bond) is numbered in a direction that gives the functional group suffix the lowest possible number.
  - For example, 1-butene signifies that the double bond is between the first and second carbons of butene;
  - 2-hexene signifies that the double bond is between the second and third carbons of hexene.

$$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH}=\overset{1}{CH_2}$$

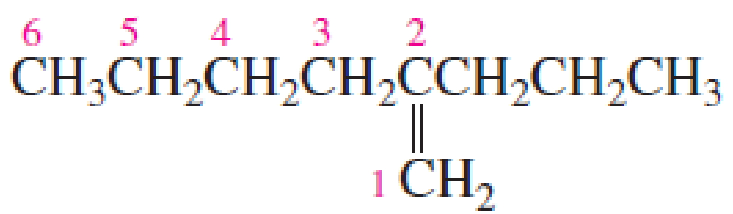
1-butene

$$\overset{1}{CH_3}\overset{2}{CH}=\overset{3}{CH}\overset{4}{CH_3}$$

2-butene

$$\overset{1}{CH_3}\overset{2}{CH}=\overset{3}{CH}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$$

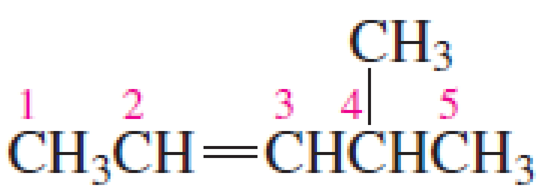
2-hexene



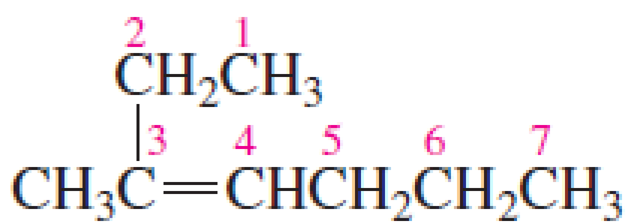
2-propyl-1-hexene

NOMENCLATURE

- The name of a substituent is cited before the name of the longest continuous chain containing the functional group, together with a number to designate the carbon to which the substituent is attached.
- The chain is still numbered in the direction that gives the *functional group suffix* the lowest possible number.



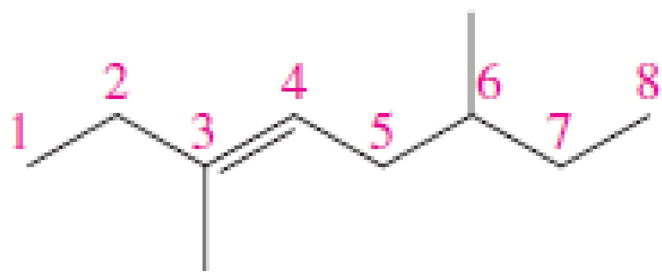
4-methyl-2-pentene



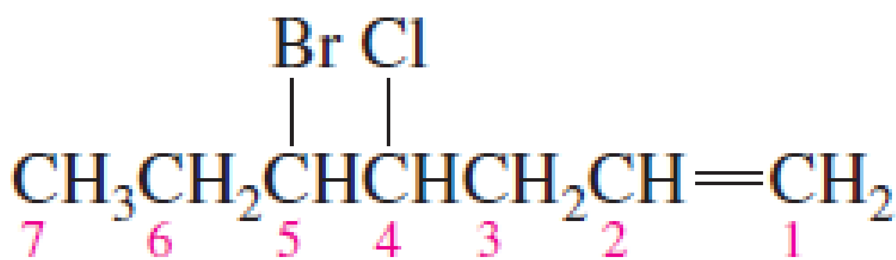
3-methyl-3-heptene

NOMENCLATURE

- If a chain has more than one substituent, the substituents are cited in alphabetical order, using the same rules for alphabetizing as mentioned earlier.
- The prefixes *di*, *tri*, *sec*, and *tert* are ignored in alphabetizing, but *iso*, *neo*, and *cyclo* are not ignored.
- The appropriate number is then assigned to each substituent.



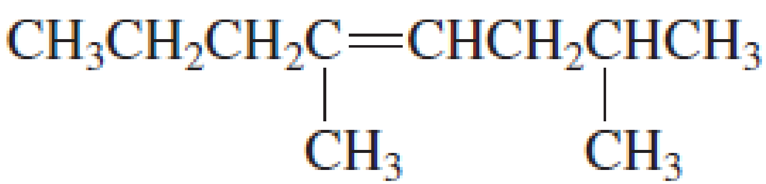
3,6-dimethyl-3-octene



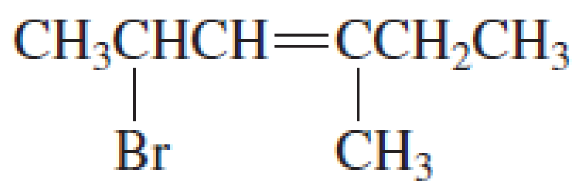
5-bromo-4-chloro-1-heptene

NOMENCLATURE

- If the same number for the alkene functional group suffix is obtained in both directions.
- The correct name is the name that contains the lowest substituent number.
- For example, 2,5-dimethyl-4-octene is a 4-octene whether the longest continuous chain is numbered from left to right or from right to left.



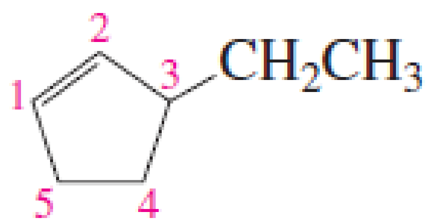
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4



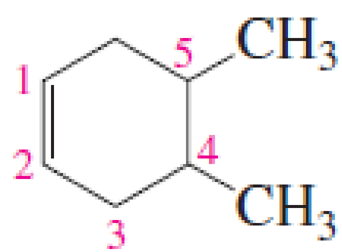
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because 2 < 3

NOMENCLATURE

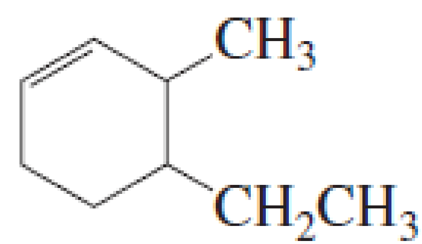
- In cyclic alkenes, a number is not needed to denote the position of the functional group, because the ring is always numbered so that the double bond is between carbons 1 and 2.



3-ethylcyclopentene



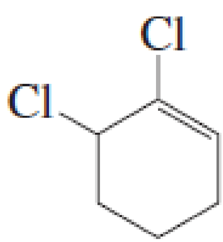
4,5-dimethylcyclohexene



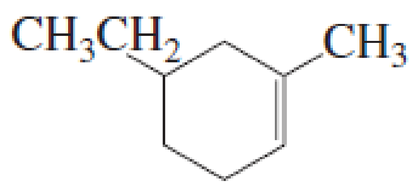
4-ethyl-3-methylcyclohexene

NOMENCLATURE

- In cyclohexenes, the double bond is between C-1 and C-2, regardless of whether you move around the ring clockwise or counterclockwise.
- Therefore, you move around the ring in the direction that puts the lowest substituent number into the name, *not* in the direction that gives the lowest *sum* of the substituent numbers.
- For example, 1,6-dichlorocyclohexene is *not* called 2,3-dichlorocyclohexene because 1,6-dichlorocyclohexene has the lowest substituent number (1), even though it does not have the lowest sum of the substituent numbers (1 + 6 = 7 versus 2 + 3 = 5).



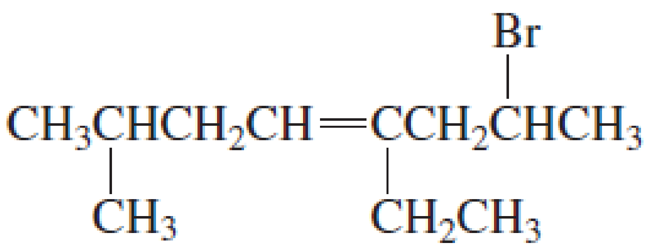
1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene
because 1 < 2



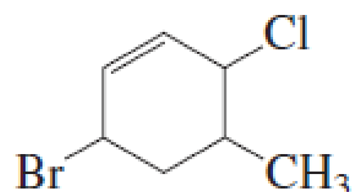
5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene
because 1 < 2

NOMENCLATURE

- If both directions lead to the same number for the alkene functional group suffix and the same low number(s) for one or more of the substituents,
- Then those substituents are ignored and the direction is chosen that gives the lowest number to one of the remaining substituents.



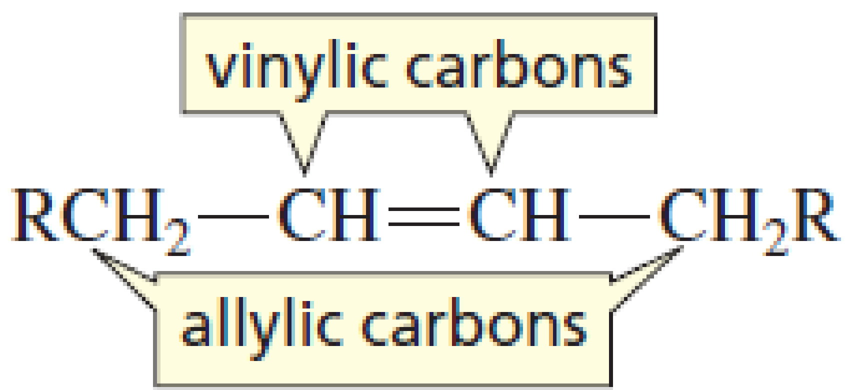
2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene
because 4 < 5



6-bromo-3-chloro-4-methylcyclohexene
not
3-bromo-6-chloro-5-methylcyclohexene
because 4 < 5

Vinylic and Allylic carbon.

- The sp^2 carbons of an alkene are called **vinylic carbons**.
- An sp^3 carbon that is adjacent to a vinylic carbon is called an **allylic carbon**.



Vinylic and Allylic carbon.

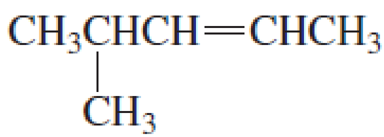
- Two groups containing a carbon–carbon double bond are used in common names—
  - The **vinyl group** and the **allyl group**.
- The vinyl group is the smallest possible group that contains a vinylic carbon; the allyl group is the smallest possible group that contains an allylic carbon.
- When “allyl” is used in nomenclature, the substituent must be attached to the allylic carbon.

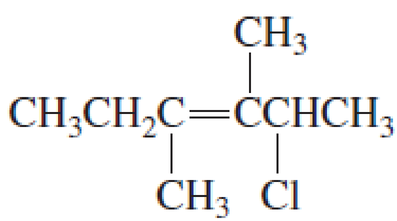
	$H_2C{=}CH{-}$	$H_2C{=}CHCH_2{-}$
	the vinyl group	the allyl group
	$H_2C{=}CHCl$	$H_2C{=}CHCH_2Br$
systematic name:	chloroethene	3-bromopropene
common name:	vinyl chloride	allyl bromide

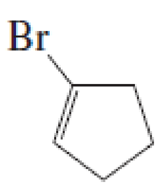
- DO YOU HAVE ANY QUESTIONS?

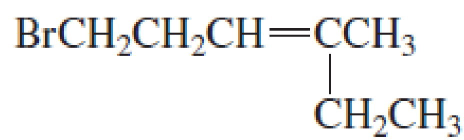
Study Questions

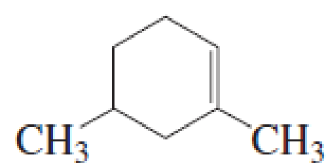
- Draw the structure for each of the following compounds:
  - 3,3-dimethylcyclopentene
  - 6-bromo-2,3-dimethyl-2-hexene
  - allyl alcohol
- Give the systematic name for each of the following compounds:

a. 

b. 

c. 

d. 

e. 

f. 

Study Questions

- Determine the molecular formula for each of the following:
  - A 5-carbon hydrocarbon with one π bond and one ring
  - A 4-carbon hydrocarbon with two π bonds and no rings
  - A 10-carbon hydrocarbon with one π bond and two rings
  - An 8-carbon hydrocarbon with three π bonds and one ring
- Determine the degree of unsaturation for the hydrocarbons with the following molecular formulas:

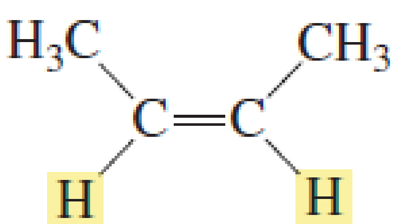
a. $C_{10}H_{16}$ b. $C_{20}H_{34}$ c. C_8H_{16} d. $C_{12}H_{20}$ e. $C_{40}H_{56}$

Determine the degree of unsaturation, and then draw possible structures, for compounds with the following molecular formulas:

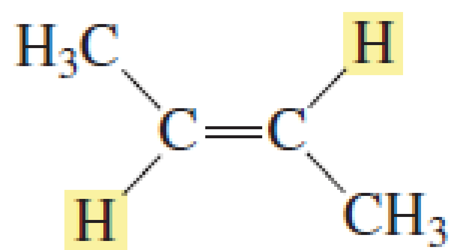
a. C_3H_6 b. C_3H_4 c. C_4H_6

Geometrical isomers or **cis–trans isomers.**

- Because there is an energy barrier to rotation about a carbon–carbon double bond, an alkene such as 2-butene can exist in two distinct forms:
- The hydrogens bonded to the carbons can be on the same side of the double bond or on opposite sides of the double bond.
- The isomer with the hydrogens on the same side of the double bond is called the **cis isomer**
- The isomer with the hydrogens on opposite sides of the double bond is called the **trans isomer**.
- A pair of isomers such as *cis*-2-butene and *trans*-2-butene is called **cis–trans isomers** or **geometric isomers**.
- Cis–trans isomers have the same molecular formula, but differ in the way their atoms are arranged in space



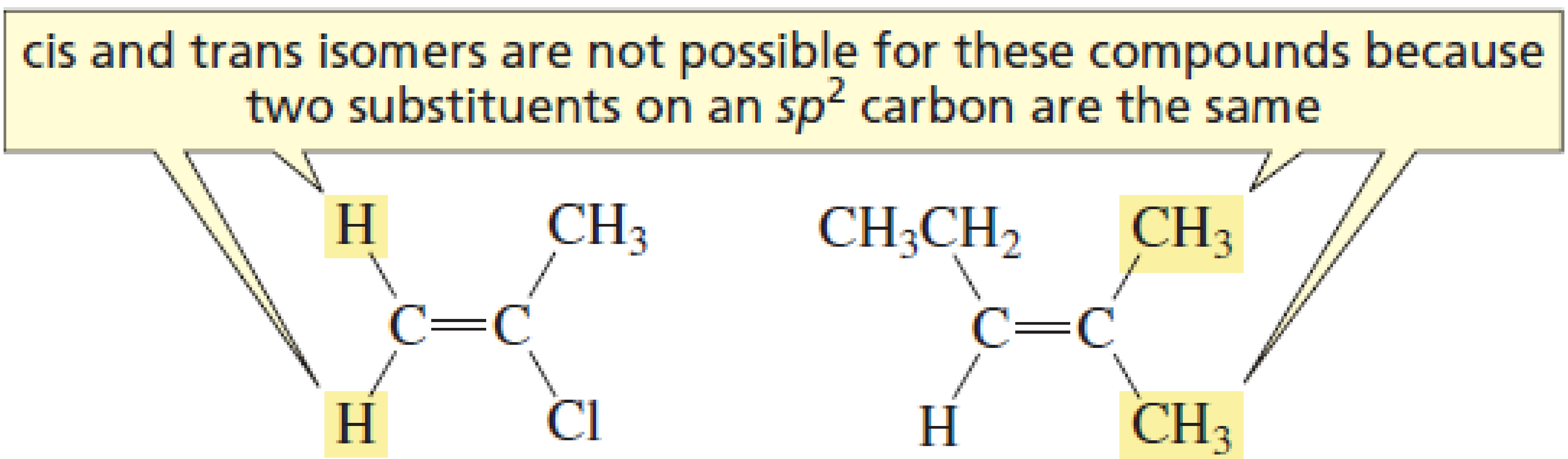
cis-2-butene



trans-2-butene

Geometrical isomers or **cis–trans isomers**.

- If one of the carbons of the double bond is attached to two identical substituents, there is only one possible structure for the alkene.
- In other words, cis and trans isomers are not possible for an alkene that has identical substituents attached to one of the double-bonded carbons.



Study Questions

- Which of the following compounds can exist as cis–trans isomers?
- For those compounds, draw and label the cis and trans isomers.

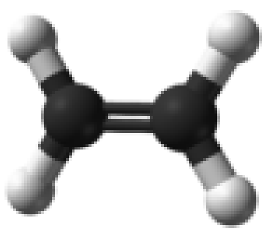
1. $CH_3CH{=}CHCH_2CH_3$
2. $CH_3\underset{\substack{|\\ CH_3}}{C}{=}CHCH_3$
3. $CH_3CH{=}CHCH_3$
4. $CH_3CH_2CH{=}CH_2$

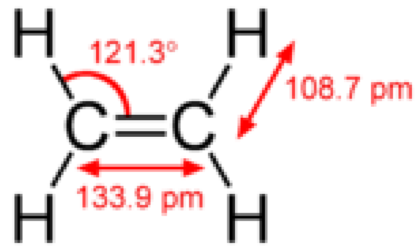
Ethene

- **Ethylene** (IUPAC name: **ethene**) is a hydrocarbon with the formula C_2H_4 or $H_2C{=}CH_2$.
- It is a colorless flammable gas with a faint "sweet and musky" odor when pure.
- It is the simplest alkene and the simplest unsaturated hydrocarbon
- Ethylene is widely used in chemical industry.
- Ethylene is also an important natural plant hormone, used in agriculture to force the ripening of fruits.

Ethene

- Ethylene has four hydrogen atoms bound to a pair of carbon atoms that are connected by a double bond.
- All six atoms that comprise ethylene are coplanar. The H-C-H angle is 120° typical of sp^2 hybridized carbon.
- The molecule is also relatively rigid:
- Rotation about the C-C bond is a high energy process that requires breaking the π-bond.
- The π-bond in the ethylene molecule is responsible for its useful reactivity.
- The double bond is a region of high electron density, thus it is susceptible to attack by electrophiles.





Reactions

- Major reactions of ethylene include:
- Polymerization
- Oxidation
- Halogenation and Hydrohalogenation
- Alkylation
- Hydration
- Oligomerization
- Hydroformylation

Preparation

- It can be produced in the laboratory via dehydration of ethanol with sulfuric acid or in the gas phase with aluminium oxide.
- Industrially, Ethylene is produced in the petrochemical industry by steam cracking
- Also by catalytic cracking of high molecular weight hydrocarbons.

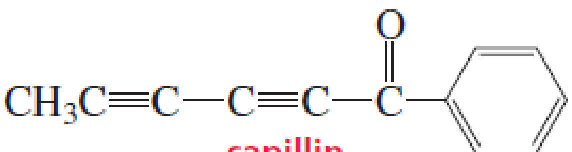
Uses

- In the manufacture of many important polymers like polyethene and polyvinyl chloride (PVC). These polymers are used in the manufacture of raincoats, shoe soles, pipes and floor tiles.
- To prepare epoxyethane which is used in the manufacture of detergents.
- To make ethyle glycol which is used to prepare Terylene
- To prepare other important chemicals like ethyl alcohol (C_2H_5OH), acetaldehyde (CH_3CHO) etc.
- As a general anaesthetic.

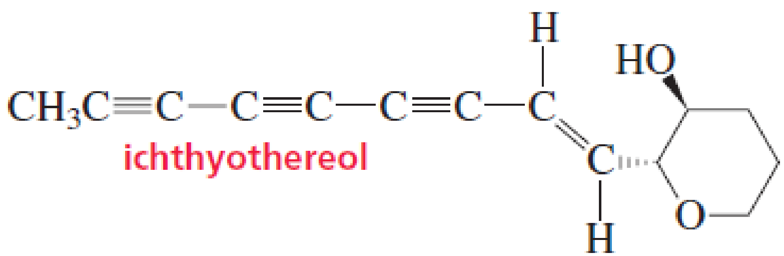
- DO YOU HAVE ANY QUESTIONS?

- **Alkynes**

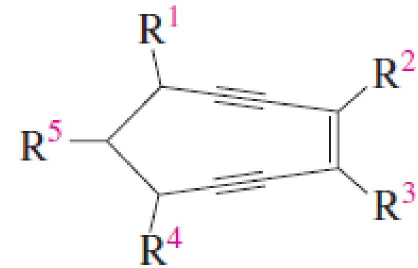
Alkynes



capillin

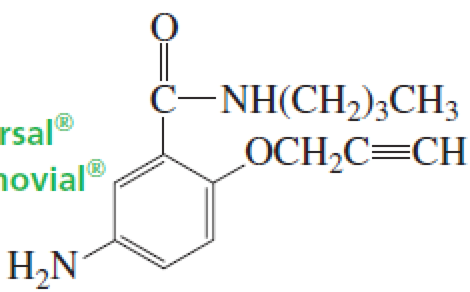


ichthyothereol



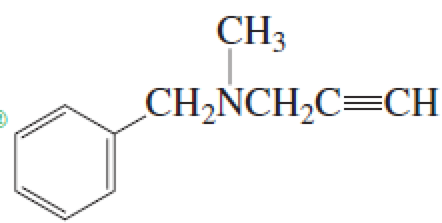
an enediyne

Parsal®
Sinovial®



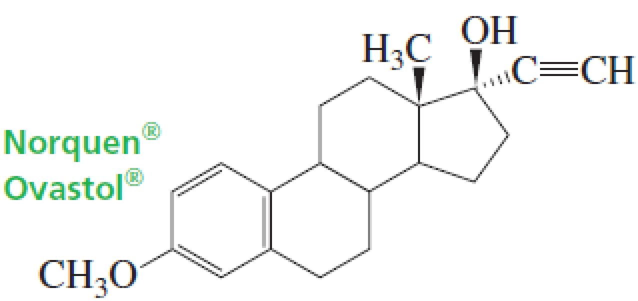
parsalmide
an analgesic

Eudatin®
Supirdyl®



pargyline
an antihypertensive

Norquen®
Ovastol®



mestranol
a component in oral contraceptives

Alkynes

- A**lkynes** are hydrocarbons that contain a carbon–carbon triple bond.
- Because of its triple bond, an alkyne has four fewer hydrogens than the corresponding alkane.
- Therefore, the general molecular formula for an acyclic (noncyclic) alkyne is C_nH_{2n-2} and that for a cyclic alkyne is C_nH_{2n-4}
- There are only a few naturally occurring alkynes. Examples include capillin, which has fungicidal activity, and ichthyothereol, a convulsant used by the Amazon Indians for poisoned arrowheads.
- A class of naturally occurring compounds called enediynes has been found to have powerful antibiotic and anticancer properties.

Nomenclature

- The systematic name of an alkyne is obtained by replacing the "**ane**" ending of the alkane name with "**yne**."
- Analogous to the way compounds with other functional groups are named, the longest continuous chain containing the carbon–carbon triple bond is numbered in the direction that gives the alkyne functional group suffix as low a number as possible.
- If the triple bond is at the end of the chain, the alkyne is classified as a **terminal alkyne**.
- Alkynes with triple bonds located elsewhere along the chain are called **internal alkynes**.
- For example, 1-butyne is a terminal alkyne, whereas
- 2-pentyne is an internal alkyne.

	$HC{\equiv}CH$	$CH_3CH_2C{\equiv}CH$	$CH_3C{\equiv}CCH_2CH_3$	$CH_3CH(CH_2CH_3)C{\equiv}CCH_3$
Systematic:	ethyne	1-butyne	2-pentyne	4-methyl-2-hexyne
Common:	acetylene	ethylacetylene	ethylmethylacetylene	*sec*-butylmethyl-acetylene
		a terminal alkyne	an internal alkyne	

Nomenclature

- In common nomenclature, alkynes are named as *substituted acetylenes*.
- The common name is obtained by citing the names of the alkyl groups, in alphabetical order, that have replaced the hydrogens of acetylene.
- If the same number for the alkyne functional group suffix is obtained counting from either direction along the carbon chain, the correct systematic name is the one that contains the lowest substituent number.
- If the compound contains more than one substituent, the substituents are listed in alphabetical order.

Nomenclature

$$CH_3CH(Cl)CH(Br)C{\equiv}CCH_2CH_2CH_3$$

1 2 3 4 5 6 7 8

3-bromo-2-chloro-4-octyne
not 6-bromo-7-chloro-4-octyne
because 2 < 6

$$CH_3CH(CH_3)C{\equiv}CCH_2CH_2Br$$

6 5 4 3 2 1

1-bromo-5-methyl-3-hexyne
not 6-bromo-2-methyl-3-hexyne
because 1 < 2

The triple-bond-containing propargyl group is used in common nomenclature. It is analogous to the double-bond-containing allyl group discussed in Alkenes.

$HC{\equiv}CCH_2{-}$
propargyl group

$H_2C{=}CHCH_2{-}$
allyl group

$HC{\equiv}CCH_2Br$
propargyl bromide

$H_2C{=}CHCH_2OH$
allyl alcohol

Study Questions

- Draw the structure for each of the following compounds.
  - 1-chloro-3-hexyne
  - propargyl chloride
  - cyclooctyne
  - 4,4-dimethyl-1-pentyne
  - isopropylacetylene
  - dimethylacetylene
- Draw the structures and give the common and systematic names for the seven alkynes with molecular formula C_6H_{12}.

Study Questions

- Give the systematic name for each of the following compounds:

a. $BrCH_2CH_2C\equiv CCH_3$

b. $CH_3CH_2\underset{|}{\underset{Br}{C}}HC\equiv CCH_2\underset{|}{\underset{Cl}{C}}HCH_3$

c. $CH_3OCH_2C\equiv CCH_2CH_3$

d. $CH_3CH_2\underset{|}{\underset{CH_2CH_2CH_3}{C}}HC\equiv CH$

- Which would you expect to be more stable, an internal alkyne or a terminal alkyne? Why?

Ethyne

- **Acetylene** (systematic name: **ethyne**) is the chemical compound with the formula C_2H_2.
- It is a hydrocarbon and the simplest alkyne.
  - It is a colorless gas
  - It is widely used as a fuel and a chemical building block.
  - It is unstable in pure form and thus is usually handled as a solution.
  - Pure acetylene is odorless, but commercial grades usually have a marked odor due to impurities.
- As an alkyne, acetylene is unsaturated because its two carbon atoms are bonded together in a triple bond.
- The carbon–carbon triple bond places all four atoms in the same straight line, with CCH bond angles of 180°.

Preparation

- Acetylene is mainly manufactured by the partial combustion of methane

$$2CH_4 ==> HCCH + 3H_2$$

- As a side product in the ethylene stream from cracking of hydrocarbons.

$$3C_4H_{10} + 2H_2O ==> 2HCCH + 2C_2H_4 + 2CH_4 + 2CO + 7H_2$$

- It was prepared by the hydrolysis of calcium carbide, a reaction discovered by Friedrich Wöhler in 1862.

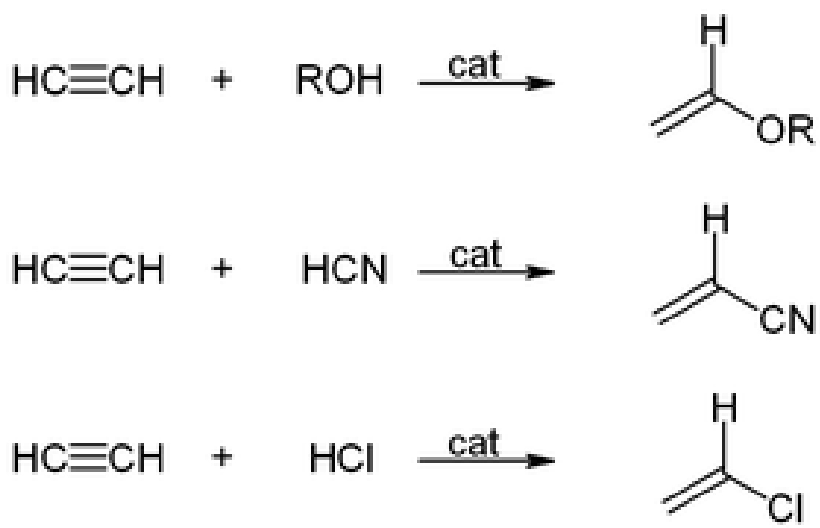
$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Reactions and Applications

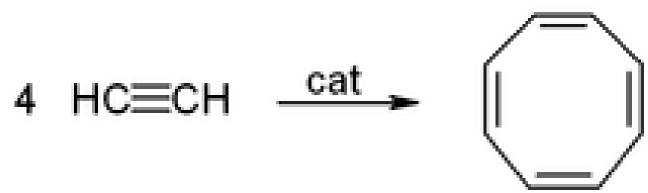
- An application is the conversion of acetylene to ethylene for use in making a variety of polyethylene plastics.
- An important reaction of acetylene is its combustion, the basis of the acetylene welding technologies.
- Its major applications involve its conversion to acrylic acid derivatives.
- Compared to most hydrocarbons, acetylene is relatively acidic, though it is still much less acidic than water or ethanol. Thus it reacts with strong bases to form acetylide salts.
  - For example, acetylene reacts with sodium amide in liquid ammonia to form sodium acetylide, and with butyllithium in cold THF to give lithium acetylide.

- Acetylides of heavy metals are easily formed by reaction of acetylene with the metal ions. Several, e.g., silver acetylide (Ag_2C_2) and copper acetylide (Cu_2C_2), are powerful and very dangerous explosives.

- in the presence of metal catalysts, acetylene can react to give a wide range of industrially significant chemicals.
  - With alcohols, hydrogen cyanide, hydrogen chloride, or carboxylic acids to give vinyl compounds



- With aldehydes to give ethynyl diols, in the Favorskii reaction:
- With carbon monoxide to give acrylic acid, or acrylic esters, which can be used to produce acrylic glass:
- Cyclicization to give benzene, cyclooctatetraene, or hydroquinone:



Uses of Ethyne

- As the fuel for the oxyacetylene blow-lamp used in cutting and welding metals.
- To prepare ethanal (i.e. acetaldehyde), and
- many important organic chemicals, including vinyl chloride monomer, which is used in the manufacture of the industrially important plastic polyvinyl chloride, PVC.

- DO YOU HAVE ANY QUESTIONS?