Chapter 2
Unsaturated Hydrocarbons

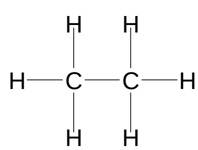
Chapter Objectives:

- Learn to recognize the difference between saturated and unsaturated hydrocarbons.
- Learn to recognize the alkene, alkyne, and aromatic functional groups.
- Learn the IUPAC system for naming alkenes, alkynes, and aromatic rings.
- Learn the important physical properties of the unsaturated hydrocarbons.
- Learn the major chemical reaction of alkenes, and learn how to predict the products of halogenation, hydrogenation, addition of acids, and hydration reactions.
- Learn the important characteristics of addition polymers.

Mr. Kevin A. Boudreaux
Angelo State University
CHEM 2353 Fundamentals of Organic Chemistry
Organic and Biochemistry for Today (Seager & Slabaugh)
www.angelo.edu/faculty/kboudrea

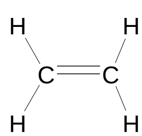
Unsaturated Hydrocarbons

- **Saturated Hydrocarbons** — contain only carbon-carbon single bonds.

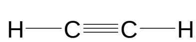


Alkanes

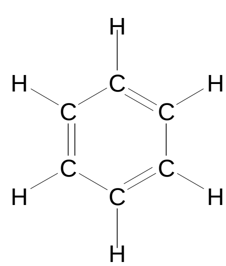
- **Unsaturated Hydrocarbons** — contain carbon-carbon double or triple bonds (more hydrogens can be added).



Alkenes



Alkynes



Aromatics

2

Alkenes

3

Alkenes

- **Alkenes** contain **carbon-carbon double bonds**.
  - General formula: C_nH_{2n} (for one double bond)
  - Suffix = **-ene**
- In the carbon-carbon double bond, two pairs of electrons are being shared, leaving the carbon free to bond to two other things.

$CH_2{=}CH_2$ — ethylene, C_2H_4

$CH_2{=}CH{-}CH_3$ — propylene, C_3H_6

$CH_2{=}CH{-}CH_2{-}CH_3$ $\quad$ $CH_3{-}CH{=}CH{-}CH_3$ $\quad$ $CH_2{=}C(CH_3){-}CH_3$

C_4H_8

4

IUPAC Nomenclature of Alkenes

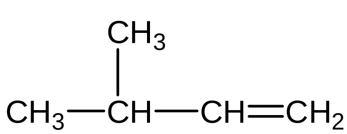
- **Step 1.** Identify and name the longest continuous chain of C atoms **which contains the double bond(s)** (**#C + -ene**).
- **Step 2.** Number the longest chain so that the C's joined by the double bond have the lowest numbers possible. If the double bond has the same position starting from either end, use the positions of the substituents to determine beginning of the chain.
- **Step 3.** Locate the double bond by the lower-numbered carbon atom joined by the double bond (e.g., 1-butene).
- **Step 4.** Locate and name attached groups.
- **Step 5.** Combine the names for the attached groups and the longest chain into the name.

5

Examples: Nomenclature of Alkenes

- Provide acceptable IUPAC names for the following molecules:

$CH_3—CH_2—CH{=}CH_2$ $\qquad$ $CH_3—CH{=}CH—CH_3$

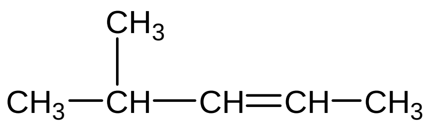


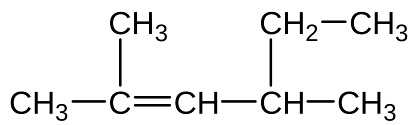
$CH_2{=}CH—CH_2—CH_2—Br$

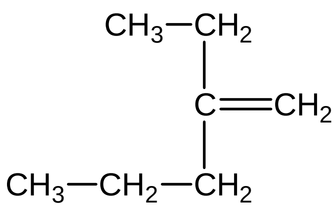
6

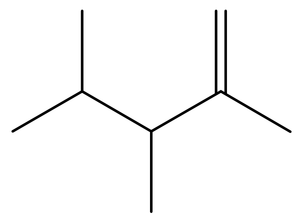
Examples: Nomenclature of Alkenes

- Provide acceptable IUPAC names for the following molecules:





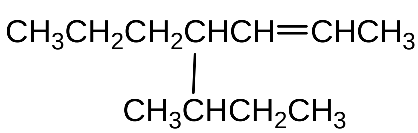


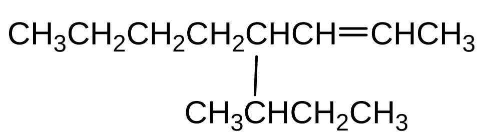


7

Examples: Nomenclature of Alkenes

- Provide acceptable IUPAC names for the following molecules:





8

IUPAC Nomenclature of Alkenes

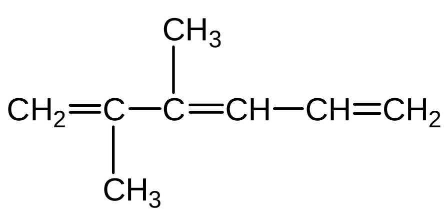
- If there is more than one double bond:
  - a **counting prefix** (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix **-ene** to indicate the number of double bonds (*di*ene, *tri*ene, *tetra*ene, etc.).
  - Usually, an "a" is placed before the counting prefix to make pronunciation easier (e.g., but*a*diene).
  - The starting position of each double bond is indicated by the lower number, separated by commas (e.g., *1,3*-butadiene).
- For cycloalkenes, the ring is named as **cyclo-** + **#C** + **-ene**; one of the carbons of the double bond must be numbered "1."

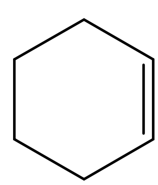
Examples: Nomenclature of Alkenes

- Provide acceptable IUPAC names for the following molecules:

$CH_2{=}CH{-}CH{=}CH_2$

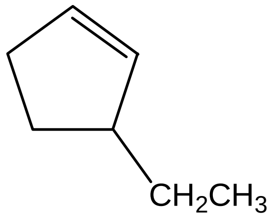
$CH_3{-}CH{=}C{=}CH_2$

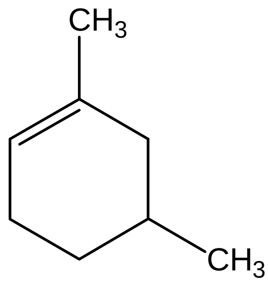


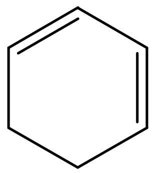


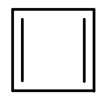
Examples: Nomenclature of Alkenes

- Provide acceptable IUPAC names for the following molecules:









11

Examples: Nomenclature of Alkenes

- Draw structural formulas for the following molecules:
  – 2-methyl-2-butene

  – 4-methyl-1-pentene

  – 2-methyl-3-pentene (what's wrong with this name?)

12

Examples: Nomenclature of Alkenes

- Draw structural formulas for the following molecules:
  - 4-ethyl-3-hexene (what's wrong with this name?)
  - 2,3,4-trimethyl-1,3-pentadiene
  - 1,6-dimethylcyclohexene

13

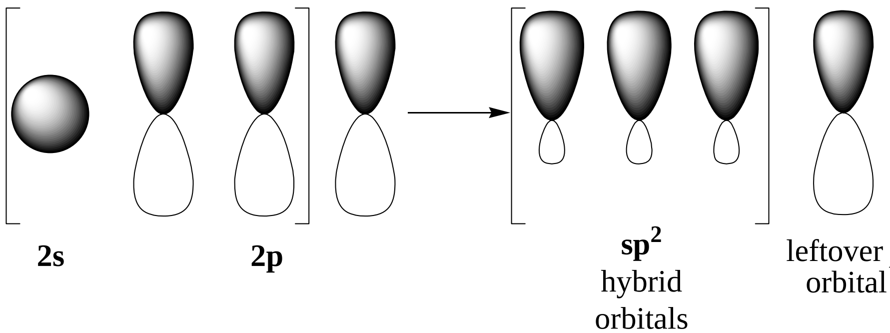
Examples: Nomenclature of Alkenes

- Draw structural formulas for the following molecules:
  - 1,1-dimethyl-2-cyclohexene (what's wrong with this name?)
  - 5-ethyl-1,3-cyclopentadiene

14

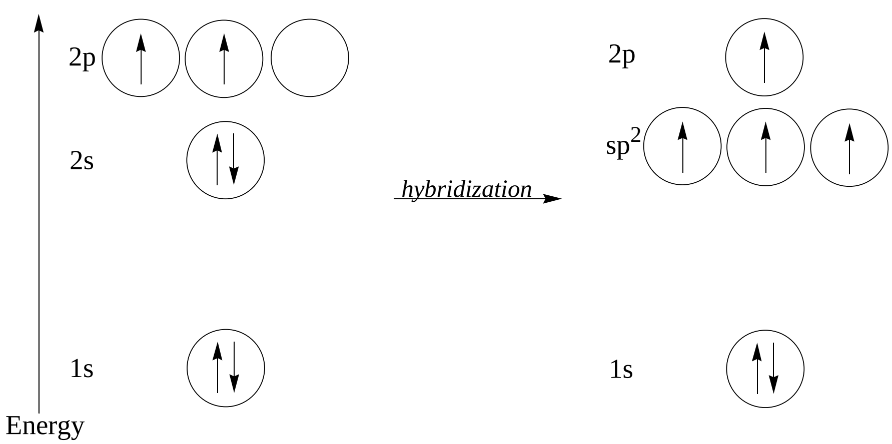
Hybridization of Alkenes

- When a carbon is connect to three other things (that is, one of the bonds is a double bond), the molecule is modeled by combining the 2*s* and two of the 2*p* orbitals to produce **three *sp*^{2} orbitals**.
- Since only two of the 2*p* orbitals were hybridized, there is **one leftover *p* orbital** in an *sp*^{2}-hybridized carbon atom.



15

Hybrid Orbitals

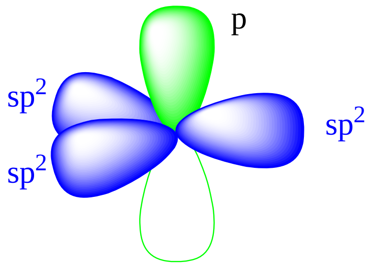


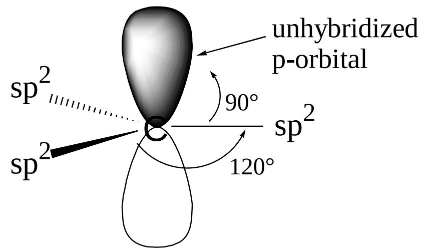
- All three *sp*^{2} orbitals are at the same energy level, with one electron in each hybrid orbital, and one in the slightly higher-energy unhybridized 2*p* orbital.

16

The Shape of an sp² Carbon

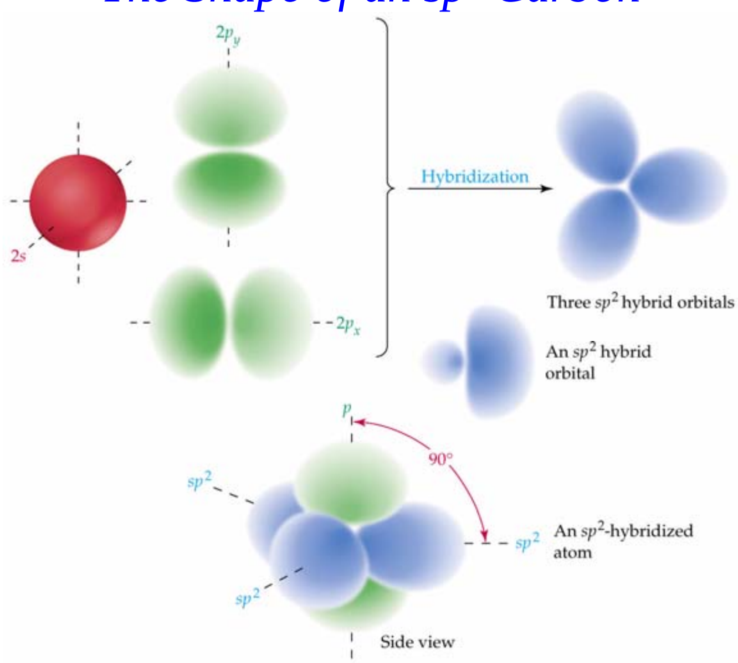
- The *sp*² orbitals are arranged in a **trigonal planar** shape around the central carbon atom, with bond angles of **120º**.
- The unhybridized *p* orbital is perpendicular to this plane.





17

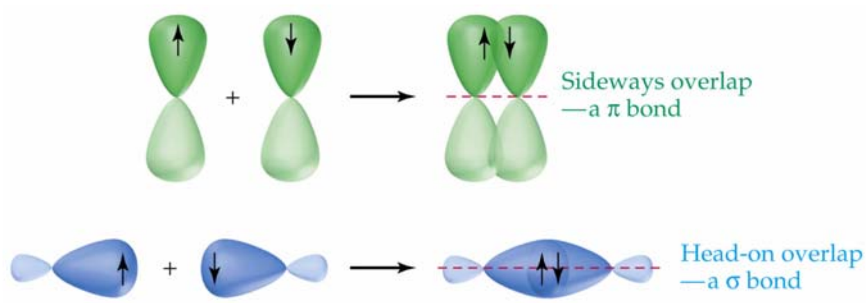
The Shape of an sp² Carbon



18

Sigma and Pi Bonds

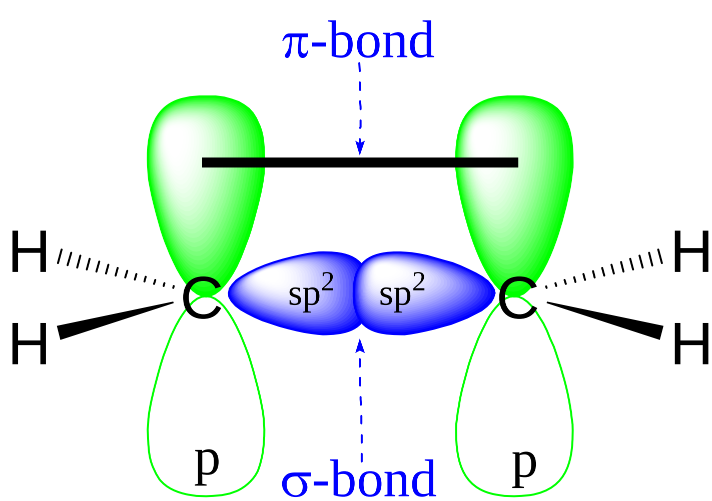
- When two *sp*^{2}-hybridized carbons are next to each other, two kinds of orbital overlap take place:
  - *end-on-end overlap* of the *sp*^{2} orbitals to make a **σ-bond** (sigma bond).
  - *side-to-side overlap* of the unhybridized *p* orbitals to make a **π-bond** (pi bond).



19

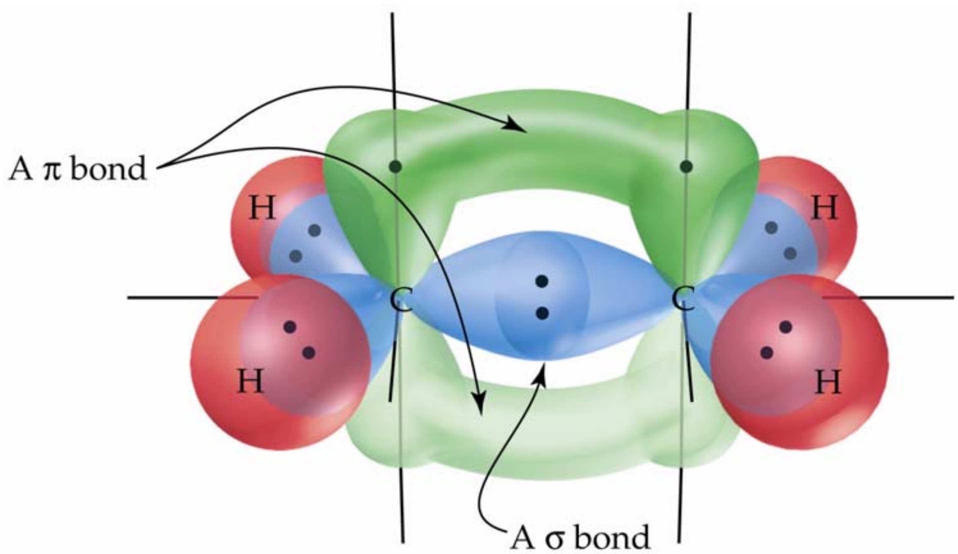
Bonding in Ethylene

- Because of the π-bond, *free rotation is not possible* around carbon-carbon double bonds.



20

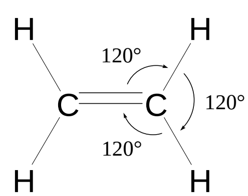
Bonding in Ethylene

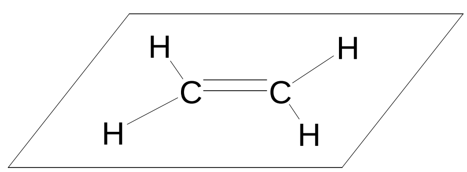


21

The Shape of the Ethylene Molecule

- Since each carbon in the double bond is trigonal planar in shape, the entire ethylene molecule is a flat molecule, with the atoms separated by bond angles of 120°.

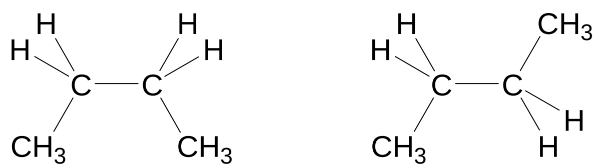




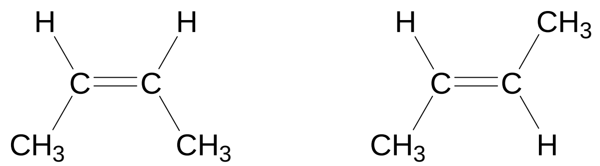
22

Geometric Isomers in Alkenes

- Because free rotation is not possible around double bonds, there are two different forms of 2-butene, which are **geometric isomers** (or **cis/trans** isomers) of each other:



same molecule

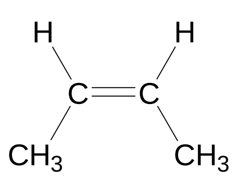


different molecules

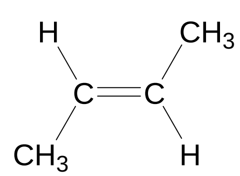
23

Geometric Isomers in Alkenes

- The geometric isomers have to have different names, since they are different molecules:
  - the prefix ***cis-*** is used when the arms of the longest chain are on the **same side** of the double bond
  - the prefix ***trans-*** is used when they are on **opposite sides** of the double bond.



cis-2-butene



trans-2-butene

- Geometric isomers have overall different molecular shapes, and may have drastically different chemical and physical properties.

24

Examples: Geometric Isomers

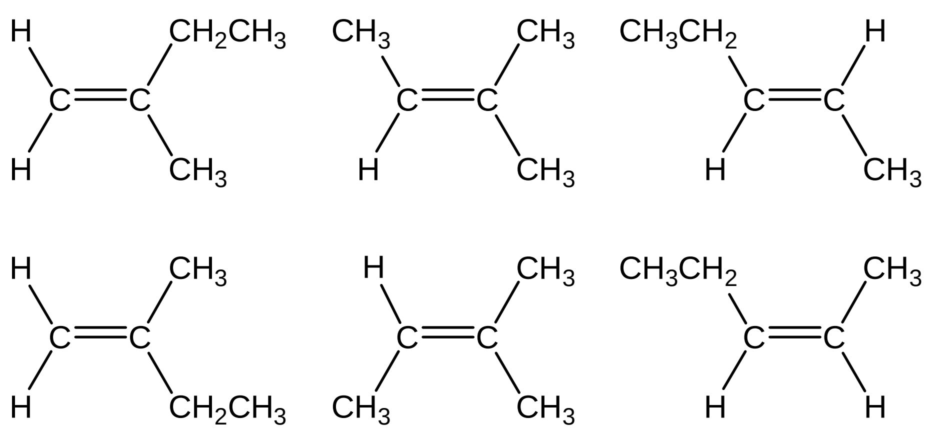
- Are the following molecules geometric isomers of each other, or are they the same molecule?

– (Any time both carbons in a double bond have two different things attached to them, geometric isomers can exist.)

25

Examples: Geometric Isomers

- Which of the following molecules are structural isomers of each other, which are geometric isomers of each other, and which are the same molecule?



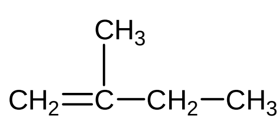
26

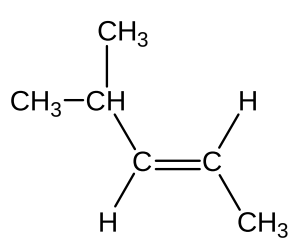
Examples: Geometric Isomers

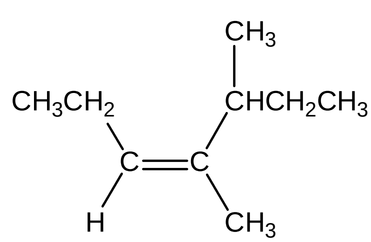
- Draw structural formulas for the following molecules:
  - Cl—CH=CH—CH_3 (draw and name both geometric isomers)
  - *cis*-2-pentene
  - *trans*-3-methyl-3-hexene

Examples: Geometric Isomers

- Provide IUPAC names for the following molecules:



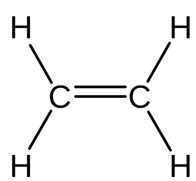




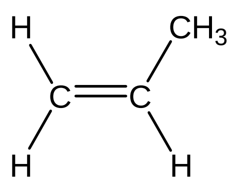
Some Important Alkenes

29

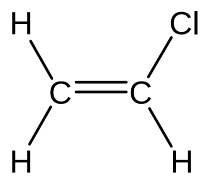
Some Important Alkenes



Ethylene (**ethene**)
Used in the manufacture of the plastic *polyethylene*. The release of ethylene stimulates the beginning of the ripening process in many plants; some plants can be picked while unripe (when they are less fragile), and exposed to ethylene gas to cause ripening once they reach their destination



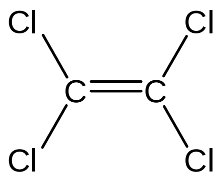
Propylene (**propene**)
Produced in the cracking of petroleum; used in the manufacture of the plastic *polypropylene*.



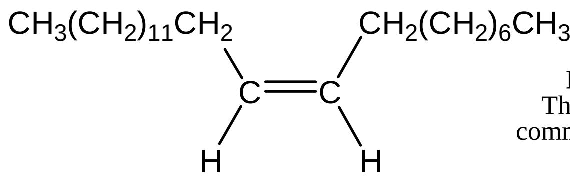
Vinyl chloride (**chloroethene**)
A carcinogenic gas manufactured from ethylene; used in the manufacture of the plastic *polyvinyl chloride* (PVC).

30

Some Important Alkenes



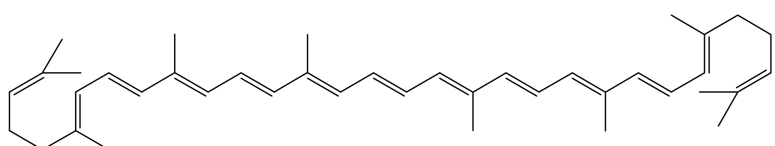
Tetrachloroethylene
Better known as *perchloroethylene* ("Perc"); a non-flammable organic solvent, widely used in dry cleaning; it is also used as an industrial solvent, degreaser, and paint remover.



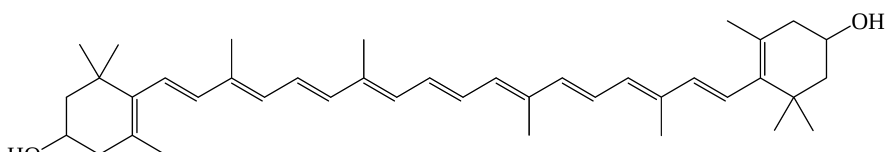
Muscalure (***cis*-9-tricosene**)
The sex pheromone of the female common housefly (*Musca domestica*).

31

Some Important Alkenes



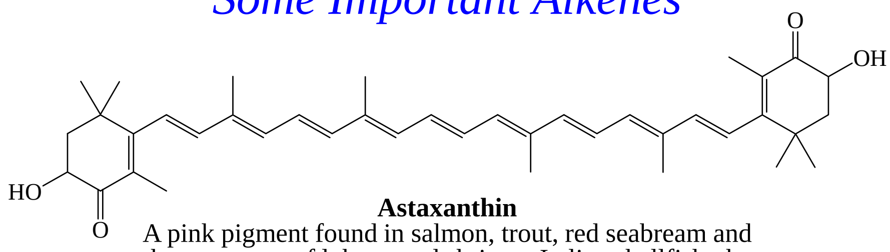
Lycopene
A red pigment found in tomatoes, watermelon, guava, papaya, pink grapefruit, apricots, and rosehips; lycopene is a good antioxidant, and is more readily absorbed from cooked tomatoes and tomato paste, especially if the foods contain fat.



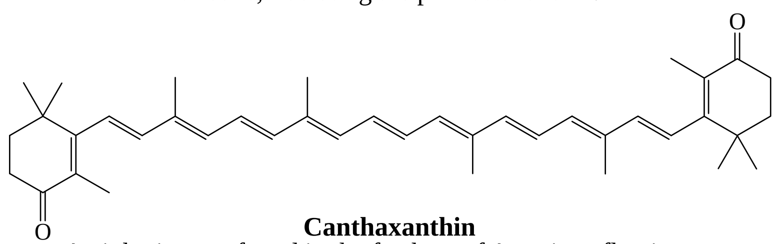
Zeaxanthin
A yellow pigment found in corn, egg yolk, orange juice, mangoes; also contributes to the yellowish color of animal fats. It is also found in the macula region of the retina (macula lutea, "yellow spot"), where it filters out some blue and UV light, acting like internal sunglasses; macular degeneration is the most common cause of blindness in the elderly.

32

Some Important Alkenes



Astaxanthin
A pink pigment found in salmon, trout, red seabream and the carapaces of lobster and shrimp. In live shellfish, the astaxanthin is wrapped in a protein which gives it a blackish color; when the shellfish are boiled, the protein uncoils, liberating the pink astaxanthin.

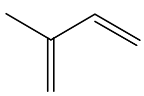


Canthaxanthin
A pink pigment found in the feathers of American flamingos. It is obtained from shrimp in their diet; flamingos in captivity lose their pink color if they are not supplied with shrimp.

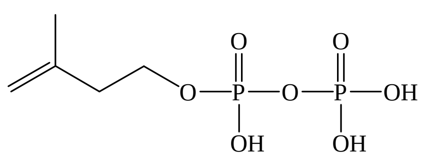
33

Terpenes and Essential Oils

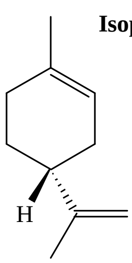
Terpenes are a diverse group of molecules which are biologically synthesized from **isoprene** units. They are found in many plants, and often have distinctive flavors and aromas. They are often components of *essential oils*, so named because they have a characteristic "essence" or fragrance. Many of these molecules are components of common foods and perfumes. (Lycopene and its related compounds are also terpenes.)



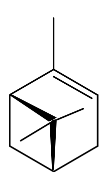
Isoprene



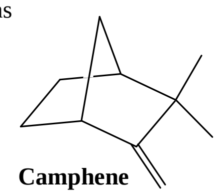
Isopentenyl pyrophosphate
precursor for the natural synthesis of terpene hydrocarbons



(*R*)-(+)-Limonene
citrus fruits



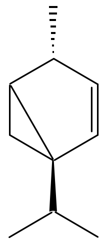
α-Pinene
turpentine



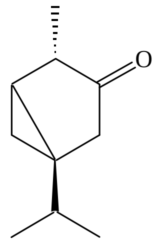
Camphene
turpentine, cypress oil, oil of citronella

34

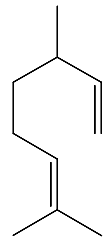
Terpenes and Essential Oils



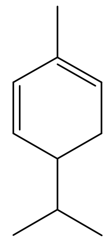
Thujene
oil of thuja, sage,
tansy, and wormwood



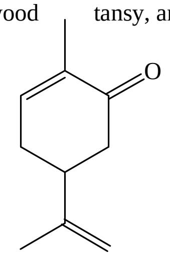
Thujone
oil of thuja, sage,
tansy, and wormwood



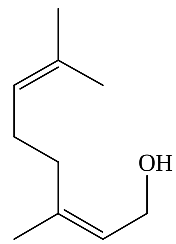
β-Myrcene
oil of bay



α-Phellandrene
eucalyptus



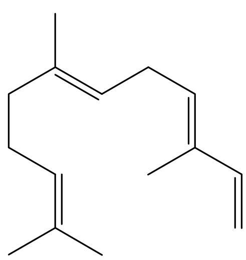
Carvone
d-isomer, caraway seed oil
l-isomer, spearmint oil



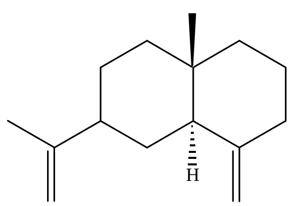
Geraniol
citronella oil, pomerosa oil, geraniums,
roses (with 2-phenylethanol)

35

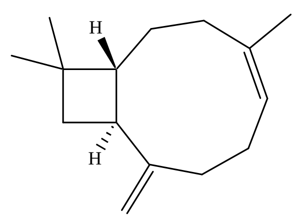
Terpenes and Essential Oils



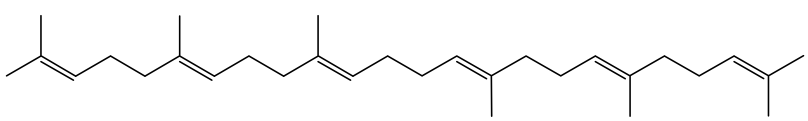
α-Farnesene
A waxy substance found
on the outer skin of apples.



β-Selinene
found in oil of celery



Caryophyllene
found in oil of cloves

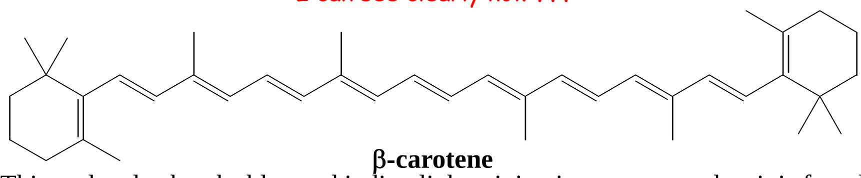


Squalene
Squalene is found in shark liver oil, and is also a major
component of the lipids on the surface of human skin. It is
a precursor for the biosynthesis of cholesterol.

36

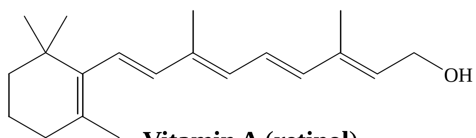
The Chemistry of Vision

"I can see clearly now . . ."



β-carotene

This molecule absorbs blue and indigo light, giving it an orange color; it is found in carrots, yams, mangoes, and persimmons. The yellow color of butter and animal fats comes from carotene and related molecules. Carotene is found along with chlorophyll in photosynthetic organisms; it protects cells by reacting with O_2 molecules. The yellow color of autumn leaves is due to the carotene, which is unmasked as the chlorophyll in the leaves breaks down.



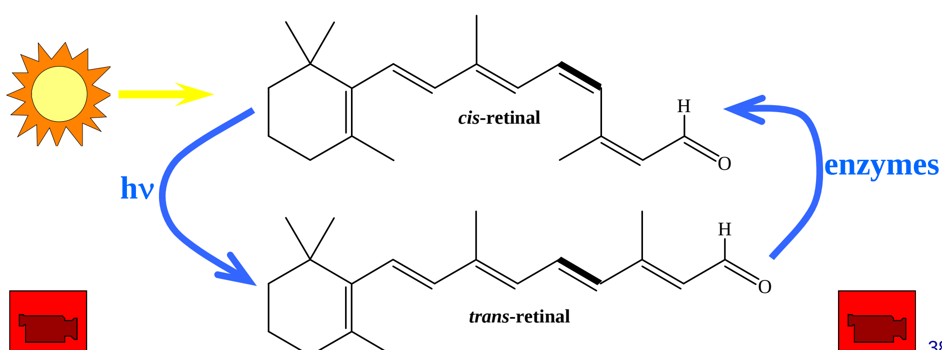
Vitamin A (**retinol**)

A fat-soluble vitamin; a metabolic product of carotene, found in liver, egg yolks, butter, and milk. The oxidized form, **retinal**, combines with the protein **opsin** to form **rhodopsin**, the primary light-gathering pigment in vertebrate retinas; also involved in cell growth and maintenance of healthy skin tissue.

37

The Chemistry of Vision

In the rod and cone cells in the retina of the eye, retinal in rhodopsin is found "at rest" in the *cis* form. When it absorbs a photon (hν) of light, one of the π-bonds is broken, causing the molecule to rotate and lock into the *trans* form, which has a completely different shape. This starts a long chain of chemical processes which eventually results in a visual image in the brain. The *trans*-retinal molecule is then twisted back into the *cis* form by a set of enzymes. When you look directly at a very bright light, the "afterimage" that you see in front of your eyes is the result of a large amount of *cis*-retinal having been transformed into *trans*-retinal all at once; the enzymes take a little bit of time to go through and "reset" all of these molecules back to the *cis* form.



38

Physical and Chemical Properties of Alkenes

39

Physical Properties of Alkenes

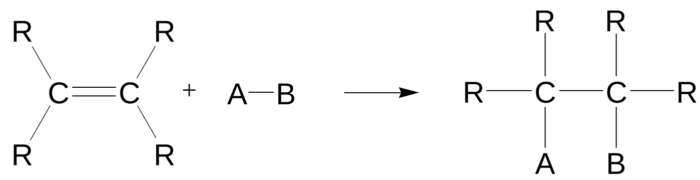
- Many of the physical properties of alkenes are similar to those of alkanes.
  - Alkenes are nonpolar compounds.
    - insoluble in water.
    - soluble in nonpolar solvents.
  - They are less dense than water.
- Range of physical states:
  - $\leq$ 4 C's — gases
  - 5 - 17 C's — liquids
  - $\geq$ 18 C's — solids
- The chemical properties of alkenes, however, are *completely* different from those of alkanes.

40

Reactions of Alkenes — Addition Reactions

- Most reactions of alkenes can be classified as **addition reactions**, in which both parts of a reactant are added to the carbon-carbon double bond:

General Reaction:

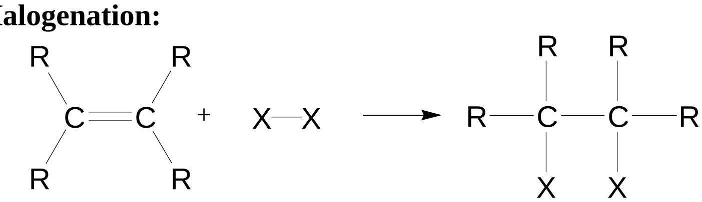


41

Halogenation of Alkenes

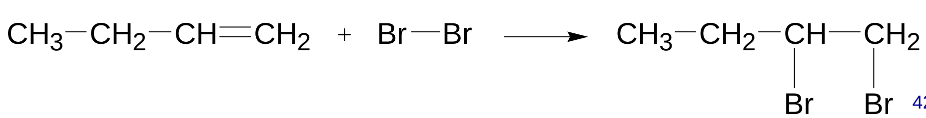
- In a **halogenation reaction**, an alkene reacts with molecular bromine (Br_2) or chlorine (Cl_2) to form an **alkyl halide** (or haloalkane).

Halogenation:



X = Cl or Br

a **haloalkane**
or
alkyl halide

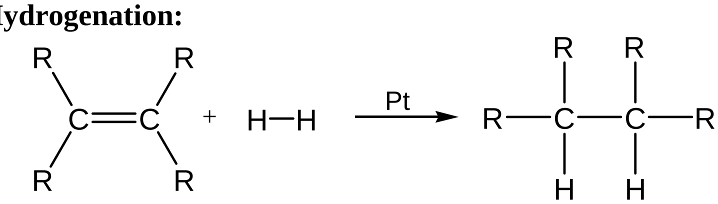


42

Hydrogenation of Alkenes

- In a **hydrogenation reaction**, a hydrogen atom is added to each carbon of the double bond, converting the alkene into an alkane.
- The reaction only takes place in the presence of a metal catalyst (usually Pt).
- This same process is used to produce *hydrogenated* vegetable oils such as margarine and shortening.

Hydrogenation:



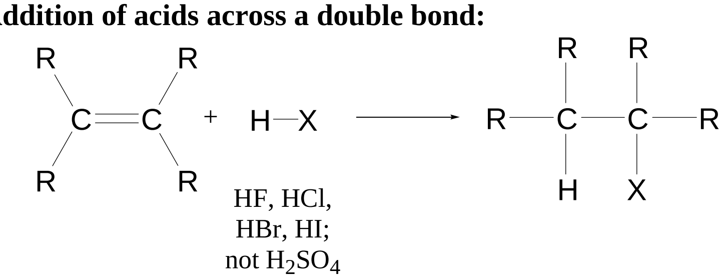
$$CH_3-CH=CH-CH_3 + H-H \xrightarrow{Pt} CH_3-CH_2-CH_2-CH_3$$

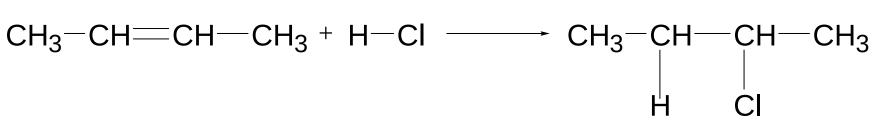
43

Addition of Acids

- Acids (HF, HCl, HBr, and HI) can add to a double bond to produce an alkyl halide.

Addition of acids across a double bond:

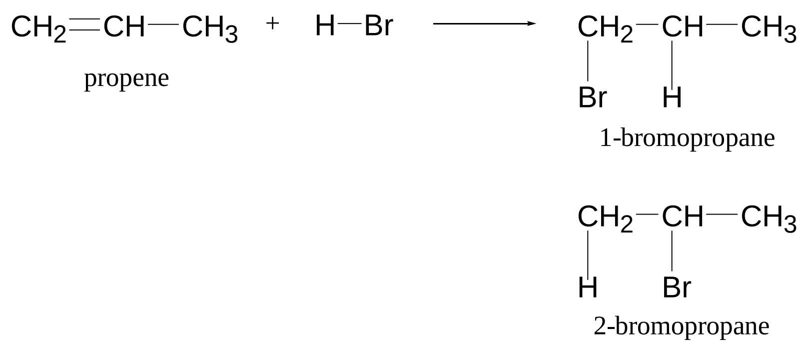




44

Addition of Acids

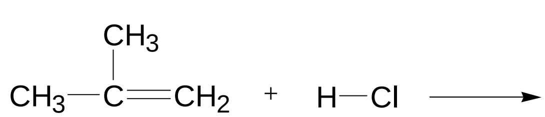
- If the alkene is unsymmetrical, there are two possible products in this kind of reaction:

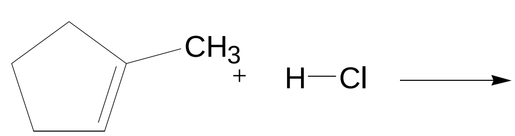


- The **major product** of the reaction is predicted using *Markonikov's Rule*:

Addition of Acids: Markonikov's Rule

- **Markonikov's Rule** (Vladimir Markonikov, 1869): when a molecule of the form H-X adds to a double bond, the hydrogen becomes attached to the carbon atom that is already bonded to the most hydrogen atoms. ("The rich get richer")

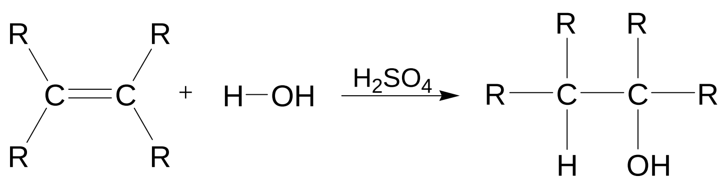




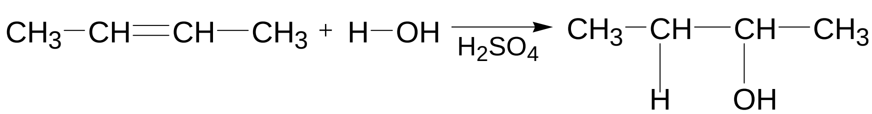
Hydration of Alkenes

- In a **hydration** reaction, the elements of water are added to an alkene, producing an **alcohol** as the product.
- This reaction requires the presence of a strong acid catalyst (usually H_2SO_4).

Hydration of an Alkene:



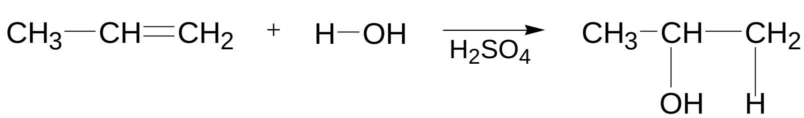
an alcohol



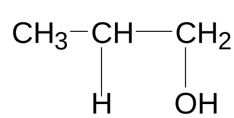
47

Hydration of Alkenes

- This reaction also follows Markonikov's Rule.



major product

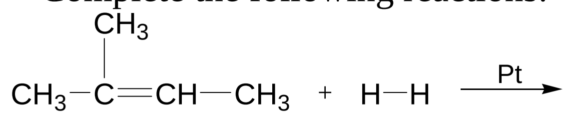


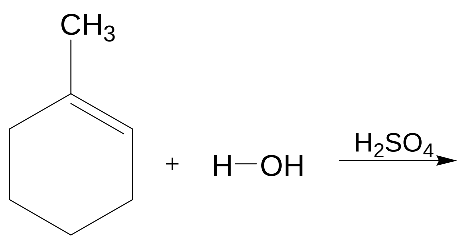
minor product

48

Examples: Reactions of Alkenes

- Complete the following reactions:

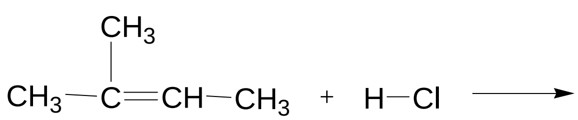


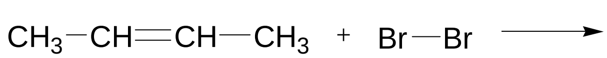


49

Examples: Reactions of Alkenes

- Complete the following reactions:



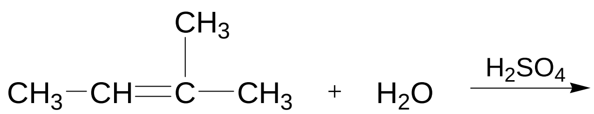


50

Examples: Reactions of Alkenes

- Complete the following reactions:

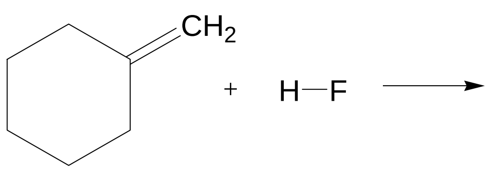
$$CH_3-CH=CH_2 + H-H \longrightarrow$$

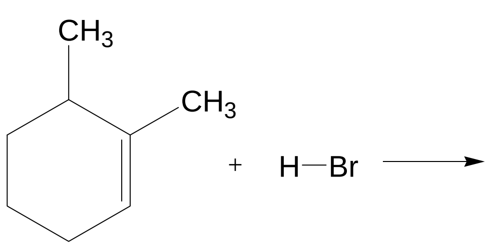


51

Examples: Reactions of Alkenes

- Complete the following reactions:





52

Addition Polymers

53

Addition Polymers

- **Polymers** are long, chain-like organic molecules built up from simpler subunits called **monomers**.

$$\underset{\text{monomer}}{n\ \mathrm{A}} \longrightarrow \underset{\text{polymer}}{\mathrm{—A—A—A—A—A—A—}} = \left(\mathrm{A}\right)_n$$

- In **addition polymers**, every atom in the reacting molecules becomes incorporated into the resulting polymer molecule. In most addition polymers, the monomer contains a double bond.

$$CH_2{=}CH_2 \quad CH_2{=}CH_2 \quad CH_2{=}CH_2 \quad CH_2{=}CH_2$$

ethylene

$$\downarrow$$

$$\leftarrow CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2 \rightarrow$$

polyethylene

54

The Complexity of Polymers

Amorphous Polymers ⟷ **Complex Polymers**

- **Amorphous Polymers (Plastics)**
  - These polymers are very simple, usually consisting of one or two repeating subunits, and have no complex three-dimensional structure.
  - Examples include polyethylene, rubber, saran, Teflon, nylon, polyesters, etc.
- **Complex Polymers**
  - These polymers often consist of a number of repeating subunits, and do have complex linear and three-dimensional structures.
  - Examples include proteins and enzymes, DNA, RNA.

Some Common Addition Polymers

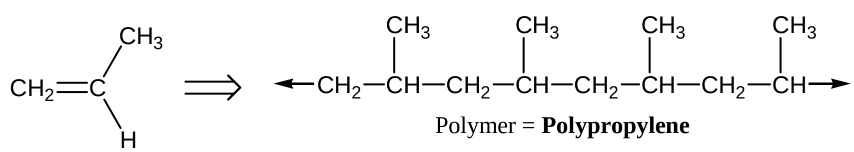
$$n\ CH_2{=}CH_2 \xrightarrow[\text{and/or heat}]{\text{catalyst}} \left(CH_2{-}CH_2\right)_n$$

Ethene (Ethylene) — Polymer = **Polyethylene** (Polyethene, Polythene)

HDPE LDPE

n = 10,000 - 30,000 = low-density polyethylenes (LDPE)
n = 10,000 - 50,000 = high-density polyethylenes (HDPE)
n = up to 200,000 = ultrahigh-molecular-weight polyethylenes (UHMWPEs)

Polyethylene is useful in food storage containers, plastic wraps and films, garbage bags, insulation for electrical wiring, squeeze bottles, etc.



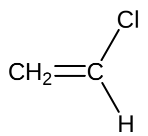
Polymer = **Polypropylene**

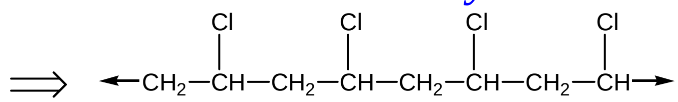
Propene (Propylene)

PP

Polypropylene (**PP**) forms a more orderly polymer than polyethylene, and is much harder, and is stable at higher temperatures (which makes it possible to use in sterilizable storage containers). It is used in fibers, indoor-outdoor carpets, bottles, artificial turf, etc.

Some Common Addition Polymers



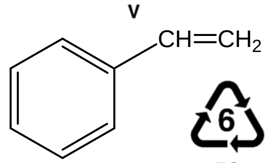


Polymer = **Polyvinyl chloride (PVC)**

Chloroethene
(vinyl chloride)

Polyvinyl chloride (**PVC, V**) is an extremely stable plastic, and is very resistant to degradation. It is also resistant to absorbing water and other solvents, and so is useful in plumbing applications, garden hoses, synthetic leather, etc.

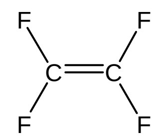
3
V



6
PS

Styrene
Polymer = **Polystyrene**

When styrene is polymerized in the presence of a foaming agent (CFCs, low-MW hydrocarbons), **styrofoam** is produced; this material is a good insulator against heat and cold.

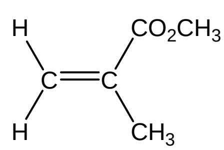


Tetrafluoroethylene
Polymer = **Teflon**

Teflon is extremely stable because of the very strong C—C and C—F bonds; grease and oils cannot bond to the carbon chain through the fluorine atoms, and so Teflon forms slick, nonstick coatings.

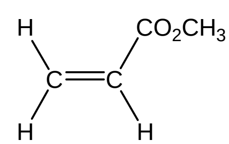
57

Some Common Addition Polymers



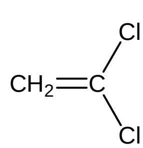
Methyl methacrylate
Polymer = **Poly(methyl methacrylate)**

This polymer has a chaotic internal structure that makes it transparent to light. It is used in airplane windows, contact lenses, fiber optics, etc. It is known by the trade names Lucite, Plexiglass, and Perspex.



Methyl acrylate
Polymer = **Poly(methyl acrylate)**

This plastic forms a milky emulsion in water, to which pigments can be added to form *acrylic paints*. When the water evaporates, the polymer remains behind, holding the pigments in a rubbery, flexible film.

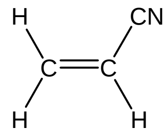


Vinylidene chloride
Polymer = **Saran A**

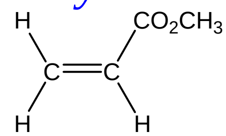
Saran A is made from pure vinylidene chloride; **Saran B** is a *copolymer* of vinylidene chloride and vinyl chloride. These substances form dense solids having high melting points and impermeability to gases; they are useful in food packaging and storage ('Saran wrap').

58

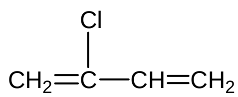
Some Common Addition Polymers



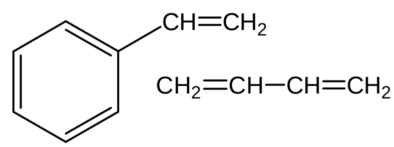
Acrylonitrile
Polymer = **Polyacrylonitrile**
This polymer forms fibers which can be used in carpets and fabrics. It is known by the trade names Orlon, Acrilan, and Creslan.



Vinyl acetate
Polymer = **Polyvinyl acetate (PVA)**
This polymer is used in adhesives, latex paints, wood glue / carpenter's glue, safety glass, textile coatings, etc.



Chloroprene
Polymer = **Polychloroprene**
When cross-linked with ZnO, this polymer forms a material called *neoprene rubber*, which is very resistant to oil and gasoline.

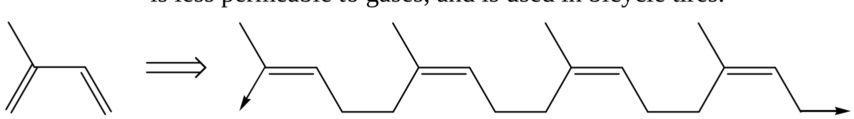


Styrene + butadiene
Polymer = **Styrene butadiene rubber (SBR)**
These monomers form a copolymer which, when cross-linked with peroxides, forms a very tough, heat-stable rubber; used in automobile tires.

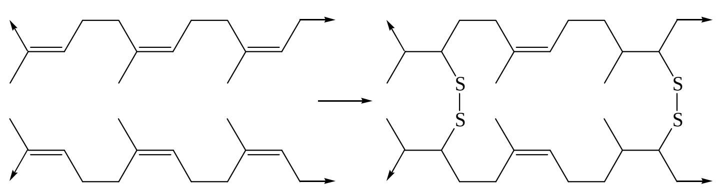
59

Rubber

Polyisoprene (**"natural rubber"**)
A polymer found in the rubber tree, *Heva brasiliensis*; formed by polymerizing isoprene. The name "rubber" was given to this compound by Joseph Priestly for its ability to rub out pencil marks. It is tough and brittle when cold, but softens and becomes sticky at higher temperatures. The rubber can be further hardened by the *vulcanization* process (Charles Goodyear, 1839), which involves heating the rubber with sulfur, which links separate polyisoprene molecules through dissulfide bridges (—S—S—) through the reactive double bonds. Depending on the catalyst used, a rubber which is either all *cis*-double bonds or all *trans*-double bonds (gutta percha) can be formed. Copolymerization of isoprene with isobutylene results in **butyl rubber**, which is less permeable to gases, and is used in bicycle tires.



Isoprene **Polyisoprene**



60

Alkynes

61

Alkynes

- **Alkynes** contain carbon-carbon triple bonds.
  - – General formula: C_nH_{2n-2} (for one triple bond)
- The nomenclature system for alkynes is identical to that of alkenes, except the suffix **-yne** is used to indicate a the triple bond. Alkynes do not have *cis*- and *trans*- isomers.

$H-C\equiv C-H$

Acetylene
(ethyne)

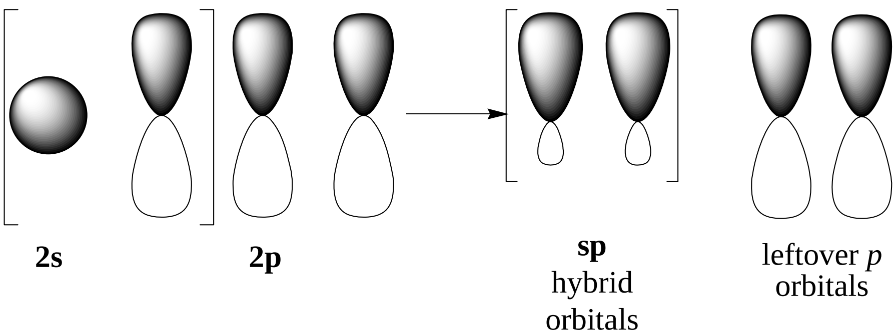
$CH_3CH_2-C\equiv C-H$

$CH_3CH_2-C\equiv C-CH(CH_2CH_2CH_3)CH_2CH_2CH_2CH_3$

62

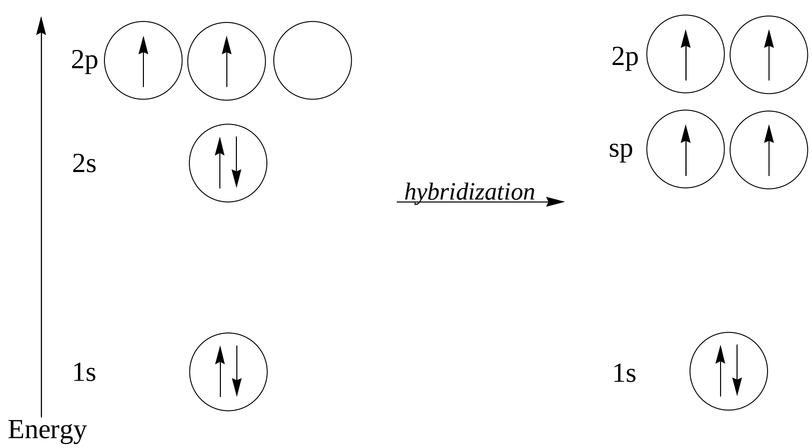
Hybridization of Alkynes

- When a carbon is connect to two other things (that is, one of the bonds is a triple bond), the molecule is modeled by combining the 2*s* and one of the 2*p* orbitals to produce **two *sp* orbitals**.
- Since only one of the 2*p* orbitals was hybridized, there are **two leftover *p* orbitals** in an *sp*-hybridized carbon atom.



63

Hybrid Orbitals

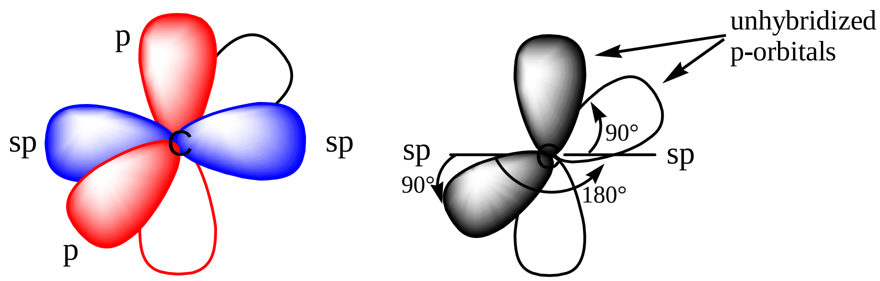


- Both *sp* orbitals are at the same energy level, with one electron in each hybrid orbital, and one in each of the unhybridized 2*p* orbitals.

64

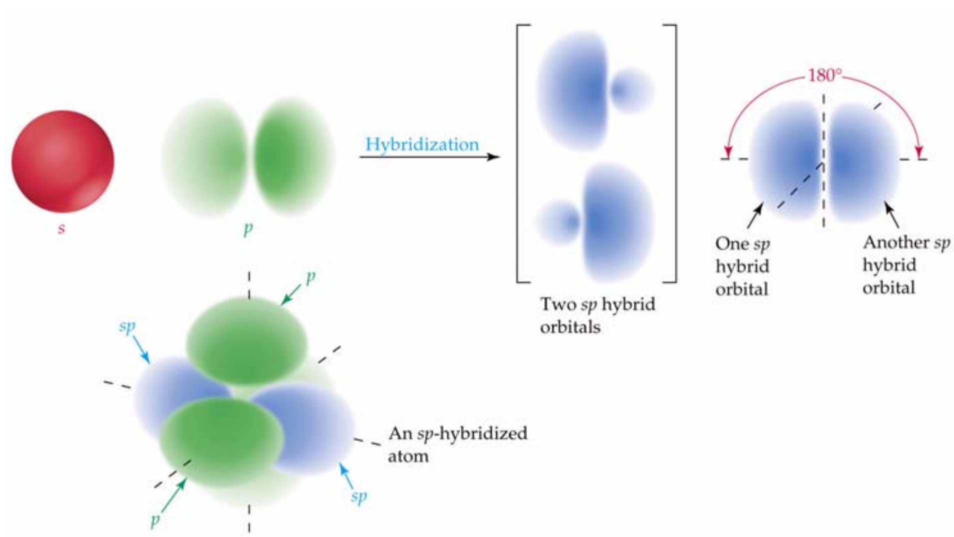
The Shape of an sp Carbon

- The *sp* orbitals are arranged in a **linear** shape around the central carbon atom, with bond angles of **180º**.
- One of the unhybridized *p* orbitals is perpendicular to the line formed by the *sp* orbitals, and the other unhybridized *p* orbital is perpendicular to the plane formed by the other orbitals.



65

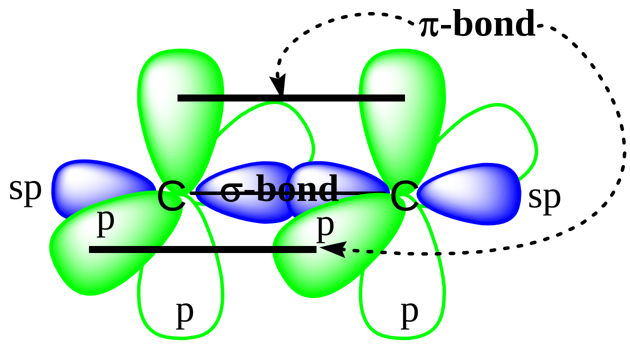
Bonding in Acetylene



66

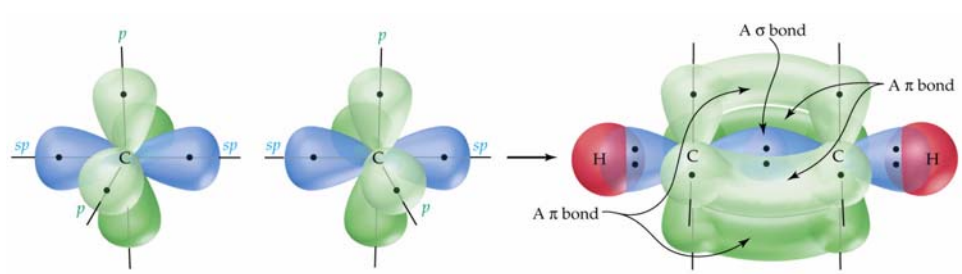
Bonding in Acetylene

- When two *sp*-hybridized carbons are next to each other, three orbital overlaps take place:
  - *end-on-end overlap* of the *sp* orbitals to make a **σ-bond**.
  - *side-to-side overlap* of both sets of unhybridized *p* orbitals to make **two π-bonds**.



67

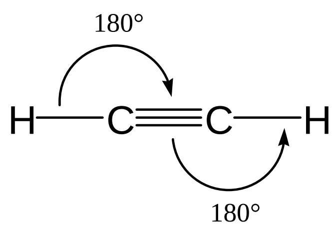
Bonding in Acetylene



68

The Shape of the Acetylene Molecule

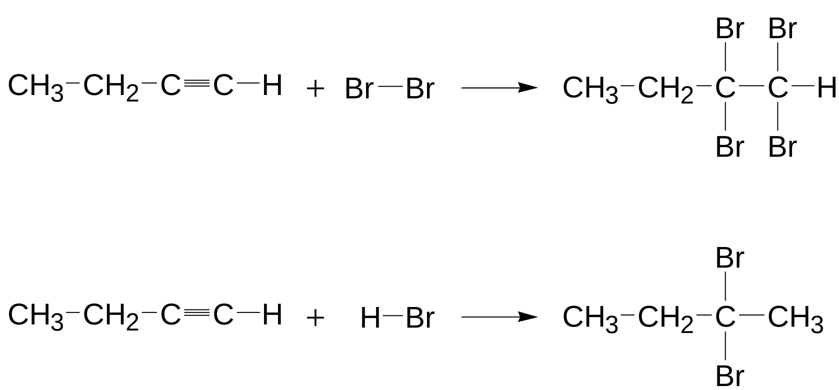
- Since each carbon in the double bond is linear in space, the entire acetylene molecule is a **linear** molecule.



69

Reactions of Alkynes

- Anything an alkene does, an alkyne does twice:



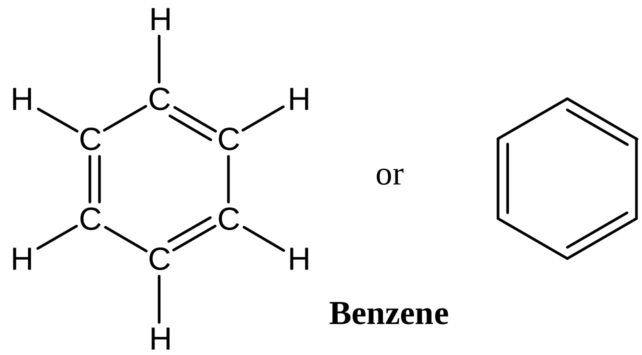
70

Aromatic Compounds

71

Aromatic Compounds

- **Aromatic compounds** are those that contain the **benzene ring** (C_6H_6) or its structural relatives.
- **Aliphatic compounds** do not contain benzene rings.

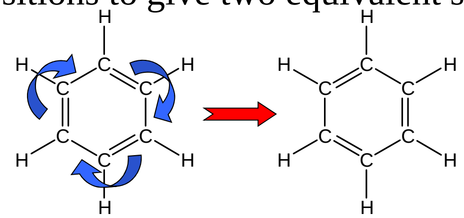


Benzene

72

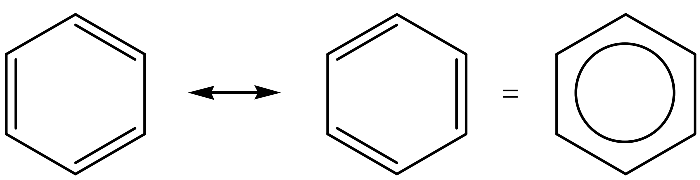
The Structure of Benzene

- The name "aromatic" originally referred to fragrant oils having similar chemical properties (such as oil of wintergreen, vanilla extract, etc.), including a very low carbon-to-hydrogen ratio.
- The molecular structure of benzene was a puzzle for a long time after its discovery; although the formula indicates the presence of double bonds, benzene does not undergo the typical alkene reactions.
- The ring structure of benzene was proposed by August Kekulé in 1865; he suggested that the double bonds switch positions to give two equivalent structures:



73

The Resonance Structures of Benzene



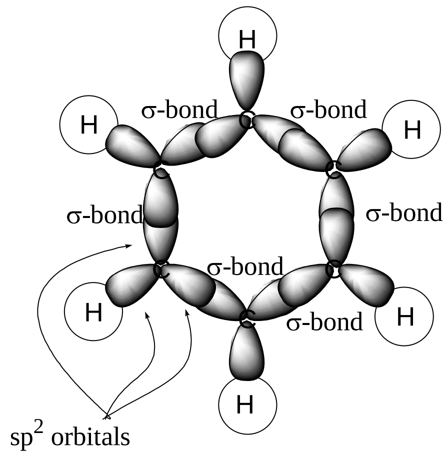
Kekulé structures

- In reality, the double bonds and single bonds in benzene do not change position. The two Kekulé structures for benzene are **resonance structures**, meaning that each individual structure is fictitious.
- The benzene ring is sometimes represented as a hexagon with a circle inside, which emphasizes that all of the positions on the benzene ring are equivalent.

74

Hybridization of Aromatic Compounds

- All six carbons in the benzene ring are *sp*^{2} hybridized; because all of the carbons are trigonal planar, the benzene ring is flat.

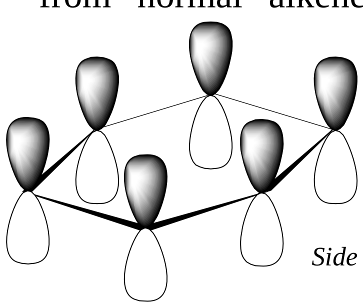


Top view

75

Hybridization of Aromatic Compounds

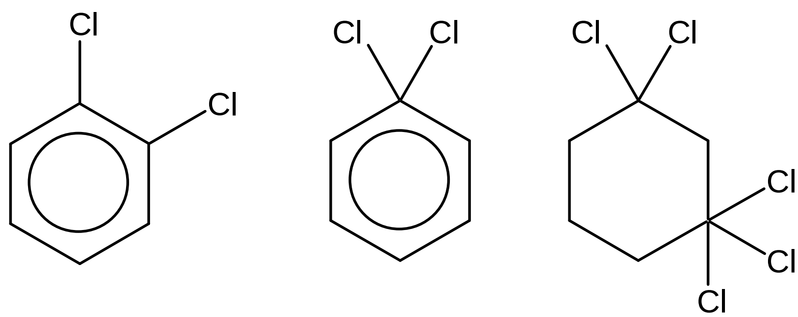
- The unhybridized *p* orbitals are perpendicular to the plane of the carbon atoms; all six *p* orbitals overlap side-to-side around the ring.
  - The 3 π-bonds are **delocalized** around the ring.
  - The 6 electrons in these bonds move freely around the entire benzene molecule.
  - Benzene thus has completely different chemistry from “normal” alkenes.

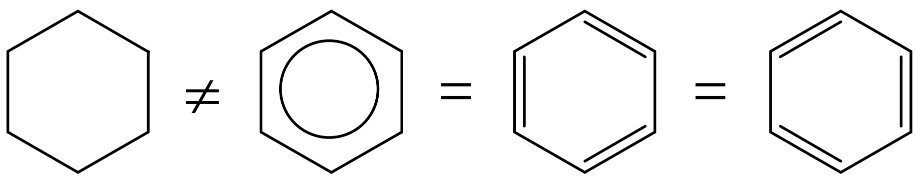


Side view

76

Some Common Aromatic Mistakes

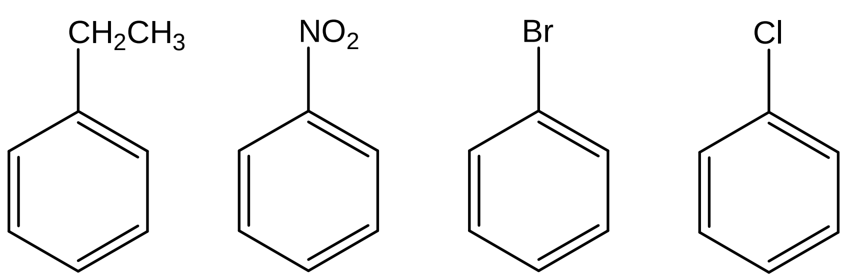




77

Nomenclature of Benzene Derivatives

- **Rule 1.** When a single hydrogen of the benzene ring is replaced, the compound can be named as a derivative of benzene.

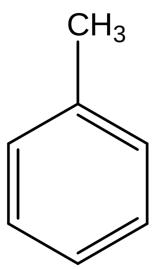


ethylbenzene nitrobenzene bromobenzene chlorobenzene

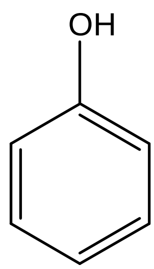
78

Nomenclature of Benzene Derivatives

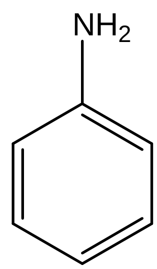
- **Rule 2.** A number of benzene derivatives are known by their common (trivial) names rather than by their formal IUPAC names.



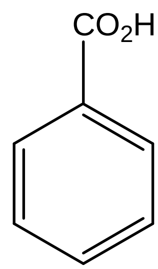
toluene



phenol



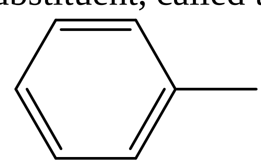
aniline

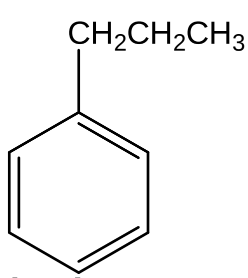


benzoic acid

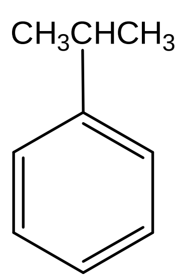
Nomenclature of Benzene Derivatives

- **Rule 3.** Compounds formed by replacing a hydrogen of benzene with a more complex hydrocarbon group can be named by naming the benzene ring as the substituent, called the **phenyl** group.

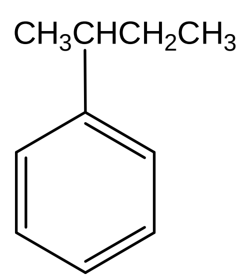
 = C_6H_5— = **phenyl group**



1-phenylpropane
(propylbenzene)



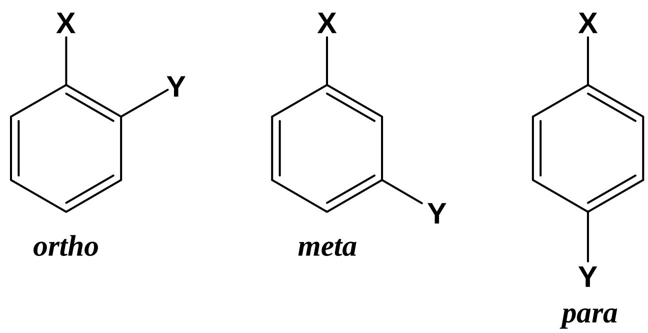
2-phenylpropane
(isopropylbenzene)



2-phenylbutane
(sec-butylbenzene)

Nomenclature of Benzene Derivatives

- **Rule 4.** When two groups are attached to a benzene ring, three isomeric structures are possible:

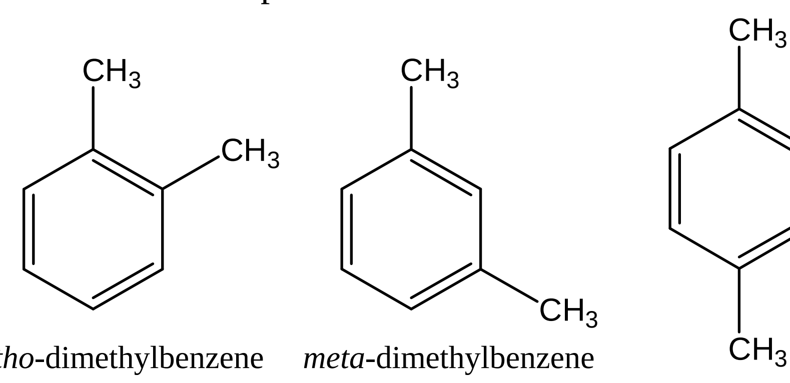


- In naming these compounds, either the ortho / meta / para prefixes may be used, or position numbers (begin numbering at the group which comes first in alphabetical order)

81

Nomenclature of Benzene Derivatives

- **Rule 4.** examples



ortho-dimethylbenzene
1,2-dimethylbenzene
ortho-methyltoluene
2-methyltoluene

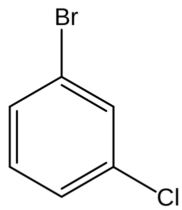
meta-dimethylbenzene
1,3-dimethylbenzene
meta-methyltoluene
3-methyltoluene

para-dimethylbenzene
1,4-dimethylbenzene
para-methyltoluene
4-methyltoluene

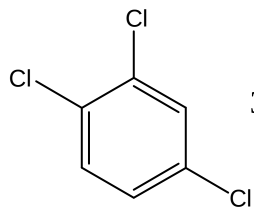
82

Nomenclature of Benzene Derivatives

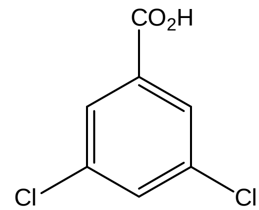
- **Rule 5.** When two or more groups are attached to the benzene ring, their positions can be indicated by numbering the carbon atoms of the ring to obtain the lowest possible numbers for the attachment positions. Groups are arranged in alphabetical order.



meta-bromochlorobenzene
1-bromo-3-chlorobenzene



1,2,4-trichlorobenzene

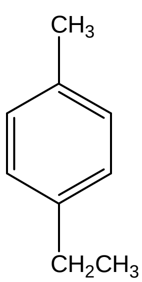


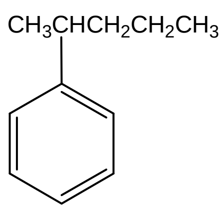
3,5-dichlorobenzoic acid

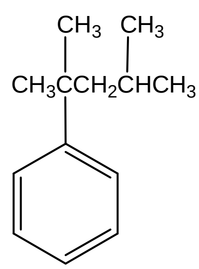
83

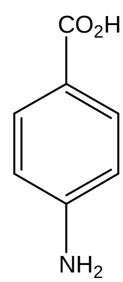
Examples: Nomenclature of Aromatic Rings

- Provide IUPAC names for the following molecules:





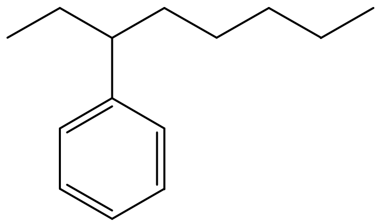


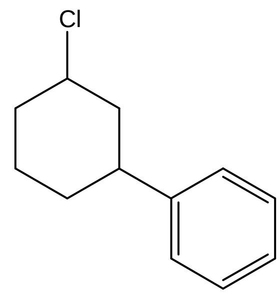


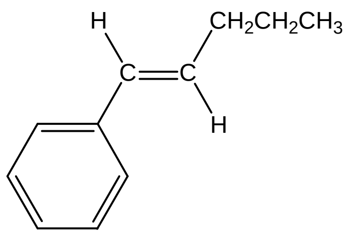
84

Examples: Nomenclature of Aromatic Rings

- Provide IUPAC names for the following molecules:



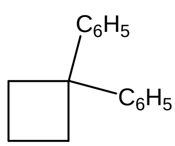


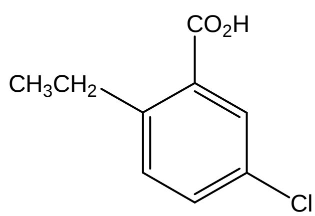


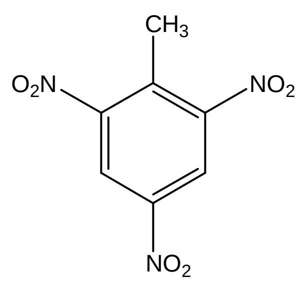
85

Examples: Nomenclature of Aromatic Rings

- Provide IUPAC names for the following molecules:







86

Examples: Nomenclature of Aromatic Rings

- Draw structural formulas for the following molecules:
  - – *meta*-ethyltoluene
  - – 2,5-dibromobenzoic acid
  - – *para*-nitrophenol

87

Examples: Nomenclature of Aromatic Rings

- Draw structural formulas for the following molecules:
  - – 3-phenylheptane
  - – butylbenzene
  - – 1,4,5-tribromobenzene (what's wrong with this name?)

88

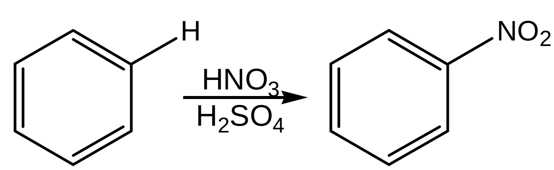
Physical Properties of Aromatic Compounds

- Just like alkanes and alkenes, aromatic compounds are **nonpolar**, and therefore **insoluble in water** (unless other substituents, such as OH groups, are present). They are also usually less dense than water.
- Many aromatic compounds are obtained from petroleum and coal tar.
- Benzene and toluene are commonly used as solvents, and are the starting materials for the synthesis of other useful organic compounds.
- Some foods contain aromatic compounds, which can be synthesized by some plants. Some aromatic amino acids and vitamins are listed as *essential*, because we lack the ability to synthesize them, and must obtain them from our diet.

89

Chemical Properties of Aromatic Compounds

- Aromatic compounds are chemically stable (unlike alkenes). They do **NOT** undergo any of the reaction of alkenes which we have discussed.
- The major reaction of interest is a substitution reaction in which a hydrogen is replaced by some other group:

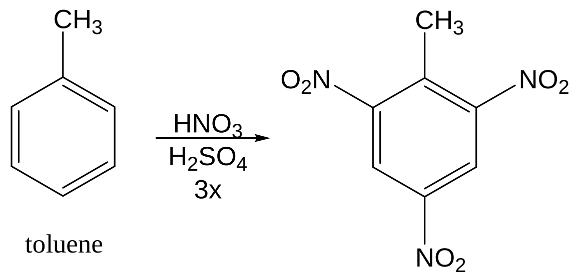


a **nitration** reaction

  – This is an industrially important reaction, because there are mechanisms for converting the nitro group to many other possible functional groups.

90

The Big Bang

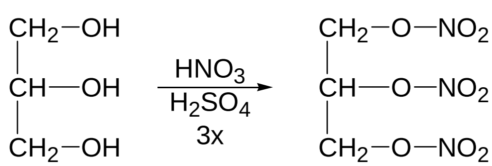


toluene

2,4,6-trinitrotoluene (TNT)
A powerful explosive; a sharp pressure wave from a detonator causes the molecule to rearrange into carbon dioxide, water vapor, nitrogen (N_2), and other gases, which expand rapidly and destructively

91

The Big Bang



glycerol / glycerin

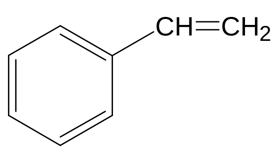
Nitroglycerin
An oily, colorless, extremely unstable liquid; it is usually mixed with an absorbent material, such as clay, to make **dynamite** (Alfred Nobel, 1866)

92

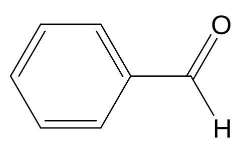
Some Important Aromatic Compounds

93

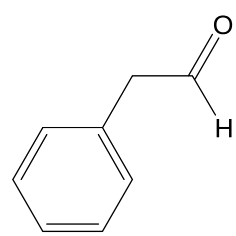
Some Important Aromatic Compounds



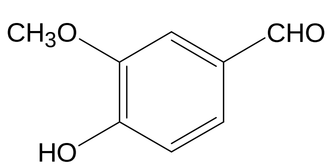
Styrene
Used to make polystyrene and styrofoam



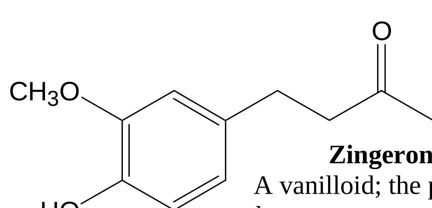
Benzaldehyde
Odor of almonds and cherries; also found in peach and apricot pits



Hyacinthin
Floral scent found in hyacinth



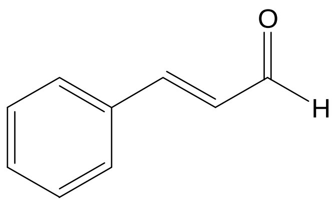
Vanillin
Essential component of *oil of vanilla*; parent compound of the *vanilloids*



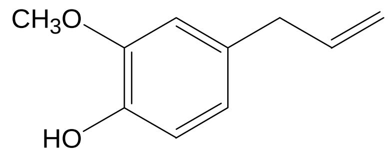
Zingerone
A vanilloid; the pungent, hot component of ginger

94

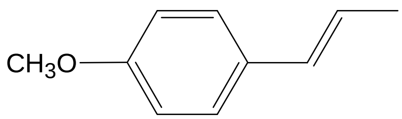
Some Important Aromatic Compounds



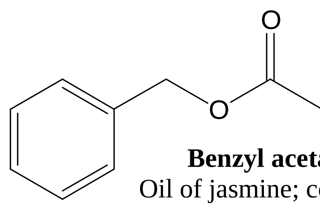
Cinnamaldehyde
Found in oil of cinnamon; has a *carminative* action (releases hydrogen sulfide, methane, and hydrogen from the intestine and stomach in one direction or the other)



Eugenol
Found in oil of bay (bay leaves), oil of cloves, allspice (combines the flavors of cinnamon, nutmeg and cloves), carnations; shifting the location of the double bond produces isoeugenol, the odor of nutmeg



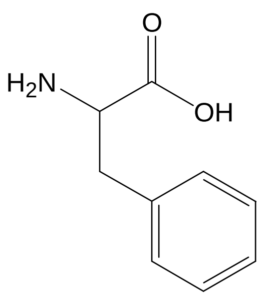
Anethole
Oil of aniseed, fennel, tarragon



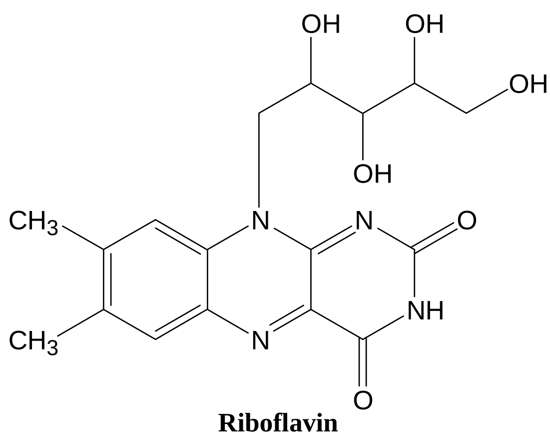
Benzyl acetate
Oil of jasmine; common ingredient in perfumes

95

Aromatic Rings in the Diet



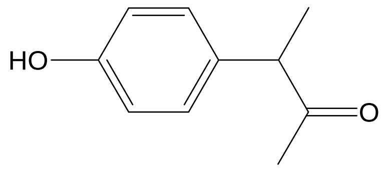
Phenylalanine
An essential amino acid; also found in *aspartame* (Nutra-Sweet)



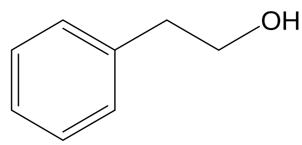
Riboflavin
Vitamin B_2; found in milk, meat, eggs, dark green vegetables, bread, beans, and peas; forms the coenzymes FMN and FAD, which are hydrogen transporters; deficiency results in dermatitis

96

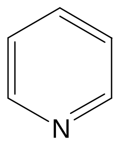
Interesting Odors



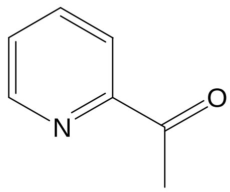
3-(*para*-hydroxyphenyl)-2-butanone
Odor of raspberries



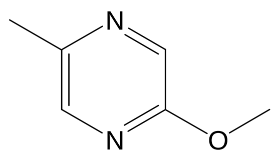
Phenylethanol
Along with geraniol, found
in the fragrance of roses



Pyridine



Methyl 2-pyridyl ketone
Odor of popcorn

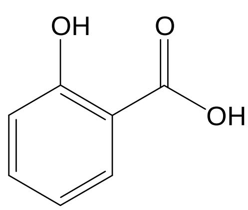


2-Methoxy-5-methylpyrazine
Odor of peanuts

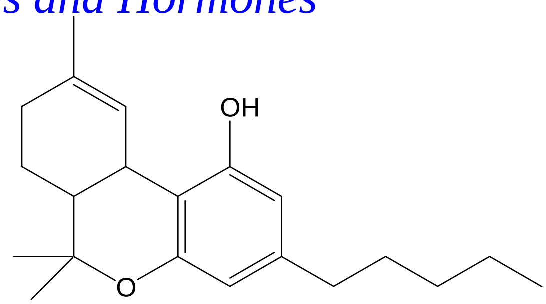
Pyrzazines also contribute to the odors of crusty bread, rum, whisky, chocolate, and some uncooked vegetables, including peppers.

97

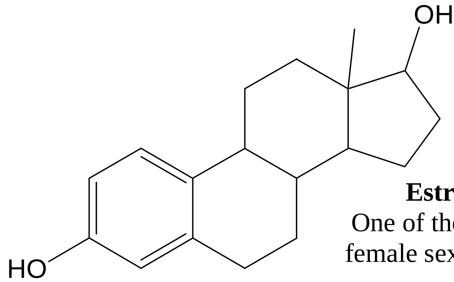
Drugs and Hormones



Salicylic acid
Analgesic, antipyretic, and
anti-inflammatory drug
found in willow bark



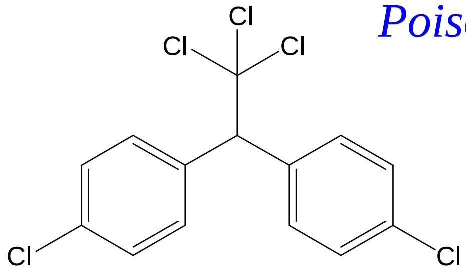
Tetrahydrocannabinol (THC)
Active component of cannabis



Estradiol
One of the principal
female sex hormones

98

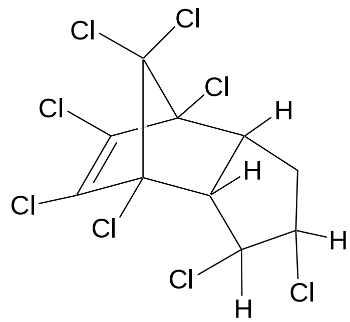
Poisons



Dichlorodiphenyltrichloroethane (DDT)

1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane

A very powerful insecticide discovered in 1939; it is toxic to insects, but not to mammals. DDT was widely used to kill mosquitoes that spread malaria, and was also effective against the insects that spread sleeping sickness and typhus. Unfortunately, DDT persists in the environment for a long time, and its accumulation in wildlife lead to decreases in the populations of several bird species. In 1972, DDT was banned by the Environmental Protection Agency.

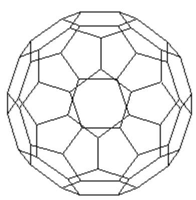


Chlordane

Used as a pesticide on some crops, and was also used to kill termites. Because of concerns about its toxicity, it was banned by the EPA in 1988.

99

Fullerenes



Buckminsterfullerene (C_{60})

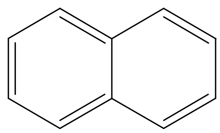
A soccer-ball shaped molecule consisting of 60 carbon atoms, discovered in the 1980s by H. W. Kroto (Univ. of Sussex), R. E. Smalley, and R. F. Curl (Rice University) (Nobel Prize in Chemistry, 1996). They named the structure after the architect R. Buckminster Fuller, because the shape reminded them of his geodesic dome designs. Similar spherical-shaped carbon-only molecules, such as C70, are often referred to as fullerenes or “buckyballs.” All of the carbon atoms in in these molecules are sp^2 hybridized, and the entire molecule is somewhat aromatic. The fullerenes are considered another allotrope (stable structural form) of carbon, in addition to graphite and diamond.

Nanotubes are cylindrical versions of the fullerenes; they look something like a chain link fence rolled into a cylinder, with a dome-shaped cap on the end (half of a buckyball). Nanotubes (also known as "buckytubes") are extremely strong, as well as being very lightweight (since they are made of nothing but carbon atoms). These materials are being tested for potential use in many materials; some nanotubes also conduct electricity, leading to some potential applications in circuit design and electronics.

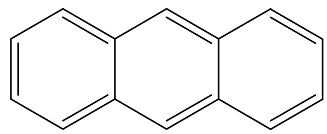
100

Polycyclic Aromatic Hydrocarbons (PAH)

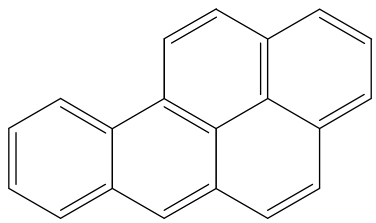
- **Polycyclic aromatic hydrocarbons** consist of two or more benzene rings fused together; they produced when organic compounds are heated to high temperatures, and are present in tobacco smoke, car exhaust, and sometimes in heavily browned foods.



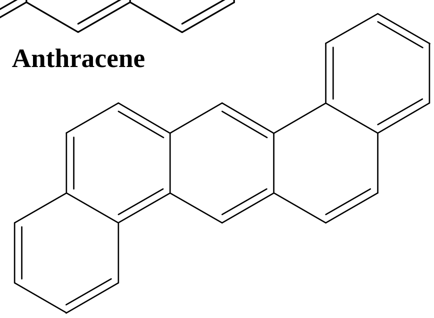
Naphthalene



Anthracene



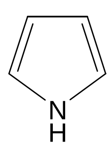
Benzo[*a*]pyrene



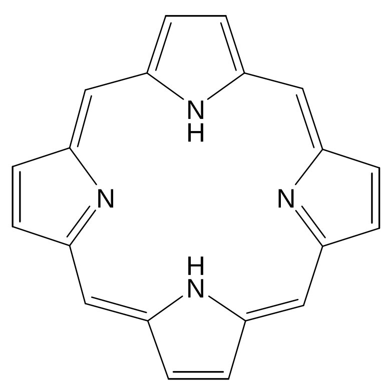
Dibenz[*a,h*]anthracene

101

Aromatic Rings That Don't Look Like Benzene



pyrrole

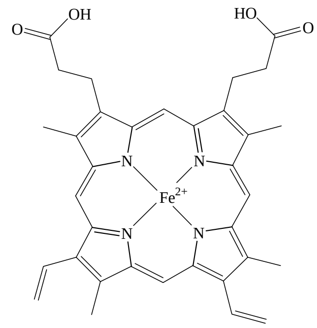


porphyrin

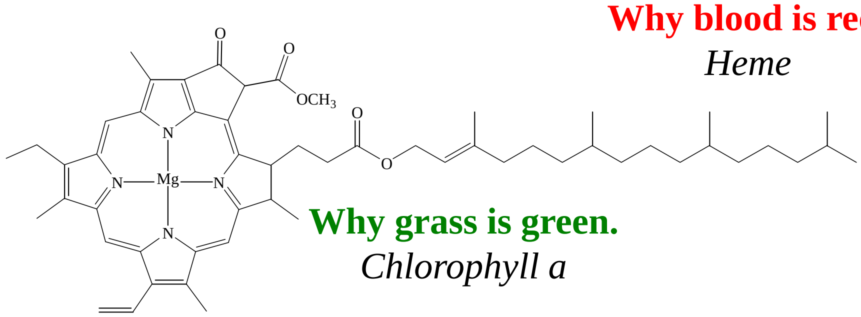
102

Why Grass is Green and Blood is Red

Why **grass** is **green**,
or why our **blood** is **red**
Are mysteries which
none have reach'd unto.
John Donne,
"Of the Progress of the Soul"



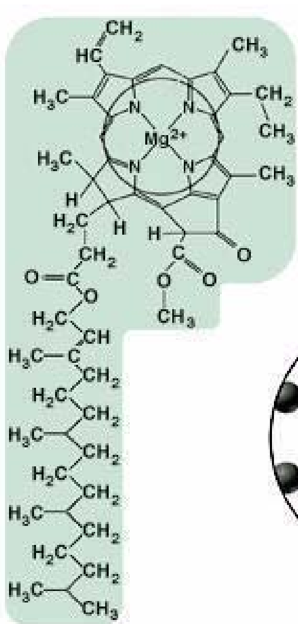
Why blood is red.
Heme

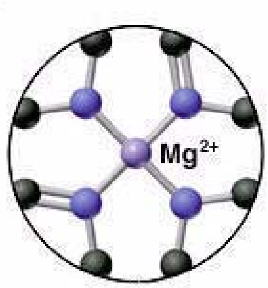


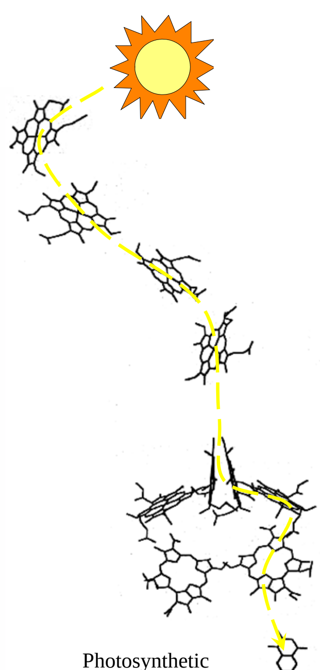
Why grass is green.
Chlorophyll a

103

Chlorophyll





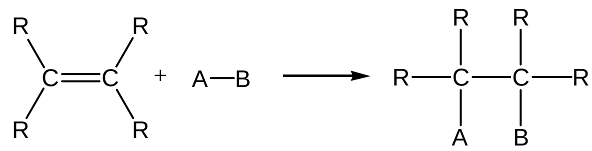


Photosynthetic
Reaction Center of
a cyanobacterium

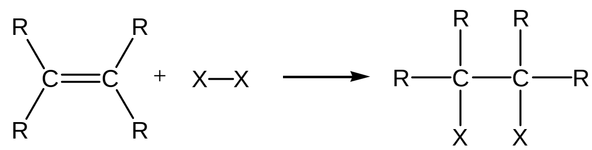
104

Reactions of Alkenes

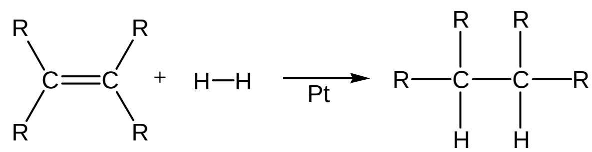
General Reaction:



Halogenation: (X = Br or Cl)

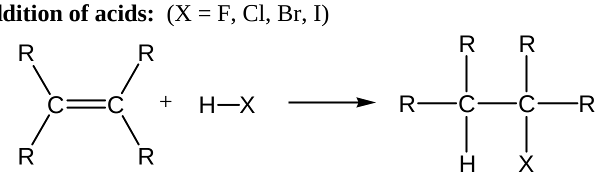


Hydrogenation:

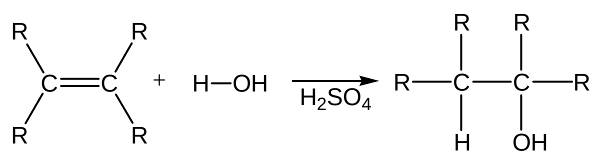


105

Addition of acids: (X = F, Cl, Br, I)



Hydration:



an <u>alcohol</u>

These two reactions obey **Markonikov's Rule:** when a molecule of the form H-X adds to a double bond, the hydrogen becomes attached to the carbon atom that is already bonded to the most hydrogen atoms. ("The rich get richer")

106