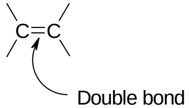
Unsaturated Hydrocarbons

- ❑Alkenes
- ❑Alkynes

Introduction to Alkenes

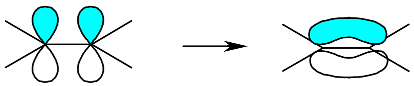
- An **alkene**, **olefin**, or **olefine** is an unsaturated chemical compound containing at least one carbon-to-carbon double bond.



- The simplest acyclic (without a ring) alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula $\mathbf{C_nH_{2n}}$.

Properties of Alkenes

- Double bonds can be described in terms of overlapping atomic orbitals, except that unlike a single bond (which consists of a single sigma bond), a carbon-carbon double bond consists of one sigma bond and one pi bond.

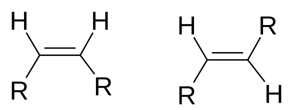


Properties of Alkenes

- This double bond is stronger than a single covalent bond (611 kJ/mol for C=C vs. 347 kJ/mol for C—C) and also shorter with an average bond length of 1.33 Angstroms (133 pm).
- Rotation about the carbon-carbon double bond is restricted because it involves breaking the pi bond, which requires a large amount of energy (264 kJ/mol in ethylene).

Properties of Alkenes

- substituted alkenes may exist as one of two isomers called a *cis* isomer (i.e. hydrogen atoms on the same side of the double bond) and a *trans* isomer (i.e. hydrogen atoms on opposite sides of the double bond) .



Cis Trans

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IUPAC Nomenclature

- To form the root of the IUPAC names for alkenes, simply change the -an- infix of the parent to -en-. For example, **CH_3-CH_3** is the alkane *ethANe*. The name of **CH_2=CH_2** is therefore *ethENe*.
- In higher alkenes, where isomers exist that differ in location of the double bond, the following numbering system is used:

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- Number the longest carbon chain that contains the double bond in the direction that gives the carbon atoms of the double bond the lowest possible numbers.
- Indicate the location of the double bond by the location of its first carbon
- Name branched or substituted alkenes in a manner similar to alkanes.
- Number the carbon atoms, locate and name substituent groups, locate the double bond, and name the main chain

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E, Z notation

- When an alkene has more than one substituent (especially necessary with 3 or 4 substituents), the double bond geometry is described using the labels *E* and *Z*.
- These labels come from the German words "entgegen" meaning "opposite" and "zusammen" meaning "together".

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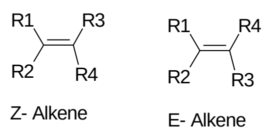
E, Z notation

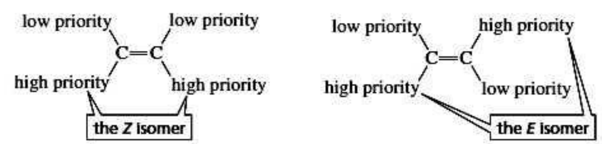
- Alkenes with the higher priority groups on opposite sides are designated *E*.

R1 > R2 and R3 > R4



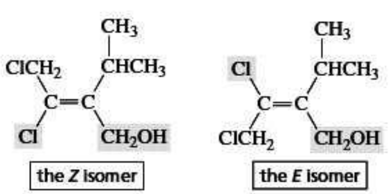
E, Z notation rules

- **Rule 1.** The relative priorities of the two groups depend on the atomic numbers of the atoms that are bonded directly to the carbon. The greater the atomic number, the higher is the priority.



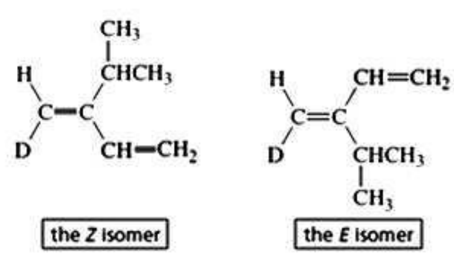
E, Z notation rules

- Rule 2: If the two substituents bonded to an carbon start with the same atom (there is a tie), you must move outward from the point of attachment and consider the atomic numbers of the atoms that are attached to the "tied" atoms.



E, Z notation rules

- Rule 3. In the case of isotopes (atoms with the same atomic number, but different mass numbers), the mass number is used to determine the relative priorities.



Properties of Alkenes

- The physical properties of alkenes are comparable with alkanes.
- The physical state depends on molecular mass (gases from ethene to butene - liquids from pentene onwards).
- The simplest alkenes, ethene, propene and butene are gases.

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Properties of Alkenes

- Linear alkenes of approximately five to sixteen carbons are liquids, and higher alkenes are waxy solids
- Boiling points of alkenes depends on more molecular mass(chain length). The more intermolecular mass is added, the higher the boiling point. Intermolecular forces of alkenes gets stronger with increase in the size of the molecules.

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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:
  - ≤ 4 C's — gases
  - 5 - 17 C's — liquids
  - ≥ 18 C's — solids

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Properties of Alkenes

Compound	Boiling points (ºC)
Ethene	-104
Propene	-47
Trans-2-Butene	0.9
Cis-2-butene	3.7
Trans 1,2-dichlorobutene	155
Cis 1,2-dichlorobutene	152
1-Pentene	30
Trans-2-Pentene	36
Cis-2-Pentene	37
1-Heptene	115
3-Octene	122
3-Nonene	147
5-Decene	170

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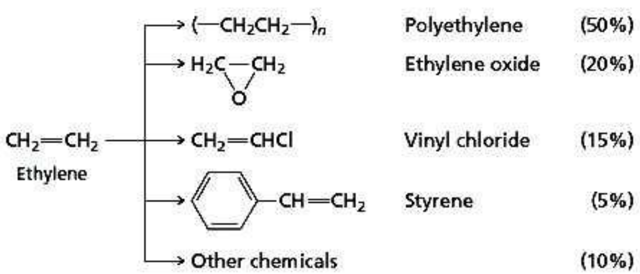
Properties….

- Low boiling points, increasing with mass.
- Branched alkenes have lower boiling points.
- Less dense than water.
- Slightly polar. Pi bond is polarizable, so instantaneous dipole-dipole interactions occur.
- Alkyl groups are electron-donating toward the pi bond, so may have a small dipole moment

Uses of Ethylene and Proplylene

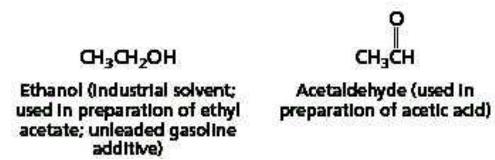
- Approximately 90% of ethylene is used for the preparation of four compounds: (polyethylene, ethylene oxide, vinyl chloride, and styrene), with polymerization to polyethylene accounting for half the total. Both vinyl chloride and styrene are polymerized to give poly(vinyl chloride) and polystyrene, respectively

Uses of Ethylene (Ethene)



Uses of Ethylene (Ethene)

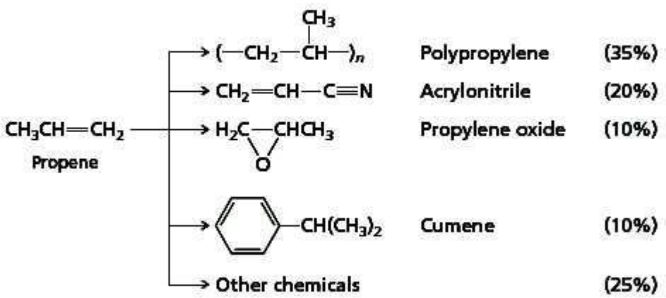
- Ethylene oxide is a starting material for the preparation of ethylene glycol for use as an antifreeze in automobile radiators and in the production of polyester fibers
- Among the “other chemicals” prepared from ethylene are ethanol and acetaldehyde



Uses of Propylene (propene)

- The major use of propene is in the production of polypropylene. Two other propene-derived organic chemicals, acrylonitrile and propylene oxide, are also starting materials for polymer synthesis. Acrylonitrile is used to make acrylic fibers and propylene oxide is one component in the preparation of *polyurethane* polymers.

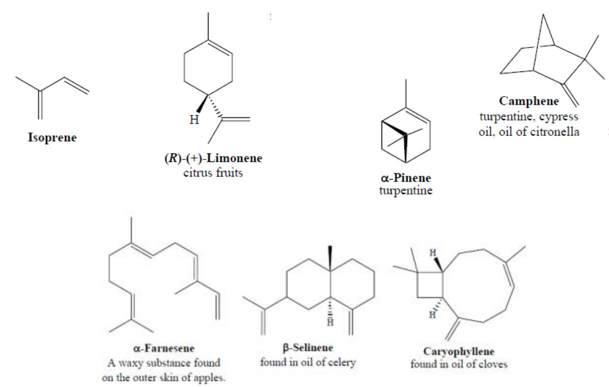
Uses of Propylene (propene)



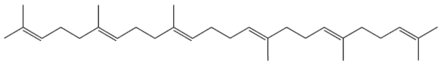
Terpenes and Essential Oils

- 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.)

Terpenes and Essential Oils



Terpenes and Essential Oils



- **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

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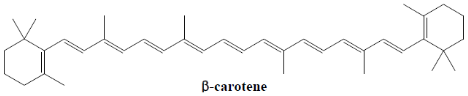
β-carotene



- 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 O2 molecules.
- The yellow color of autumn leaves is due to the carotene, which is unmasked as the chlorophyll in the leaves breaks down.

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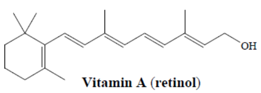
Vitamin A



- A fat-soluble vitamin; a metabolic product of carotene, found in liver, egg yolks, butter, and milk. It 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.

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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 (hv) 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 *transretinal* molecule is then twisted back into the *cis form by another enzyme.*

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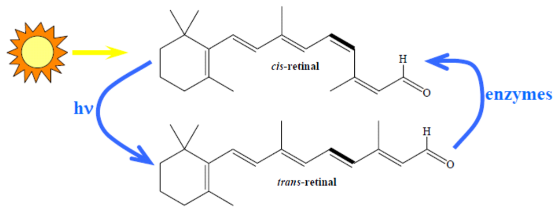
The Chemistry of Vision

- 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.



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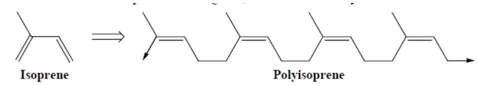
Rubber

- **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.



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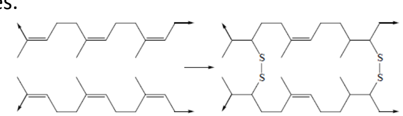
Polyisoprene ("natural rubber")

- 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 can be formed.* Copolymerization of isoprene with isobutylene results in **butyl rubber, which** is less permeable to gases, and is used in bicycle tires.



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Alkynes

- Alkyne is a hydrocarbon (i.e. contains carbon and hydrogen atoms) that have at least one triple bond between two carbon atoms, with the formula $\mathbf{C_nH_{2n-2}}$.

  $$—C\equiv C—$$

- The C≡C bond distance of 121 pm (picometers) is much shorter than the C=C distance in alkenes (134 pm) or the C-C bond in alkanes (153 pm)

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Terminal and internal alkynes

- Internal alkynes feature carbon substituents on each acetylenic carbon.
- Terminal alkynes have at least one hydrogen atom bonded to a sp hybridized carbon (those involved in the triple bond.

$H-C\equiv C-R$	$R-C\equiv C-R$
A terminal alkyne	An internal alkyne

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IUPAC nomenclature of alkynes

$H-C\equiv C-H$	**Ethyne**
$CH_3C\equiv C-H$	**Propyne**
$CH_3CH_2C\equiv C-H$	**1-Butyne**
$CH_3CH_2CH_2C\equiv C-H$	**1-Pentyne**
$CH_3C\equiv C-CH_3$	**2-Butyne**
$CH_3CH_2C\equiv C-CH_3$	**2-Pentyne**

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IUPAC names of Alkynes

- The IUPAC name depends on whether it is a terminal or an internal akyne.
- For example: 1-butyne is a terminal alkyne, whereas 2-pentyne is an internal alkyne.

	$HC\equiv CH$	$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}\equiv\overset{1}{C}H$	$\overset{1}{C}H_3\overset{2}{C}\equiv\overset{3}{C}\overset{4}{C}H_2\overset{5}{C}H_3$	$\overset{4}{C}H_3\overset{4}{C}H(\overset{5}{C}H_2\overset{6}{C}H_3)\overset{3}{C}\equiv\overset{2}{C}\overset{1}{C}H_3$
Systematic:	**ethyne**	**1-butyne**	**2-pentyne**	**4-methyl-2-hexyne**
Common:	**acetylene**	**ethylacetylene**	**ethylmethylacetylene**	***sec*-butylmethyl-acetylene**
		a terminal alkyne	**an internal alkyne**	

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Properties of Alkynes

- Due to their low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes.
- They are insoluble in water, but quite soluble in the usual organic solvents of low polarity: e.g. ether, benzene, and carbon tetrachloride. They are less dense than water, with relative densities ranging from 0.67 to 0.77. Their boiling points show the usual increase with increasing carbon number, and the usual effects of chain-branching (lower melting and boiling points due to increased surface area).

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Boiling points of some alkynes

H−C≡C−H	Ethyne	-84
CH_3C≡C−H	Propyne	-23
CH_3CH_2C≡C−H	1-Butyne	8
$CH_3CH_2CH_2C$≡C−H	1-Pentyne	39
CH_3C≡C−CH_3	2-Butyne	27
CH_3CH_2C≡C−CH_3	2-Pentyne	55

Industrial Uses of Acetylene

- The alkyne of chief industrial importance is the simplest member of the family: acetylene.
- It is used primarily for oxyacetylene gas welding and metal cutting due to the high temperature of the flame. The combustion of acetylene with oxygen produces a flame of over 3300°C (5972°F), releasing 11.8 kJ/g.
- Oxyacetylene is the hottest burning of all fuel gases.

Manufacture of Acetylene

- The principal **raw materials** for acetylene manufacture are **calcium carbonate** (limestone) and **coal**. The calcium carbonate is first converted into calcium oxide and the coal into coke. Then these two are reacted with each other to form calcium carbide and carbon monoxide:

$$CaO + 3C \dashrightarrow CaC_2 + CO$$

- Calcium carbide (or calcium acetylide) and water are then reacted by any of several methods to produce acetylene and calcium hydroxide.

Manufacture of Acetylene

- Calcium carbide synthesis requires an extremely high temperature (~ 2000 °C) so the reaction is performed in an electric arc furnace. This reaction was an important part of the industrial revolution in chemistry that occurred as a product of massive amounts of cheap hydroelectric power liberated from Niagara Falls before the turn of the (19th)century.
- Acetylene can also be manufactured by the cracking of hydrocarbons, as well as by the controlled, high-temperature (~ 1500 °C) partial oxidation of methane.

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

$$6\,CH_4 + O_2 \dashrightarrow 2\,C_2H_2 + 2\,CO + 10\,H_2$$