

Unsaturated hydrocarbons. Double and triple bonds in our carbon backbone.



version 1.0

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Ch09

Alkenes & Alkynes

- Definition and bond angles.
- Uses and Properties
- Saturation
- Naming
 - Chain alkenes & alkynes.
 - Cycloalkenes & cycloalkynes.
- Aromatic Compounds
 - Benzene
 - Delocalizatized structure
 - Substituted aromatics
 - Basic compounds
 - Multiple substitutions



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- Cis & Trans Isomers
 - Isomers
 - Structural
 - Stereo
 - Cis-Trans Isomers
 - Restricted bond rotation.
 - Naming
- Reactions with Alkenes
 - Bromination
 - Hydrogenation
 - Hydration
 - Structural Isomers
 - Selectivity
 - Formation of Alcohols









- Hydrocarbons are molecules composed of only hydrogen and carbon.
- Carbons form four bonds.
- Alkanes are hydrocarbons that have only carbon-carbon single bonds.
- Alkenes are hydrocarbons that have one or more carboncarbon double bonds.
 - Carbons that form double bonds are said to have a sp² shape.
 - The bonds connected to a sp² carbon have a 120° angle between them.
- Alkynes are hydrocarbons that have one or more carboncarbon triple bonds.
 - Carbons that form triple bonds are said to have a sp shape.
 - The bonds connected to a sp carbon form a single line, they have a 180° angle around the carbon.
- Alkenes and alkynes have unique properties.





Bond angles = 120° Ethene





Alkenes in Biochemistry.



Ethene, the simplest alkene is a plant hormone, it causes fruit to ripen.

Plastic bags from the supermarket are made of polyethylene (many ethenes stuck together).

The longer you leave fruit in those bags, the faster that hormone will cause them to ripen.





Ethene





Bombykol, sex attractant for the silkworm moth

Alkene structures are important in many biological structures, like the pheromone of silkworm moths.



Alkynes in Industry

- Burning alkynes produces *less* heat than alkanes.
 - But they also produce less gases.
- The gases produced in burning alkynes have more heat *per mole* of product
 - Those gases have a higher temperature.
- Alkynes burn hotter.
- If you want to put heat into your house, burn an alkane.
- If you want to create gases to push pistons in your car, burn an alkane.
- But if you want concentrated heat to cut metal, burn an alkyne.
 - Like ethyne (also called acetylene).

 $\begin{array}{l} CH_{3}CH_{3} + \frac{7}{2}O_{2} \longrightarrow 2CO_{2} + 3H_{2}O \qquad \Delta H^{\circ} = -1561 \text{ kJ} (-373 \text{ kcal}) \\ -1561 \text{ kJ divided by 5 moles of products} = -312 \text{ kJ/mol of products} \\ (-75 \text{ kcal/mol of products}) \end{array}$

 $\begin{array}{rcl} H_2C = CH_2 + 3 O_2 &\longrightarrow& 2 CO_2 + 2 H_2O & \Delta H^\circ = -1410 \text{ kJ } (-337 \text{ kcal}) \\ &-1410 \text{ kJ divided by 4 moles of products} = -352 \text{ kJ/mol of products} \\ & (-84 \text{ kcal/mol of products}) \end{array}$

 $HC \equiv CH + \frac{5}{2}O_2 \longrightarrow 2 CO_2 + 1 H_2O \qquad \Delta H^\circ = -1326 \text{ kJ} (-317 \text{ kcal})$ -1326 kJ divided by 3 moles of products = -442 kJ/mol of products(-106 kcal/mol of products)







Saturated & Unsaturated

- We describe hydrocarbons are either saturated or unsaturated.
- Saturated hydrocarbons are hydrocarbons with only single carbon-carbon bonds.
 - This means they have the most hydrogens their carbon skeletons can possibly have.
 - Alkanes are saturated hydrocarbons.
- Unsaturated hydrocarbons have double and triple carbon-carbon bonds.
 - Unsaturated hydrocarbons are not saturated with hydrogen, their carbon skeletons could hold more hydrogen.
 - > Alkenes & Alkynes are unsaturated hydrocarbons.
- Hydrocarbons can be monounsaturated (one unsaturation) or polyunsaturated (more than one unsaturation).
- Each unsaturation in a compound reduces the number of hydrogen atoms in the molecular formula by 2.





- Alkenes and alkynes are named using the same rules as alkanes, but the carbon backbone has some additional considerations.
- Choose the the longest chain that contains the double or triple bond(s) as your backbone.
 - Even if you would get a longer chain otherwise.
 - We'll stick to the more simple structures.
 - We won't be considering cases where you cannot identify a single chain with all unsaturations.
 - We won't ask you to choose between a ring or a chain with unsaturations.
- Numbering your backbone.
 - You have to give the address of the unsaturation(s) as part of the backbone name.
 - Unsaturations are numbered by the first carbon in their double or triple bond.
 - The unsaturation takes priority in assigning numbers.
 - If you have a choice between assigning simpler numbers to the unsaturation or to substituents
- We identify the unsaturation with the suffix:
 - -ene for a double bond (alkenes)
 - -yne for a triple bond (alkynes)

(you can't have a double bond with one atom)	6 = hex—
2 = eth—	7 = hept-
3 = prop—	8 = oct-
4 = but—	9 = non—
5 = pent—	10 = dec—



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$$CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$$

$$CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$$
 hexyne

$$CH_3 - CH_2 - C \equiv C - CH_2 - CH_3 - hexyne$$

$$1 \qquad 2 \qquad 3 \qquad 4 \qquad 5 \qquad 6$$



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4-methyl-2-pentene 4-methylpent-2-ene

> The address of the unsaturation can be written either before the backbone or before the suffix.





2-Pentene (or Pent-2-ene) not 3-Pentene

(start numbering from the end that gives you the smallest numbers)



1,3-Heptadiene (or Hept-1,3-diene)

(use greek prefixes for multiple unsaturations)

Br

6-Bromo-3-heptyne not 2-Bromo-4-heptyne

(having the lower number on the suffix is more important that having the lower number on the substituents)



Oct-5-en-2-yne (or 5-Octen-2-yne) not 5,2-Octenyne

(if you have double **and** triple bonds: 1. use both suffixes 2. only the last one ends in "e" 3. alphabetize the suffixes 4. addresses stay with each suffix)



6-chloro 6-chloro

non

3-en

7-yn

6,6-Dichloro-1,3-nonadien-7-yne or 6,6-Dichloronona-1,3-dien-7-yne

(not 6,6-Dichloro-1,3,7-nonadienyne)



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- Cycloalkenes & Cycloakynes are ring systems with a double or triple bond between atoms of the ring.
- There are **very few** cycloalkynes (the linear arrangement of four atoms makes ring formation difficult).
- Cycloalkenes & Cycloalkynes are named the same as cycloalkanes, except:
 - If there is no substituent, the double or triple bond requires no number.
 - The alkane ring is replaced.
 - In alkene & alkyne rings the same prefixes are used to indicated the number of carbons, the suffice -ene or -yne is used.
 - The first atom in each double or triple bond is atom #1.
 - The numbering continues so that the substituents get the lowest possible numbers.



Cyclooctyne



4-chlorocyclohexene



4-methyl-3-chloropentene



(you can't have a ring with one atom)	6 = hex—
(you can't have a ring with two atoms)	7 = hept—
3 = prop—	8 = oct—
4 = but—	9 = non—
5 = pent—	10 = dec—

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Benzene

- A unique substances was isolated by Michael Faraday in 1825.
 - Benzene is composed of six hydrogen and six carbon atoms connected in a ring.
 - All twelve atoms are coplanar.
 - Lewis Structure analysis suggests this structure would be composed of alternating double bonds.
 - Crystal structure though shows six equal bond lengths.
 - Not alternating single and double bonds.
- Benzene is often written as a hexane ring with a circle in the center, to indicate it's resonance nature.







Structures for benzene





Skeletal formula for benzene ring



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Aromatic Compounds

- Benzene and compounds built on the benzene ring have distinct fragrances.
- Collectively, these are known as aromatic compounds.
- The most basic aromatics have important common names:
 - Toluene is benzene with a methyl substituent.
 - Aniline is benzene with an amine substituent.
 - Phenol is benzene with an alcohol substituent.

(we will discuss amines and alcohols in more detail in upcoming chapters)





Substituted Aromatics

- Aromatics are named using either benzene or another simple aromatic as the backbone.
- If there is only one substituent on the benzene ring, no number is required.
- Otherwise numbering starts with the defining substituent on the simple aromatic, or largest substituent (on benzene).



Substituted Aromatics

- Aromatics are named using either benzene or another simple aromatic as the backbone.
- If there is only one substituent on the benzene ring, no number is required.
- Otherwise numbering starts with the defining substituent on the simple aromatic, or the atom with the highest atomic number (on benzene).



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Reminder!

Structural Isomers

- Isomers are substances that have the same molecular formula but other differences.
- Structural isomers have...
 - the same composition (formula)
 - different connectivity (structure)
- Structural isomers <u>are different substances</u>.
 - A chemical change is required to convert between structural isomers – you have to break and make bonds.
 - This is not the same as conformational changes where you just rotate along bonds.
 - Structural isomers may have different properties:
 - Different boiling point.
 - Different density.
 - Different melting point.
 - Structural isomers have the same composition, so they do have some things in common.
 - The same chemical formula.
 - The same molar mass.





Boiling point: -1.0 °C Density: 0.579 g/mL Melting point: -140 °C

C₄H₁₀ Molar mass: 58.12 g/mol

СН₃—СН₂—СН₂—СН₃



Boiling point: -11.7 °C Density: 2.064 g/mL Melting point: -159.6 °C

C₄H₁₀ Molar mass: 58.12 g/mol



Molar mass: 56.11 g/mol

Stereo Isomers

- Isomers are substances that have the same molecular formula but other differences.
- Structural isomers have...
 - the same composition (formula)
 - different connectivity (structure)
- Stereo isomers have...
 - the same composition (formula)
 - the same connectivity (structure)
 - different shape (sketch)
- Stereo isomers <u>are different substances</u>.
 - This is not the same as conformational changes where you just rotate along bonds.
 - Stereo isomers may have different properties:
 - Different boiling point.
 - Different density.
 - Different chemical reactivity.
 - Structural isomers have the same composition and connectivity so they do have some things in common.
 - The same chemical formula.
 - The same molar mass.
 - The same bond orders.



Stereo Isomers

- There are different kinds of stereoisomers. There are different issues that can cause two substances with the same composition and connectivity to be locked into different shapes.
- Double bonds are one of these issues.
- Cis-Trans isomers (or geometric isomers) are isomers that differ only because of how atoms are attached to a double bond.
- Cis-trans isomers are one kind of stereo isomer.
- Molecules cannot rotate around double bonds the way they can rotate around single bonds.
 - This produces two possible isomers, two different substances, that have the same:
 - composition (formula)
 - connectivity (structure)
 - In 2-butene for example the two end carbon atoms can be:
 - on the same of the double bond
 - on opposite sides of the double bond
- Why are these not conformations?
 - Covalent bonds exist because of overlap between the orbitals of adjacent atoms.
 - Some overlap allows rotation (single bonds do).
 - Allowing conformations to interconvert.
 - Some overlap does not (double bonds do not).
 - Locking substances into one shape or the other.
 - The only way to interconvert cis-trans isomers is to break bonds, to make a chemical change.



Double Bonds Have Restricted Rotation





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Naming Cis-Trans Isomers

- The concept of stereo isomers can quickly take us beyond the scope of this class.
- We will confine our discussions of geometric isomers to cis trans relationships within the backbone of the hydrocarbon.
- There is more than one way to indicate the stereochemistry of a double bond.
- We will use only the cis-trans naming convention.
- Cis isomers are isomers where the two hydrogens on a double bond are on the same side.
 - Prefix the full name of the substances with "cis".



cis-2-Pentene or cis-Pent-2-ene

- Trans isomers are isomers where the two hydrogens on a double bond are on opposite sides.
 - Prefix the full name of the substances with "trans".



trans-2-Pentene or trans-Pent-2-ene



Naming Cis-Trans Isomers

Name the following alkenes, use the correct cis-trans prefixes.



trans-3-octene







trans-2-heptene



cis-3-heptene



Naming Cis-Trans Isomers

Name the following alkenes, use the correct cis-trans prefixes.



trans-2-Pentene (or Pent-2-ene)



trans,trans-1,3-Heptadiene (or *trans,trans*-Hept-1,3-diene) *not trans-1,trans-3-Heptadiene*

(the *cis-trans* prefixes are attached to the name, not the address)

trans-4,4-Dichloro-2-heptene *not* 4,4-Dichloro-trans-2-heptene

(the *cis-trans* prefix goes in front of the entire name, including any other substituents)



cis-1-Propene (or cis-Prop-1-ene)

(look at the hydrogens on the double bond we will not consider the stereochemistry of a double bond that has less than two hydrogens)

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Types of Reactions

- Organic chemists describe and group chemical reactions into different classes to organize their palette or collection of tools.
- Some reaction types you're already familiar with are:
 - Combustion Reactions
 - Double Displacement Reactions
 - Reduction-Oxidation Reactions
 - Neutralization Reactions
- The pi-bonds in unsaturated hydrocarbons are weak and easy to break. Many chemical reactions take advantage of this to add new atoms to carbon chains at those points.
- Addition Reactions are a type of reaction that describe any reaction which adds new atoms to the carbon chain.
- We'll introduce you to a handful of very common addition reactions.





Bromination

- Bromination is the addition of bromine to a carbon skeleton.
- These reactions occur easily when bromine is mixed with an alkene.
- Bromination is an addition reaction.
- Bromination can be used to test hydrocarbons for unsaturations.
 - Bromine does not react with an alkane because the alkane contains only single C-C bonds which cannot add the bromine. Alkanes merely dilute the red-brown bromine color to an orange or yellow color in the absence of a strong catalyst.
 - Due to their C=C double bonds which can be broken, alkenes react readily with bromine to produce saturated dibromoalkanes. When an alkene is reacted with bromine, the red-brown color of the bromine is immediately lost due to the reaction of the bromine.





 $Br_2 + Alkane \quad Br_2 + Alkene$





Hydrogenation

- Hydrogenation is the addition of hydrogen to a carbon skeleton.
- The reaction between hydrogen and alkenes is less favorable than with bromine. But occurs with a catalyst like Pd, Ni or Pt.
- Hydrogenation is an addition reaction.

 $+ H_2$

+ H₂

 $+ H_2$

+ H₂



Double bond (alkene)

Single bond (alkane)



Hydration

- Hydration is the addition of the atoms of water to a carbon skeleton.
- Acid is used as a catalyst to drive this reaction.
- Hydration is an addition reaction.

 $+ H_2O$

 $+ H_2O$

 H^{+}

H₂O



difference)

OH ← Functional group

Η

Oxidation with $KMnO_4$

- The per oxy-ion of manganese in water, permanganate ion, adds two OH groups to alkene carbons.
- Acid is used as a catalyst to drive this reaction.
- This is an addition reaction.



- Permanganate can be used to test hydrocarbons for unsaturations.
 - The permanganate ion is dark purple in solution. If it's consumed by an alkene, it produces a colorless ion.
 - The disappearance of permanganate color indicates the presence of an unsaturated hydrocarbon.







Reactions of Alkenes

Predict the products or indicate the reactants required for the following reactions.



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