Chapter 13

Alkenes, Alkynes, and Aromatic Compounds

Chapter 13 suggested problems: 23, 24, 25, 26, 27, 28, 29, 34, 36, 38, 40, 44, 48, 50, 58, 60, 84, 86, 88, 90

Class Notes

I. Alkenes and alkynes: general information

   A. Unsaturated hydrocarbons that contain one or more carbon-carbon double bonds

      1. Saturated hydrocarbons: every carbon atom is bonded to the maximum number of hydrogen atoms

      2. Unsaturated hydrocarbons: one or more carbon atoms is not bonded to the maximum number of hydrogen atoms due to the presence of, for example, carbon-carbon double or triple bonds

   B. General formulas and the index of hydrogen deficiency

      1. Alkenes: same as for a cycloalkanes: C_nH_{2n}

      2. Alkynes: same as for dienes C_nH_{2n-2}

      3. General: the molecular formula provides information about the numbers and types of atoms in a compound

      4. It also provides information about the index of hydrogen deficiency, i.e., the number of pairs of hydrogen atoms the compound is missing due either to the presence of double bonds, triple bonds, and rings

         a. This index of hydrogen deficiency is also known as double bond equivalence

         b. Index = # carbons (tetravalent atoms) - (monovalent atoms/2) + (trivalent atoms/2) + 1

            i. Tetravalent atoms: C, Si

            ii. Monovalent atoms: H, halogens

            iii. Divalent atoms: O, S

            iv. Trivalent atoms: N, P

         c. The Octet Rule must be obeyed when drawing the Lewis structures that correspond to predicted structures, i.e., every atom in the structure must have an octet regardless of any resulting formal charges

d. Examples

i. Hexane C_6H_{14} I = 6 - 14/2 + 1 = 0

ii. 1-hexene C_6H_{12} I = 6 - 12/2 + 1 = 1

iii. 1-hexyne C_6H_{10} I = 6 - 10/2 + 1 = 2

iv. 1,3-hexadiene C_6H_{10} I = 6 - 6/2 + 1 = 2

v. 1,3,5-hexatriene C_6H_8 I = 6 - 8/2 + 1 = 3

vi. Cyclohexane C_6H_{12} I = 6 - 12/2 + 1 = 1

vii. Cyclohexene C_6H_{10} I = 6 - 10/2 + 1 = 2

viii. Benzene C_6H_6 I = 6 - 6/2 + 1 = 4

C. Sources: most commonly obtained from the cracking of petroleum, although there are many naturally occurring and biologically important alkenes; alkynes are less common biologically

D. Similar physical properties to those of alkanes

1. The predominant intermolecular bonding forces are dispersion forces, as is the case with alkanes
2. Nonpolar and insoluble in water
3. Flammable
4. Low toxicity
5. Much more reactive than alkanes, pi bonds serve as the focal point for reactions

E. Bonding in alkenes and alkynes: hybridization, sigma bonds, and pi bonds

1. Carbon atoms that form sigma bonds use hybridized orbitals
2. A double bond is made up of one sigma bond and one pi bond, a triple bond of one sigma bond and two pi bonds
3. Using ethylene as an example, the four C-H bonds are formed by the overlap of the H's 1s orbital and a hybrid orbital of a carbon atom
4. The orbitals of the remaining unhybridized p electrons overlap out of the plane of the bonding atoms to form the pi bond
5. Pi bonds are about 50-75% as strong as sigma bonds - due to being out of plane? slightly electron repulsion?
6. sp^2 hybridization explains the 120° angles and molecular flatness observed in the carbons involved in the double bond (trigonal planar geometry)
7. Using acetylene as an example, the two C-H bonds are formed by the overlap of the H's 1s orbital and a hybrid orbital of a carbon atom

8. sp hybridization explains the 180° angles and molecular linearity observed in the carbons involved in the triple bond (linear geometry)

II. Constitutional isomers of alkenes

A. Alkenes have more possible constitutional isomers for a given number of carbon atoms than alkanes due to variations both in the backbone arrangement and in the placement of the functional group

B. Ethene - 1 isomer

C. Propene - 1 isomer

D. Butene - 4 isomers: 1-butene, cis-2-butene, trans-2-butene, 2-methyl-1-propene

E. Pentene - 6 isomers

III. Naming alkenes and alkynes

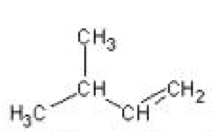
A. Simple alkenes and alkene side chains

C_2H_4	ethene	CH_2=CH-	vinyl
C_3H_6	propene	CH_2=$CHCH_2$-	allyl
C_4H_8	1-butene	CH_2=CCH_3	isopropenyl
C_5H_{10}	1-pentene	-CH_2=$CHCH_2CH_3$	butenyl
C_6H_{12}	1-hexene		
C_7H_{14}	1-heptene		
C_8H_{16}	1-octene		
C_9H_{18}	1-nonene		
$C_{10}H_{10}$	1-decene		

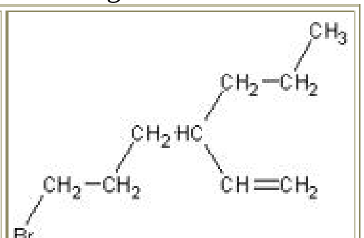
B. Identify the longest chain

C. Number the chain so that the position of the double bond is as low as possible

D. Carbon-carbon double bonds take precedence over alkyl groups and halogen atoms in determining the chain length and the direction of numbering



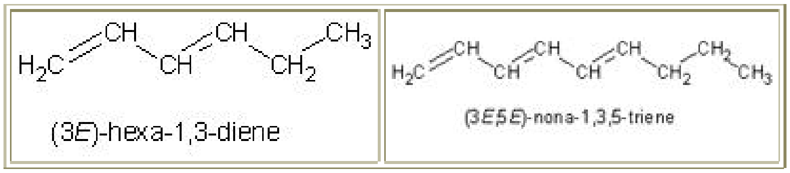
3-methyl-1-butene, not 2-methyl-3-butene



6-bromo-3-propyl-1-hexene

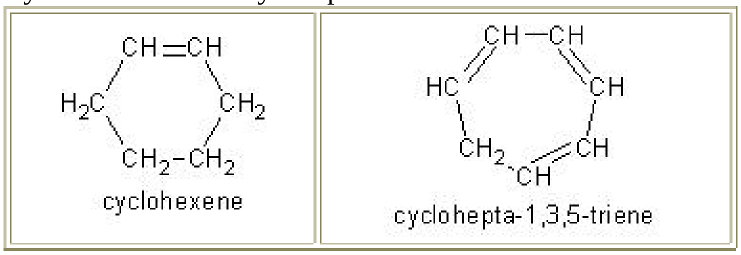
E. Hydroxyl groups outrank the double bond

F. Dienes and trienes - two and three C=C respectively, indicated with suffixes "adiene" or "atriene" rather than "ene"



(3*E*)-hexa-1,3-diene (3*E*,5*E*)-nona-1,3,5-triene

G. Cycloalkenes - use "cyclo" prefix

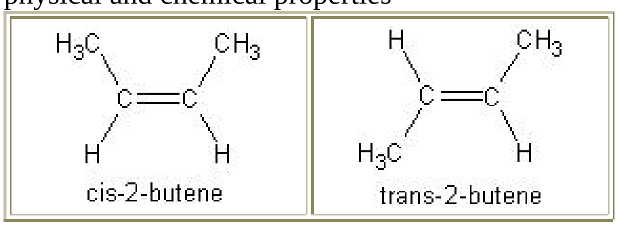


cyclohexene cyclohepta-1,3,5-triene

IV. The structure of alkenes: cis-trans isomerism

A. Rotation around carbon-carbon double bonds is restricted (i.e. does not occur under normal circumstances), as is also the case with rotation around rings

B. This means that compounds with the same molecular formulas and the same groups attached to the same carbons (i.e. the same configurations) but on different sides of a double bond will have different physical and chemical properties



cis-2-butene trans-2-butene

C. Cis-tran isomerization is only possible when each of the two carbons in the double bond have two different substituents

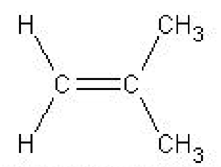
1. Used when the groups on either end of the double bond are the same or are structurally similar (Carey: 173)

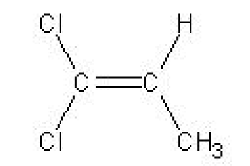
2. Cis - Latin: "on this side

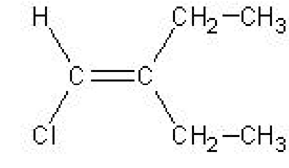
3. Trans - Latin: "across"

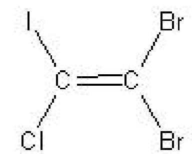
4. Examples of compounds that are cis-tran isomers include oleic acid (cis-$CH_3(CH_2)_6CH_2CH{=}CHCH_2(CH_2)_6COOH$) and cinnamaldehyde (trans-$C_6H_5CH{=}CHCHO$)

5. Examples of compounds that are not geometric isomers


2-methyl-1-propene


1 , 1 - dichloropropene


1-chloro-2-ethyl-1-butene


1,1-dibromo-2-chloro-2-iodoethylene

D. Z and E are also used in lieu of cis and trans when groups of various sizes or weights are involved or when it is not obvious when substituents are similar

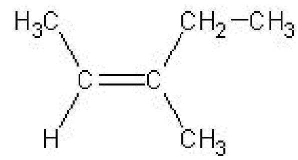
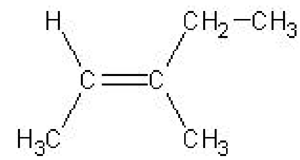
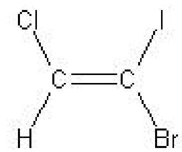
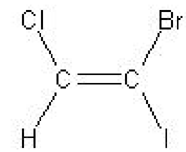
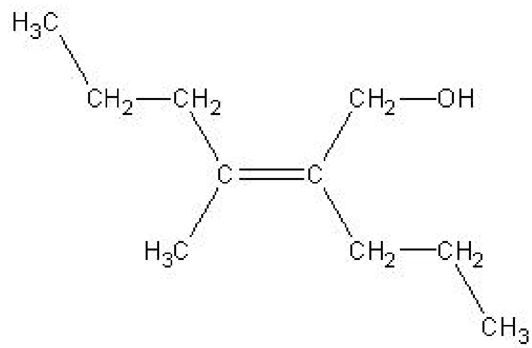
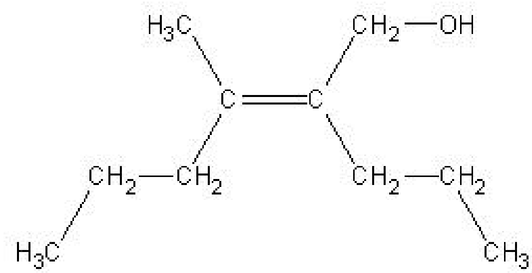
1. The Z-E system is an unambiguous system based on the atomic numbers of atoms bonding to the double-bonded carbon atoms

2. Z - zusammen: "together;" atoms or groups of highest rank (based on atomic numbers) on same side of double bond

3. E - entgegen: "opposite;" atoms or groups of highest rank (based on atomic numbers) on opposite sides of double bond

4. First the atomic numbers of the atoms bonding to the double-bonded carbon atoms is examined, and then the atomic numbers of the atoms bonded to those atoms is checked, and so on until a classification is determined

5.

 Z-3-methyl-2-pentene	 E-3-methyl-2-pentene
 Z-1-bromo-2-chloro-1-iodoethylene	 E-1-bromo-2-chloro-1-iodoethylene
 (2*Z*)-3-methyl-2-propylhex-2-en-1-ol	 (2*E*)-3-methyl-2-propylhex-2-en-1-ol

V. Addition reactions: the pi bond(s) in alkenes and alkynes results in their being much more reactive than alkanes

A. Lewis acid-base chemistry and reactions in organic chemistry

1. Acid-base theories

   a. Arrhenius theory

   b. Bronsted-Lowry theory

   c. Lewis theory

2. Nucleophile - shares an electron pair with another atom to form a new covalent bond: a Lewis base

3. Electrophile - gains an electron pair from another atom to form a new covalent bond: a Lewis acid

B. Addition reactions - general information

1. A reaction in which two molecules combine to yield a single product molecule; the reagent is simply added to the substrate molecule; resulting in the breaking of a pi bond and the formation of two sigma bonds

2. Pi electrons are not held as tightly, serve as electron source (nucleophilic)

3. Alkenes/alkynes can be attacked by electrophiles or free radicals

C. Addition of symmetric substances (H_2, halogens)

1. Hydrogenation
    a. A hydrogen molecule is broken into hydrogen atoms which add to the carbon atoms involved in the double bond
    b. Takes place at room temperature but requires a catalyst (Pt or Ni), so the process is sometimes called catalytic hydrogenation
    c. An alkane forms as a result
    d. Ex: the addition of hydrogen to 2-butene and 1-hexene
2. Halogenation
    a. A halogen molecule is broken into halogen atoms which add to the carbon atoms involved in the double bond
    b. Takes place at room temperature
    c. A vicinal dihalide is formed as a result
    d. Ex: the addition of hydrogen to 2-butene and 1-hexene

D. Addition of asymmetric substances (hydrohalides, water)

1. Markovnikov's Rule
    a. Hydrogen preferentially - but not exclusively - adds to the carbon atom with the most hydrogen atoms bonded to it
    b. This results in the formation of major (more abundant) and minor (less abundant) products
    c. Carbocation stabilization and the inductive effect: 3° > 2° > 1°
    d. Ex: the addition of HBr to ethylene and to 1-butene
2. Hydrohalogenation
    a. A molecule is broken into a hydrogen atom and a halogen atom which add to the carbon atoms involved in the double bond
    b. An alkyl halide is formed as a result
    c. Ex: the addition of hydrogen to 2-butene and 1-hexene
3. Hydration
    a. A water molecule is broken into a hydrogen atom and a hydroxide ion which add to the carbon atoms involved in the double bond
    b. Requires a acid catalyst
    c. An alcohol is formed as a result
    d. Ex: the addition of hydrogen to 2-butene and 1-hexene

VI. Oxidation of alkenes and alkynes

A. Alkenes undergo combustion reactions, in which every carbon and hydrogen atom is oxidized to its highest oxidation state

1. The concept of oxidation numbers: a brief review

2. Oxidation of an organic compound involves forming bonds between carbon and oxygen and breaking C-C and/or C-H bonds

3. The greater the oxidation state of the carbon the more C-O bonds exist

4. Maximum oxidation number of carbon is +4 (CO_2)

5. All carbon atoms are completely oxidized

B. Selective oxidation of carbon atoms involved in C-C double bonds and colorimetric functional group analysis

1. Ozone: cleaves both the sigma and the pi bond, forming two new compounds, either aldehydes or ketones

2. Potassium permanganate: results depend on conditions - can either add a hydroxyl group to both of the participating carbon atoms and form a vicinal diol, or it may form aldehydes or carboxylic acids: purple solution turns brown (M&B: 220f, March: 732f)

3. Potassium dichromate: orange solution turns green, behaves similarly to permanganate solutions with respect to its effects on the double bond

VII. Alkene polymers

A. Polymers are molecular chains

1. The basic building blocks of polymers are monomers

2. The monomers used to build the polymer are reflected in the name of the polymer

a. There are hundreds of polymers, both natural and synthetic

b. Natural: proteins, nucleic acids, rubber, cellulose, starch, etc.,

c. Recyclable polymers

code	polymer resin	description	products
1	PETE: polyethylene-terephthalate	usually clear or green; sinks (more dense) than water	soft drink, salad dressing, and peanut butter bottles
2	HDPE	semi-glossy, crinkly	toys, liquid detergent bottles, motor oil bottles, plastic bags, milk - water - juice containers
3	PVC	semi-rigid, glossy, sinks in water	clear food wrap, blister packaging, shampoo and vegetable oil bottles
4	LDPE	flexible, not crinkly	frozen-food bags, grocery bags, shrink-wrap, bread bags, garment bags
5	PP	semi-rigid, low gloss	most bottle caps, yogurt and margarine containers, medicine containers
6	PS	often brittle, glossy	insulated cups, containers, and trays, video cassette jackets and jewel cases
7	other (multi-layer plastics)	squeezable	squeezable food delivery devices

B. Many important monomers are alkenes, includes ethylene, propylene, styrene, tetrafluoroethylene, vinyl chloride, acrylonitrile (vinyl cyanide), and methyl methacrylate)

C. In addition polymerizations, the monomers add one to another to form polymers that can range from dozens to thousands of monomers in size

D. Addition polymerization requires a catalyst

E. Addition polymerization will not take place in the presence of things that add to a double bond (hydrogen, halogens, hydrohalogens, water, sulfuric acid)

VIII. Aromatic compounds

A. Aliphatic versus aromatic hydrocarbons

B. Benzene - the basic building block of aromatic compounds

1. Structure results a high degree of stability, relatively low degree of reactivity

   a. 6 co-planar sp^2 hybridized carbon atoms

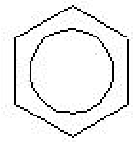
   b. Overlap of the p orbitals results in the formation of 3 pi bonds

   c. Benzene's actual structure is a combination of resonance structures

   d. Resonance structures indicate electron delocalization, which results in stabilization of the compound

   e. Due to resonance stability, benzene is about 152 kJ/mol more stable than 1,3,5-cyclohexatriene

   f. Combustion experiments corroborate that benzene is lower in energy than similar alkenes

   g. This results in the representation of benzene rings as 

2. Reactivity notes

   a. Halogens, hydrogen halides, water, and sulfuric acid do not add to the double bonds of the ring under any condition

   b. Substitution of functionalities for ring hydrogens can occur (electrophilic aromatic substitution)

IX. Isomers and names of aromatic compounds

A. Monosubstituted benzenes

1. Many are named by placing the substituent name in front of "benzene"

   a. Chlorobenzene, bromobenzene, iodobenzene

   b. Nitrobenzene

2. Common names and systematic names

   a. Toluene - methylbenzene

   b. Phenol - benzenol

   c. Aniline - benzenamine

   d. Benzoic acid - benzenecarboxylic acid

   e. Styrene - vinyl benzene

   f. Anisole - methoxybenzene

   g. Benzaldehyde - benzenecarbaldehyde

B. Disubstituted benzenes

1. The constitutional isomers of xylene (dimethyl benzene)

   a. 1,2-xylene or o-xylene

   b. 1,3-xylene or m-xylene

   c. 1,4-xylene or p-xylene

2. The o, m, p prefixes may be used in two circumstances

   a. When a disubstituted substance is named as a benzene derivative

      i. o-dichlorobenzene

b. When there are two substituents and one of them is responsible for giving benzene a common name

i. m-nitrotoluene

ii. p-chloroanisole

C. Trisubstituted benzenes and beyond

1. Numbers must be used for trisubstituted and beyond (substituents are named alphabetically)

a. 2,4,6-trinitrotoluene

b. 2,4-dichloro-1-nitrobenzene

c. 3-ethyl-2-methylaniline

D. Benzene as a substituent

1. Benzene rings as substituents are called phenyl groups

a. 2-phenylethanol

b. 1-phenylnonane

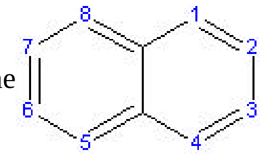
c. 1-phenyl-2-propanone

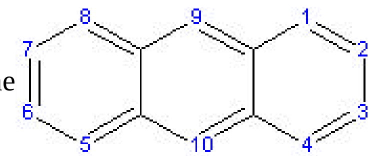
E. Polyaromatic hydrocarbons and biphenyls

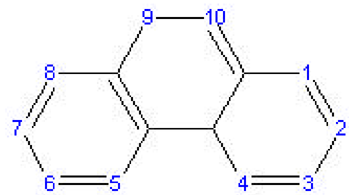
1. Two phenyl groups joined by a sigma bond are called biphenyl

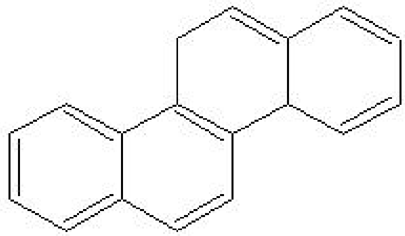
a. polychlorinated biphenyls

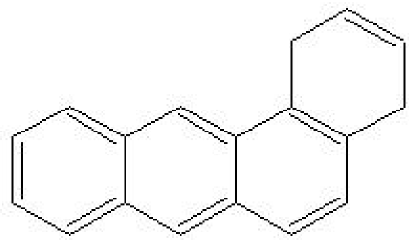
2. Two or more fused benzene rings are called polyaromatic hydrocarbons

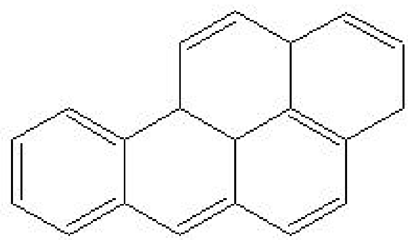
a. Naphthalene 

b. Anthracene 

c. Phenanthrene 

d. Chrysene 

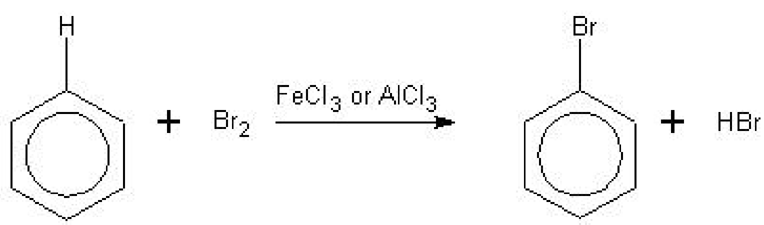
e. 1,2-benzanthracene 

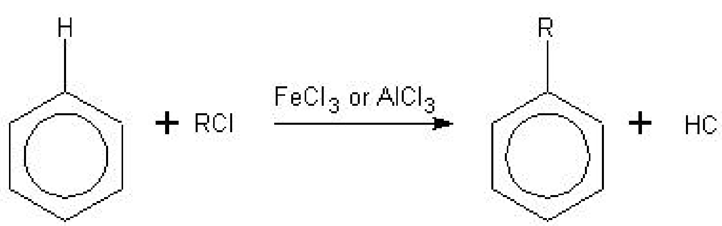
f. Benzo[a]pyrene (BAP) 

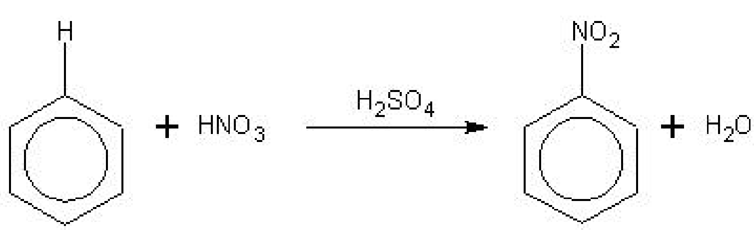
g. Chrysene, 1,2-benzanthracene, and benzo[a]pyrene are carcinogens

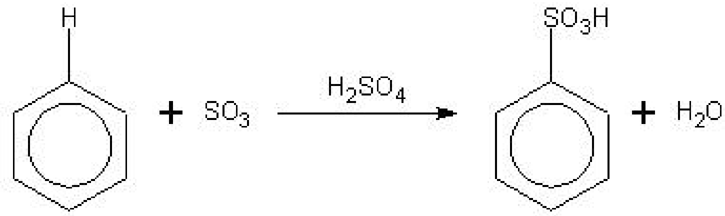
X. Reactions of aromatic compounds

A. Electrophilic aromatic substitution - the replacement of a ring hydrogen by another substituent often require a metal halide or sulfuric acid as a catalyst

1. Halogenation 

2. Alkylation 

3. Nitration 

4. Sulfonation 

B. Oxidation

1. Alkylbenzenes undergo oxidation under moderately strong oxidizing conditions, such as hot potassium permanganate or potassium dichromate

2. The benzene ring is untouched while the aliphatic moiety is oxidized completely to carbon dioxide and water

3. The carbon attached to the ring is oxidized to a carboxylic acid

C. Combustion - aromatics do undergo complete oxidation in combustion reactions, but need a good oxygen source for complete combustion

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