Chemistry 121(01) Winter 2009

Introduction to Organic Chemistry and Biochemistry
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TR 9::00 - !0:00 am & 1:00-2:00 pm.

December 19, Test 1 (Chapters 12-14)
January 2 Test 1 (Chapters 15-16)
February 6 (Chapters 17-19)
February 27, (Chapters 20-22)
March 2, 2009, Make Up Exam:
Bring Scantron Sheet 882-E

Chapter 13: Unsaturated Hydrocarbons

Sections 4.1-4.5

Chapter 13: Unsaturated Hydrocarbons

Unsaturated hydrocabons

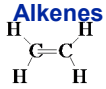
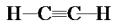
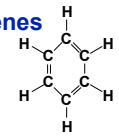
Hydrocarbons with carbon-carbon double bonds and triple bonds

double bonds: alkenes

triple bonds: alkynes

three alternating double bond in 6 carbon ring: aromatics

Unsaturated Hydrocarbons:

Alkenes	Alkynes	Arenes
		
ethene	ethyne	benzene
C_2H_4	C_2H_2	C_6H_6
C_nH_{2n} unsaturated	C_nH_{2n-2} unsaturated	C_nH_n Aromatic
alkene	alkyne	Arene
Chapters 13	Chapters 13	Chapter 13

Units of Unsaturation

Compounds that have have fewer hydrogens than saturated hydrocarbons (C_nH_{2n+2}). Two hydrogen are considered as unit of unstauration

Cycloalkane ring C_nH_{2n} (one unit of unsat.)

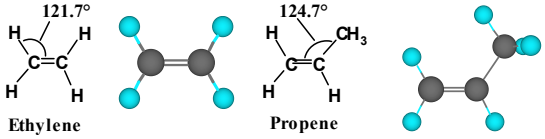
Unsaturated hydrocarbons:

= bond C_nH_{2n} (one unit of unsat.)

≡ bond C_nH_{2n-2} (two units of unsat.)

Structure of Alkenes

- **Alkene: contains a carbon-carbon double bond and has the general formula C_nH_{2n}**
- **The two carbon atoms of a double bond and the four atoms bonded to them lie in a plane, with bond angles of approximately 120°**

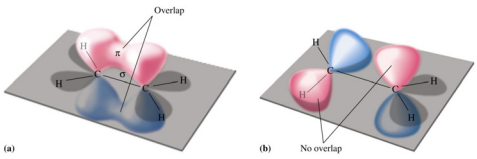


Planar Structure of Alkenes

According to the orbital overlap model, a double bond consists of

- a σ bond formed by overlap of sp^2 hybrid orbitals
- a π bond formed by overlap of parallel $2p$ orbital

Rotating by 90°breaks the pi bond

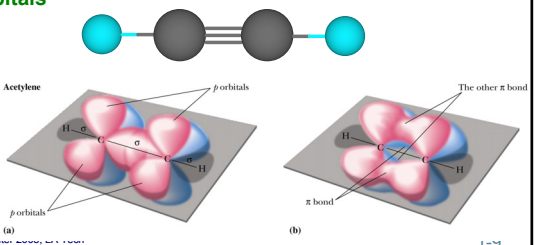


Structure of Alkynes

The functional group of an alkyne is a carbon-carbon triple bond

A triple bond consists of

- one σ bond formed by the overlap of *sp* hybrid orbitals
- two π bonds formed by the overlap of sets of parallel *2p* orbitals



Alkenes

Second members of the hydrocarbon family.

- contain only hydrogen and carbon
- have single bonds and at least one C=C double bond

All members have the general formula of

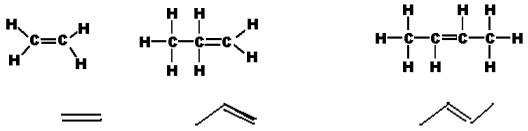
C_nH_{2n}

Twice as many hydrogen as carbon

Alkenes: Naming and Structures

One simple class of compound is the alkene which has only C, H and single bonds.

ethene	propene	2- butene
C_2H_4	C_3H_6	C_4H_8
CH_2CH_2	$CH_3CH_2CH_2$	$CH_3CH_2CHCH_3$



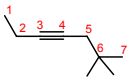
IUPAC Nomenclature of Alkenes and Alkynes

- name the longest continuous carbon chain containing the multiple bond(s) (parent chain). If cyclic, ring is the parent.
- use the infix -en- to show the presence of a carbon-carbon double bond
- use the infix -yn- to show the presence of a carbon-carbon triple bond
- number the parent chain to give the 1st carbon of the double/triple bond the lower number
- If both double and triple are present and cannot have the same #, then double bonds take priority.
- follow IUPAC general rules for numbering and naming substituents
- for a cycloalkene, the double bond must be numbered 1,2

IUPAC Nomenclature of Alkynes

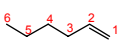
- use the infix -yn- to show the presence of a carbon-carbon triple bond
- number the parent chain to give the 1st carbon of the triple bond the lower number
- follow IUPAC rules for numbering and naming substituents

3-Methyl-1-butyne

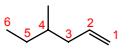


6,6-Dimethyl-3-heptyne

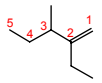
Example of IUPAC Nomenclature of Alkenes Cycloalkanes



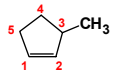
1-Hexene



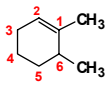
4-Methyl-1-hexene



2-Ethyl-3-methyl-1-pentene



3-Methylcyclo-pentene



1,6-Dimethylcyclo-hexene

Nomenclature of Alkenes: Common Names

Some alkenes, particularly low-molecular-weight ones, are known almost exclusively by their common names

	$CH_2=CH_2$	$CH_3CH=CH_2$	$CH_3C(CH_3)=CH_2$
IUPAC:	Ethene	Propene	2-Methylpropene
Common:	Ethylene	Propylene	Isobutylene

Alkenes

First four members of the alkanes

Name	# of C	Condensed formula
Ethene	2	$CH_2=CH_2$
Propene	3	$CH_3CH=CH_2$
2-Butene	4	$CH_3CH=CHCH_3$

Called a homologous series

- "Members differ by number of CH_2 groups"

Naming alkenes and alkynes

Find the longest carbon chain. Use as base name with an ene or yne ending.

Number the chain to give lowest number for the carbons of the double or triple bond.

Locate any branches on chain. Use base names with a yl ending.

For multiple branch of the same type, modify name with di, tri, ...

Show the location of each branch with numbers.

List multiple branches alphabetically

- the di, tri, ... don't count..

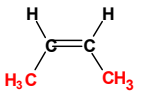
Cis and trans Geometrical isomers of alkenes

two groups are said to be located cis to each other if they lie on the same side of a plane with respect to the double bond.

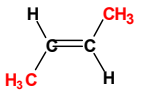
If they are on opposite sides, their relative position is described as trans.

Geometrical Stereoisomerism

Because of restricted rotation about a C-C double bond, groups on adjacent carbons are either cis or trans to each other



cis-2-Butene
mp -139°C, bp 4°C



trans-2-Butene
mp -106°C, bp 1°C

Physical Properties

Alkenes and alkynes are nonpolar compounds

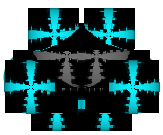
- the only attractive forces between their molecules are dispersion forces

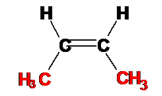
Their physical properties are similar to those of alkanes of similar carbon skeletons

- those that are liquid at room temperature are less dense than water (1.0 g/m L)
- they dissolve in each other and in nonpolar organic solvents
- they are insoluble in water

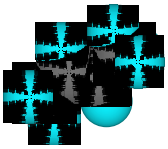
Cis-Trans Isomerism

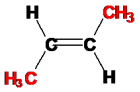
- trans alkenes are more stable than cis alkenes because of nonbonded interaction strain between alkyl substituents of the same side of the double bond





cis-2-Butene



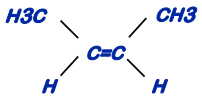


trans-2-Butene

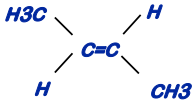
Geometric isomers

There are two possible arrangements.

Example 2-butene



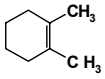
cis
Largest groups are on the same side.



trans
Largest groups are on opposite sides.

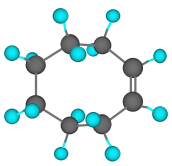
Cis-Trans Isomerism in Cycloalkenes

- the configuration of the double bond in cyclopropene through cycloheptene must be cis; these rings are not large enough to accommodate a trans double bond



- cyclooctene is the smallest cycloalkene that can accommodate a trans double bond

trans-Cyclooctene



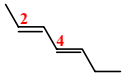
cis-Cyclooctene

Cis-Trans Isomerism

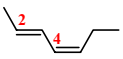
Dienes, trienes, and polyenes

- for an alkene with *n* carbon-carbon double bonds, each of which can show cis-trans isomerism, 2^n cis-trans isomers are possible
- consider 2,4-heptadiene; it has four cis-trans isomers, two of which are drawn here

Double bond	
C_2-C_3	C_4-C_5
trans	trans
trans	cis
cis	trans
cis	cis



trans,trans-2,4-heptadiene

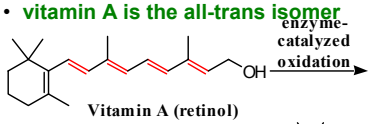


trans,cis-2,4-heptadiene

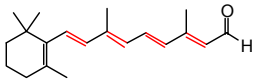
Naturally Occurring

AlkenesCis-Trans Isomerism

- vitamin A has five double bonds
- four of the five can show cis-trans isomerism
- vitamin A is the all-trans isomer



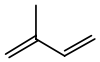
Vitamin A (retinol)



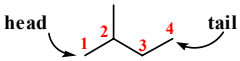
Vitamin A aldehyde (retinal)

Naturally Occurring Alkenes: The Terpenes

Terpene: a compound whose carbon skeleton can be divided into two or more units identical with the carbon skeleton of isoprene

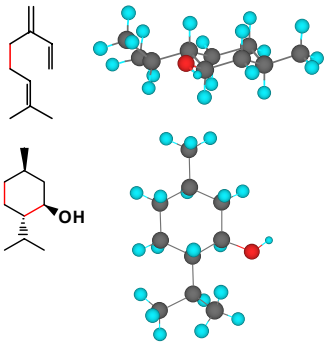


2-Methyl-1,3-butadiene
(Isoprene)



Terpenes: Polymers of Isoprene

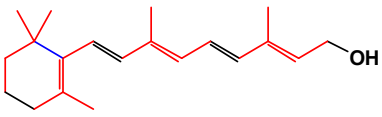
- myrcene, $C_{10}H_{16}$, a component of bayberry wax and oils of bay and verbena
- menthol, from peppermint



Terpenes

Vitamin A (retinol)

- the four isoprene units in vitamin A are shown in red
- they are linked head to tail, and cross linked at one point (the blue bond) to give the six-membered ring



Reactions of alkenes

Combustion

$$C_2H_4 + 4\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + \text{heat}$$

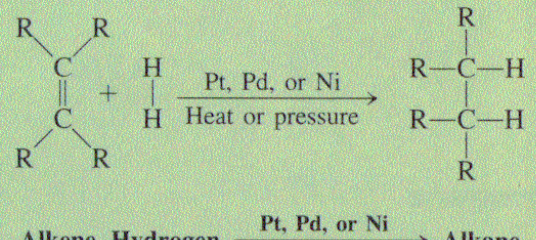
Alkynes also under go combustion reactions similarly

Addition Reactions

The exposed electrons of double bonds make alkenes more reactive than alkanes and show addition reactions.

Addition reactions of alkenes

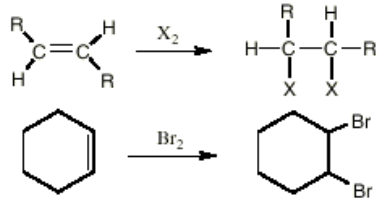
Hydrogenation:



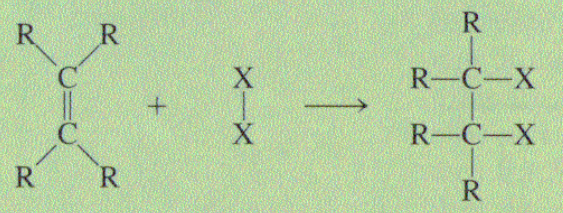
Alkene Hydrogen —(Pt, Pd, or Ni; Heat or pressure)→ Alkane

Halogenation

Halogenation - Addition of halogen to the double bond. Textbook page xx.



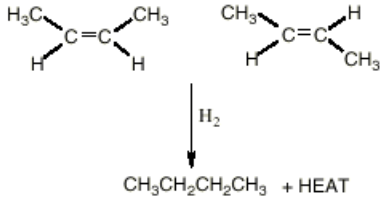
Halogenation:



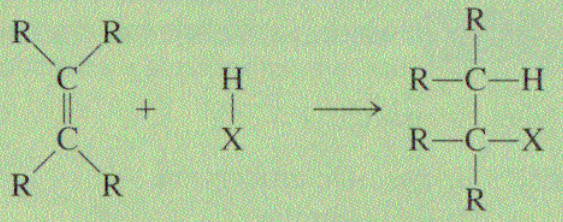
Alkene Halogen ⟶ Alkyl dihalide

Hydrogenation

Addition of hydrogen to the double bond. Textbook page 84



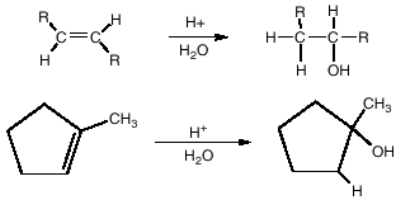
Hydrohalogenation:



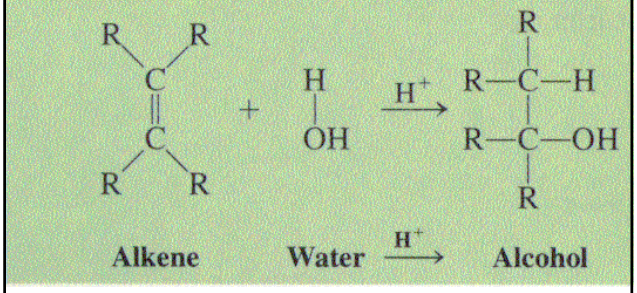
Alkene Hydrogen halide ⟶ Alkyl halide

Hydration

Addition of water to the double bond. Textbook page86.

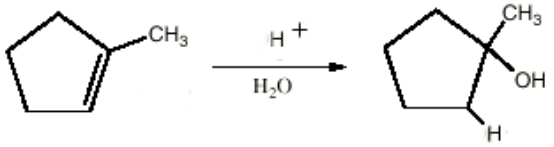


Hydration:

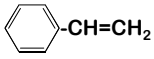
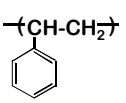


Markovnikov Rule

- Non symmetric alkene
- In hydrohalogenation and hydration reations hydrogen adds to the double-bonded carbon with the most hydrogens



Polymerization

Name	Monomer	Formula Polymer
Polypropylene	$CH_3CH=CH_2$	$-(CH(CH_3)-CH_2)-$
Polystyrene		
Polychloroprene	$H_2C=CHC(Cl)=CH_2$	$-(CH_2CH=C(Cl)CH_2)-$

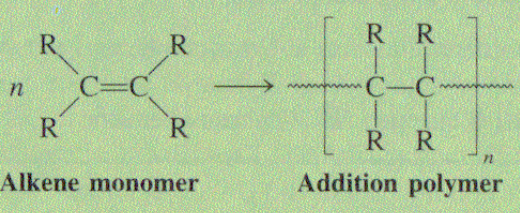
Polymers

Addition Polymers

Because the monomer units in synthetic polymers are all the same (except for copolymers), an abbreviated formula can be used.

Monomer	Polymer
Ethylene	polyethylene
	$-(CH_2-CH_2)_n-$
Vinyl chloride	poly(vinyl chloride)
	$-(CH_2-CH(Cl))_n-$

Addition Polymers of Alkenes



Reactions of alkynes

Alkynes undergo hydration, halogenation, and hydrohalogenation just like alkenes.

A special application is the carbide lamp (oxidation of alkyne).

2 C (coke) + CaO (lime) + heat

---> CaC_2 (calcium carbide) + CO

$CaC_2 + H_2O$

---> H-C≡C-H (acetylene) + $Ca(OH)^2$

Acetylene serves as combustion fuel for the carbide lamp.

Aromatic hydrocarbons

Aromatic hydrocarbons - organic compounds that had aromas and had different chemical properties from alkane

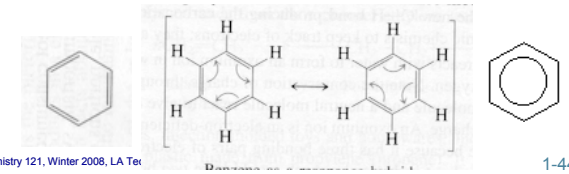
Benzene is the parent compound for the aromatic hydrocarbons. Textbook, page90.

Consider benzene. C_6H_6

Resonance Structures of Benzene

Resonance structures or contributing structures = when two or more structure can be drawn for a compound.

In thiscase, the real structure is something between the proposed structures. Textbook, page 90-91.



Naming Aromatic Hydroarbons.

Monosubstituted benzenes:

Ar-CH_2CH_3 ethylbenzene

Ar-CH_2-CH_2-CH_2-CH_3 butylbenzene

Ar-CH_3 (methylbenzene) toluene

Ar-X (halobenzene) bromobenzene,

Ar-NO_2 nitrobenzene

Ar-SO_3H benzenesulfonic acid

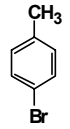
Ar-NH_2 a nitrile substituent

Nomenclature

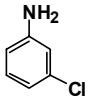
Disubstituted benzenes

- locate substituents by numbering or
- use the locators ortho (1,2-), meta (1,3-), and para (1,4-)

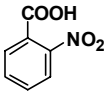
Where one group imparts a special name, name the compound as a derivative of that molecule



4-Bromotoluene (*p*-Bromotoluene)



3-Chloroaniline (*m*-Chloroaniline)



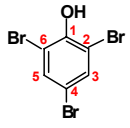
2-Nitrobenzoic acid (*o*-Nitrobenzoic acid)

Nomenclature

Polysubstituted benzenes

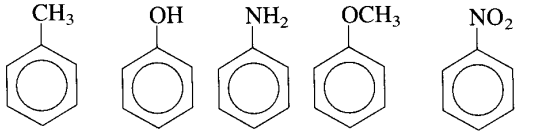
- with three or more substituents, number the atoms of the ring
- if one group imparts a special name, it becomes the parent name
- if no group imparts a special name, number to give the smallest set of numbers, and then list alphabetically

4-Chloro-2-nitro-toluene

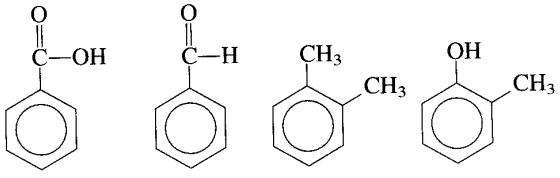


2,4,6-Tribromo-phenol

2-Bromo-1-ethyl-4-nitrobenzene



Toluene Phenol Aniline Anisole Nitrobenzene



Disubstituted benzenes:

Textbook, page 352.

2,6-dibromotoluene

p-diethylbenzene

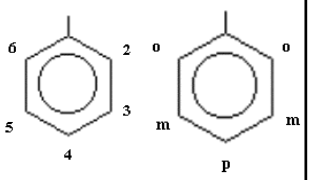
3,5-dinitrotoluene

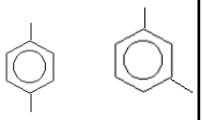
p-cholonitrobenzene

o-nitrobenzenesulfonic acid

4-benzyl-1-octene

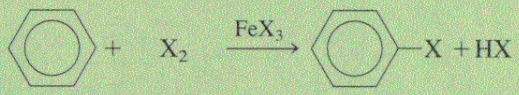
m-cyanotoluene



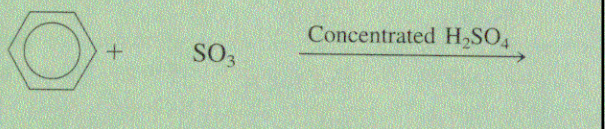


Reactions of Benzene

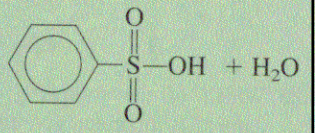
Halogenation:



Benzene **Halogen** **Halobenzene**

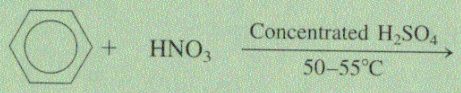


Benzene **Sulfur trioxide**

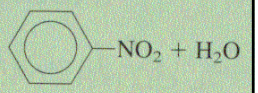


Benzenesulfonic acid

Nitration:



Benzene **Nitric acid**

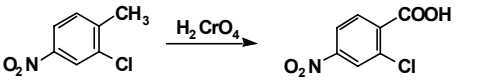


Nitrobenzene

Benzylic Oxidation

Benzene is unaffected by strong oxidizing agents such as H_2CrO_4 and $KMnO_4$

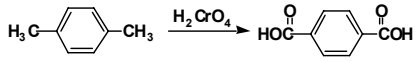
- halogen and nitro substituents are unaffected by these reagents
- an alkyl group with at least one hydrogen on the benzylic carbon is oxidized to a carboxyl group



2-Chloro-4-nitrotoluene — 2-Chloro-4-nitrobenzoic acid

Benzylic Oxidation

- if there is more than one alkyl group, each is oxidized to a -COOH group



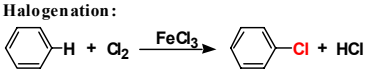
1,4-Dimethylbenzene (p-xylene) — 1,4-Benzenedicarboxylic acid (terephthalic acid)

- terephthalic acid is one of the two monomers required for the synthesis of poly(ethylene terephthalate), a polymer that can be fabricated into Dacron polyester fibers and into Mylar films

Reactions of Benzene

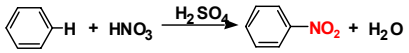
The most characteristic reaction of aromatic compounds is substitution at a ring carbon

Halogenation:



Chlorobenzene

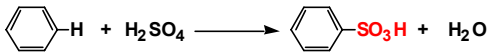
Nitration:



Nitrobenzene

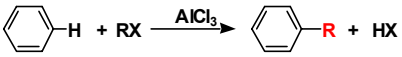
Reactions of Benzene

Sulfonation:



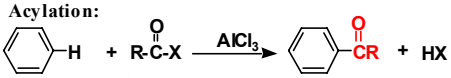
Benzenesulfonic acid

Alkylation:



An alkylbenzene

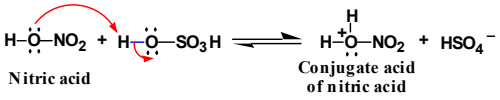
Acylation:

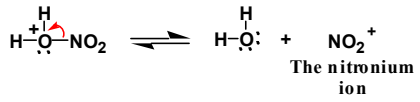


An acyl halide — An acylbenzene

Nitration

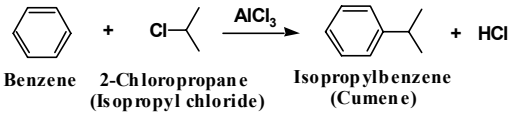
The electrophile is NO_2^+, generated in this way





Friedel-Crafts Alkylation

Friedel-Crafts alkylation forms a new C-C bond between an aromatic ring and an alkyl group



Friedel-Crafts Acylations

Treating an aromatic ring with an acid chloride in the presence of $AlCl_3$

- **acid (acyl) chloride: a derivative of a carboxylic acid in which the -OH is replaced by a chlorine**