1

Introduction to Organic Chemistry

last semester- 109 elements

this semester only 4- C, H, O, N: but arranged in a plethora of ways

Ionic compounds *vs*. Covalent compounds

solid	liquid or gas
high mp/bp	low mp/bp
conductors	insulators

2

Carbon

- Typical final exam question: diagram an atom of carbon
- group IVA
  - 4 valence electrons
  - oxidation state ±4
  - form 4 bonds in reactions
  - tetrahedral
- C-H bond nonpolar
- C-O, C-N bonds polar
- N-H, O-H bonds

3

How Can So Many Molecules be Made From So Few Elements?

- different number of C atoms

Empirical formula- C_4H_{10} (molecular formula)

Structural formula

4

Drawing Molecules

As you can see already, drawing all these C-H bonds is tedious. We will use shortcuts most of the time (not on exam 1)

Condensed (structural) formula

Line formula

- Isomers
  - iso means: something same, something different
- Functional groups (later)

5

Drawing Molecules on Paper Does not Show the 3-Dimensional Shape

The geometry around each C atom is tetrahedral (sp^3 hybrid)

6

Hydrocarbons

Contain only carbon and hydrogen (plethora of structures).

Alkanes

Alkenes

Alkynes

7

Functional Groups

- Table 11.2
- We will learn these in greater depth as we go along, for now start learning name/structure of them

1. Alkane- first topic
2. Alkyl Halide
3. Alkene
4. Alkyne

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Alkanes

meth-	1 carbon
eth-	2 carbons
prop-	3 carbons
but-	4 carbons
pent-	5 carbons
hex-	6 carbons
hept-	7 carbons
oct-	8 carbons
non-	9 carbons
dec-	10 carbons

9

Alkanes

Only *sigma* (σ) *bonds* in molecules

General formula C_nH_{2n+2}

Molecular formula

Structural formula

Condensed formula

Isomers- same formula, different structure

functional isomers

structural isomers

10

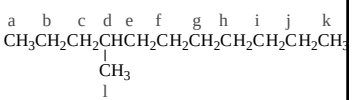
Sample Test Question (STQ)

- Tamoxifen is a molecule used in the treatment of breast cancer and has the following structure. Circle and name each functional group of the molecule.

11

Nomenclature

- Primary
- Secondary
- Tertiary
- Quaternary
- STQ: In the following molecule, list each *primary* carbon.



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IUPAC Nomenclature

1. Find the longest continuous carbon chain and use the name for the alkane with that number of carbon atoms.
2. Number the carbons in the longest continuous carbon chain from the end nearer the first R group.
3. Identify R groups by name.
4. Identify by number the carbon atom in the chain to which each substituent bonds. If the same substituent occurs more than once, identify each carbon number for that substituent, separate the numbers to commas, and use the appropriate prefix to identify how many occur in the compound.
5. Name the compound by listing the substituents preceded by a number and a hyphen, followed by the base name for the C chain. If more than one type R group, arrange in alphabetical order, ignoring prefixes except iso- and cyclo-. Connect all numbers and prefixes by hyphens.

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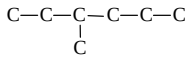
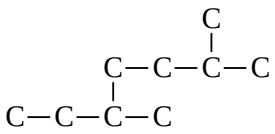
Alkane Nomenclature Examples (H's left off for speed and simplicity)



3-methylhexane

14

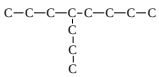
Alkane Nomenclature Examples (H's left off for speed and simplicity)



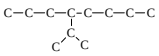
2,5-dimethylheptane

15

Alkane Nomenclature Examples (H's left off for speed and simplicity)



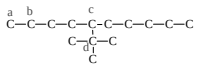
4-propylyloctane



4-isopropyloctane

16

Alkane Nomenclature Examples (H's left off for speed and simplicity)



5-t-butyldecane

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Atomic Orbitals

electron configuration of C

$1s^2,2s^2,2p^2$

We might expect C to form two bonds (the 2 unpaired p electrons)

We know that C forms 4 bonds

We might expect that CH_4 would have 1 s-s bonds and 3 s-p bonds.

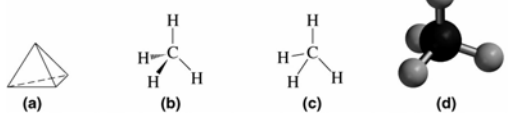
We know that all CH bonds are equivalent

18

Hybrid Atomic Orbitals

Fig. 11-3 Denniston GOB 4th Ed.

- Fig 11.3: C has 4 sp^3 hybrid orbitals
  - called sigma bonds
- pi bonds: sp^2 hybrid orbitals



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Hybrid Atomic Orbitals

Hybrid atomic orbitals is a theory used to reconcile the discrepancy between what atomic orbital theory predicts, and what is seen experimentally

hybrid	bonding	shape	rotation	bonds
sp^3	head-head	tetrahedral	free	– (single)
sp^2	sideways	triangular	rigid	= (double)
sp	sideways	linear	rigid	≡ (triple)

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Physical Properties of Alkanes

1. Nonpolar
2. Most gas or liquid, some solid.
3. Soluble in _____ solvents.
4. Not very reactive.

21

Chemical Reactions of Alkanes

1. Combustion
2. Desaturation- forms alkenes
3. Halogenation- forms alkyl halides

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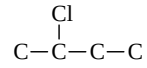
Alkyl Halides

Nomenclature

1. Chain as alkanes
2. -ine of halogen changed to –o
3. Identify attachment site

Physical Properties

1. Polar
2. Liquid instead of gas
3. Toxic, taken internally



2-chlorobutane

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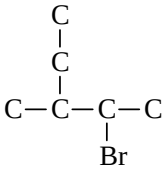
Practice Problems

Draw the structure of the following molecule, for which the correct IUPAC name is given:

2-chloro-3,3-difluorohexane.

Your friend tells you the following molecule is called 2-ethyl-3-bromobutane. What is the correct name you should give your friend?



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12.1 Alkenes: Names and Structures

Alkenes- hydrocarbons that have one or more double bonds between carbon atoms

C_nH_{2n}

Monounsaturated- one double bond

Polyunsaturated- two or more double bonds

25

Naming Alkenes

1. Find the longest continuous carbon chain that contains the double bond(s), even if it is not the longest carbon chain, and number from the end nearer the double bond.
2. Write the alkane name corresponding to the longest carbon chain, then change the *-ane* suffix to -ene.
3. Identify by number the lower-numbered carbon atom containing a double bond, followed by a hyphen directly before the alkene name; precede this by naming substituents in the usual way. If two or more double bonds occur, specify each double bond by number and use an appropriate prefix before *-ene* to indicate the number of double bonds.

26

Cis-Trans (Geometric) Isomerism

Isomer- two or more compounds with the same molecular formula but different arrangements of atoms.

Cis Trans Neither

1. R groups must be attached to different carbons
2. Larger R groups get priority

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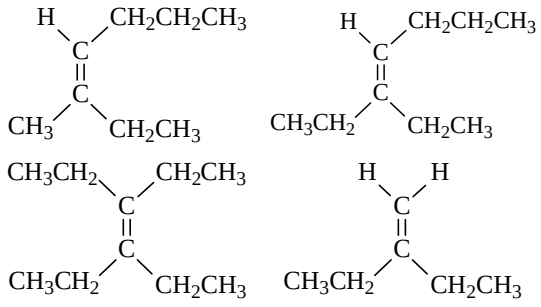
Practice Problems: Identify the following as *cis*-, *trans*-, or neither



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12.9 Alkynes: Names and Structures

Alkynes- hydrocarbons that have one or more triple bonds between carbon atoms

C_nH_{2n-2}

Named as alkenes, with the exception that *-yne* is used instead of *-ene*

29

Properties of Alkenes and Alkynes

1. nonpolar
2. less dense than alkanes
3. trend toward gas rather than liquid
4. used to make polymers

30

Reactions of Alkenes

Addition reaction- since H has been taken away to create a double bond, H or other molecules can be added across the double bond, yielding a substituted alkane.

1. catalytic hydrogenation
2. halogenation
3. addition of HCl and HBr (Markovnikonv's rule)
4. hydration (Markovnikonv's rule)
5. oxidation

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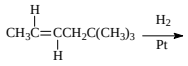
Sample Test Question

- Predict the product of the following reactions. If no reaction occurs, write “NR.” Be sure the reactions are balanced. If more than one product occurs, indicate the major product. Name the molecule(s) you arrive at as products.



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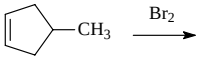
Sample Test Question

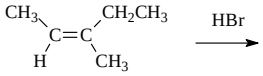
- Predict the product of the following reactions. If no reaction occurs, write “NR.” Be sure the reactions are balanced. If more than one product occurs, indicate the major product. Name the molecule(s) you arrive at as products.



33

Sample Test Question

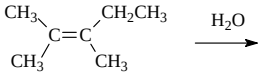
- Predict the product of the following reactions. If no reaction occurs, write “NR.” Be sure the reactions are balanced. If more than one product occurs, indicate the major product. Name the molecule(s) you arrive at as products.



34

Sample Test Question

- Predict the product of the following reactions. If no reaction occurs, write “NR.” Be sure the reactions are balanced. If more than one product occurs, indicate the major product. Name the molecule(s) you arrive at as products.



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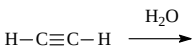
Reactions of Alkynes

Since H has been taken away to create the triple bond, just as for a double bond, the same reactions will occur for alkynes as alkenes.

The difference is, 2 moles will be added instead of 1.



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12.10 Aromatic Hydrocarbons

The aromatic compounds we will deal with are derivatives of benzene.

1. Benzene is aromatic.
2. Linked benzene rings are aromatic.
3. Substituted benzene rings are aromatic.

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What is Benzene?

- 6 carbons, each with 1 H
- alternating single and double bonds
- FLAT

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Nomenclature

1. Remember benzene, toluene, phenol, and aniline as common base names
2. o- (ortho) 1,2
   m- (meta) 1,3
   p- (para) 1,4
3. Name substituents as usual
4. phenyl group

40

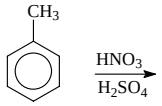
Reactions of Aromatics: Halogenation

- Difference from alkenes is that the stability of benzene makes a catalyst necessary
- Catalyst is a metal halide
- *Substitution reaction* instead of addition reaction

41

Reactions of Aromatics: Nitration

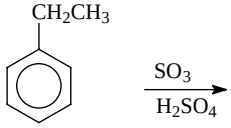
- Again a catalyst is necessary
- Nitric acid for NO_2 donor



42

Reactions of Aromatics: Sulfonation

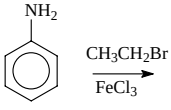
- H_2SO_4 works as catalyst for this too



43

Reactions of Aromatics: Alkylation

- Back to metal halide as catalyst
- Any alkyl halide will work



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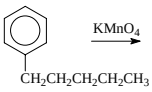
Reactions of Aromatics: Oxidation

- $KMnO_4$ very strong
- Also run in hot acid



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Alcohols

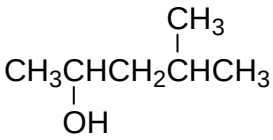
Compare this and all other functional groups to alkanes

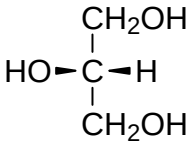
General form R-OH

46

IUPAC Nomenclature

1. Follow all the rules to determine chain base name, R groups, etc.
2. Change the final -e to -ol
3. Number from the end nearer the -OH group
4. If there are more than one -OH group, molecule is a diol (triol, etc.)





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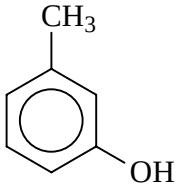
Phenols

- Talked about in aromatic section
- Phenol used as base name
- The other common name to remember is cresol



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Physical Properties of Alcohols

1. Very water soluble if small
2. High mp/bp
3. Toxic
4. H of the -OH group don't come off easily- therefore not very acidic

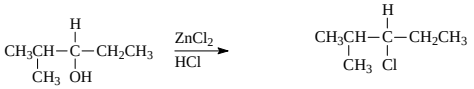
49

Chemical Properties of Alcohols

1. -OH is hard to remove
2. Three reactions
   A. Oxidation
   B. Lucas Test
   C. Dehydration- mechanism

50

Sample Test Question



- Predict the product of the above reaction.

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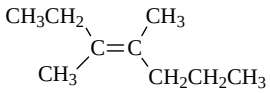
Sample Test Question

- If you want to make the following alkene, what reactant would you start with, and what reaction conditions (e.g. catalyst) would you use?



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Thiols

- R-SH instead of R-OH
- Smell bad
- oxidation to disulfides *very* important in biochemistry
- are not a major focus of the course

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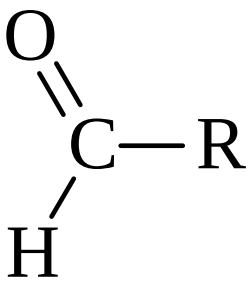
Ethers

- R-O-R
- Slightly polar (water soluble if short R groups)
- gas or liquid
- Nomenclature: name R groups alphabetically followed by ether
- don't have to know any reactions

55

Aldehydes

General form



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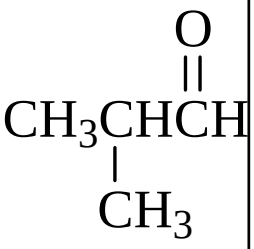
IUPAC Nomenclature

1. Follow all the rules to determine chain base name, R groups, etc.
2. Change the final -e to -al
3. Number from the aldehyde group
4. Remember benzaldehyde



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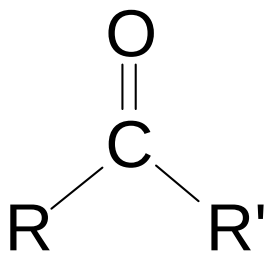
Ketones

General form



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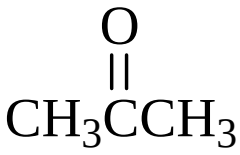
IUPAC Nomenclature

1. Follow all the rules to determine chain base name, R groups, etc.
2. Change the final -e to -one
3. Number from the end nearer the keto group
4. Remember -phenone



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The Physical Properties of Aldehydes and Ketones are Very Similar

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Chemical Properties of Aldehydes and Ketones are Very Similar

1. pi bond makes reactive
2. Oxidation Reactions- aldehydes not ketones
   A. Tollens test used to detect aldehydes
   B. Fehling's test will be used in lab
3. Addition Reactions
   A. Reduction to alcohols with a hydride
   B. Hemiacetal (hemiketal) formation

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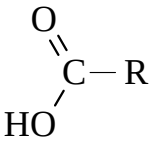
Carboxylic acids

General form



IUPAC Nomenclature

1. Follow all the rules to determine chain base name, R groups, etc.
2. Change the final *-e* to *-oic acid*
3. Number from the end nearer the acid group
4. Remember benzoic acid

62

Physical Properties of Carboxylic Acids Include Weak Acidity

Long chain fatty acids are weaker acids than short chain fatty acids.

In the acid form, fatty acids are less soluble.

The ending of the name differs depending on whether the acid group is protonated.

63

Chemical Properties of Carboxylic Acids

1. pi bond of carbonyl makes reactive
2. also have an 'alcohol group' which reacts

A. Redox Reaction

B. Acid-Base Reaction

C. Ester formation- very important to life and commercially

We will not concern ourselves acyl halides or acid anhydrides

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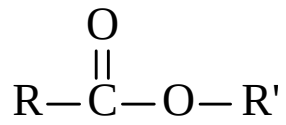
Esters

General form



IUPAC Nomenclature

1. Name the alcohol side first, ending with *-yl*
2. Name the acid side
3. End with *-anoate*

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An Important Physical Property of Esters is Fragrance

66

Chemical Properties of Esters

1. Hydrolysis
2. Saponification

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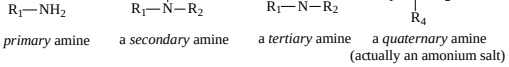
Amines

General form R–NH_2

Primary, secondary or tertiary depending on how many H are replaced with R groups



a *primary* amine — a *secondary* amine — a *tertiary* amine — a *quaternary* amine (actually an amonium salt)

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IUPAC Nomenclature - Primary Amines

1. Follow all the rules to determine chain base name, R groups, etc.
2. Consider the amine group as a substituent
3. Number from the end nearer the amine group
4. Remember aniline

69

IUPAC Nomenclature - Secondary Amines

Named similarly to ethers-

1. Name the R groups on each side
2. end with amine

70

Physical Properties of Amines

Polar, therefore water-soluble

mp/bp ~same as aldehydes (less than alcohols- can you tell me why?)

However, not the same for 1°, 2°, etc.

71

Chemical Properties of Amines

A. Acid-Base Reaction

B. Amide formation

72

Physical and Chemical Properties of Amides

Partial double bond character and *resonance structures*

Amide hydrolysis and “saponification”

73

Yea! Biochemistry is Here!