ORGANIC NOMENCLATURE

Introduction

Confusion can arise in organic chemistry because of the variety of names that have been applied to compounds; common names, trade names and systematic names are prevalent. For example, a compound of formula, C_6H_6O has variously been known as phenol, carbolic acid, phenic acid, phenyl hydroxide, hydroxybenzene, phenylic acid and oxobenzene!

To help eliminate the proliferation of many names for a compound, a systematic IUPAC naming system has been derived to uniquely name the several million organic different compounds based on considerations of their structure.

This hand-out will address the naming of simple organic compounds and is by no means complete, for instance the compound, **hexahydroazepinium-1-spiro-1'-imidazolidine-3'-spiro-1''-piperidinium dibromide** may be regarded as being too complicated for this course!

In general compounds are classified and named by consideration of:

a) the number and types of atoms that are present,
b) the bond types in the molecule, and
c) the geometry of the molecule.

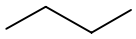
Nomenclature

As indicated previously, compounds are classified in terms of their structure and are named accordingly. The simplest classification is that of the hydrocarbons, compounds of carbon and hydrogen. Hydrocarbons are further identified as being aliphatic or aromatic (nothing to do with smell).

The aliphatics may be alkanes, alkenes or alkynes; aromatic hydrocarbons contain one or more benzene rings. It is important that students get a good grasp of the convention used in naming the simplest class, the alkanes, as the naming of other classes is an extension of alkane nomenclature.

Alkanes

- contain only C, H
- are saturated, i.e. contain only single bonds
- straight chain (normal) alkanes are named according to the number of C atoms present.
- normal alkanes form a series, a homologous series of formula C_nH_{2n+2} where n is an integer.
- these names should be memorized
- hence butane, C_4H_{10}, has the structure:



- complications set in when branching occurs. The compound below also has the formula C_4H_{10}

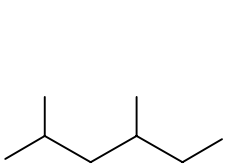
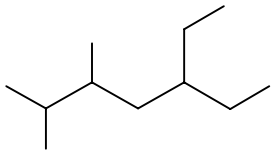
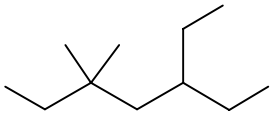
- compounds of the same formula are called isomers
- structural isomers have the same formula but different groupings branch from the main carbon chain.

Number of Carbon atoms (n)	Name
1	methane
2	ethane
3	propane
4	butane
5	pentane
6	hexane
7	heptane
8	octane
9	nonane
10	decane

Naming Alkanes

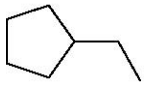
1. Name the longest continuous carbon chain in the molecule as the parent name.
2. Identify the side groups attached to this chain and place them before the parent name in alphabetical order. In general, a side group can be regarded as an alkane that is deficient in a hydrogen atom,
   alkane → alkyl group $CH_4 \rightarrow CH_3—$
   methane methyl
3. If several groups of the same kind are attached to the main chain, list the groups only once using the appropriate numerical prefix di, tri, tetra, penta, hexa, hepta, octa, nona, deca etc. to indicate how many times that side group appears.
4. Assign a number to each of the side groups to indicate where the group is attached to the main chain. Start the numbering of the main chain from whichever end of the main chain will give the lowest set of numbers. The lowest set of numbers is selected on the basis of **the lowest number at the first point of difference.**

2,4-dimethylhexane 5-ethyl-2,3-dimethylheptane 5-ethyl-3,3-dimethylheptane (**not** 3-ethyl-5,5-dimethylheptane)

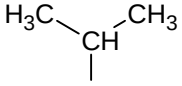
5. a) hyphens **must** separate numbers and letters
   b) commas **must** separate numbers
   c) the di, tri, tetra etc. are not included in the alphabetizing process.
   d) n, s, and t are not included in the alphabetizing process, but iso is (see next paragraph).
   e) the prefix 'cyclo' is used for cyclic alkanes.

cyclobutane ethylcyclopentane cyclohexane (not benzene)

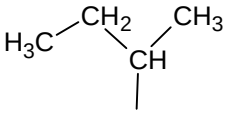




Common Side Groups

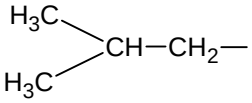
$CH_3—$ methyl $CH_3CH_2—$ ethyl $CH_3CH_2CH_2—$ propyl $CH_3\ CH_2\ CH_2CH_2—$ butyl



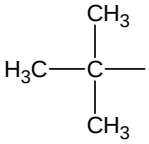
isopropyl



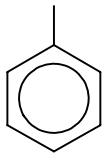
sec-butyl



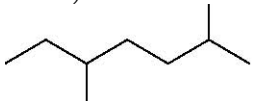
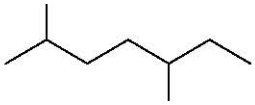
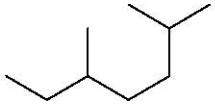
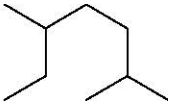
isobutyl



tert-butyl


phenyl

In identifying the longest chain in a molecule, and hence the parent name, do not be deceived by the 2-dimensional representation of the molecule. For instance, 2,5-dimethylheptane could have be drawn in the following ways (and several more).

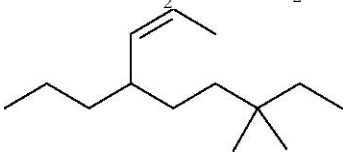





Alkenes

- hydrocarbons having at least one carbon-carbon double bond (C=C).

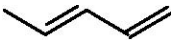
1) Select as the parent structure the longest continuous carbon chain that ontains the carbon double bond (C=C). Replace 'ane' with 'ene'.
2) Number this chain from the end that will give the C atom starting the double bond the lowest number. Prefix the name with this number.
3) Treat side-groups as for alkanes.
4) Dienes contain two double bonds, trienes have three, etc.

CH_2=CH-CH_2-CH_3 1-butene

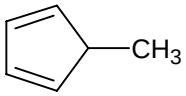


7,7-dimethyl-4-propylnon-2-ene

CH_3-CH =CH-CH_3 2-butene



1,3-pentadiene

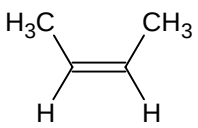


5-methylcyclopent-1,3-diene

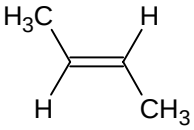
Configurational Isomerism

Structural isomerism deals with the possible different ways in which the carbon atoms are attached to each other. Configurational isomerism deals with the different arrangements in space the atoms can take in one structural isomer. This type of isomerism shows up in some alkenes and is due to the lack of free rotation about a double bond (or of the cyclic bonds in a cycloalkane).

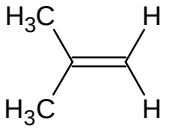
Consider the compounds:



A



B



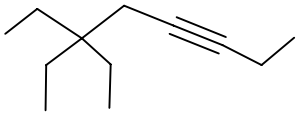
C

A and B are configurational isomers. In both A and B, the two groups attached to the carbon atom on the left side of the double bond have the same orientation in space (the methyl is up and the hydrogen is down). Now consider the two groups attached to the carbon atom on the right side of the double bond, A has a different arrangement in space than B (in A the methyl is up and in B the methyl is down). A and B are not superimposable on one another. To name the two isomers, the left side of the double bond is considered first and the two groups are prioritized based on atomic number (**the largest atomic number at the first point of difference has the highest priority**). Then the two groups on the right side of the double bond are prioritized. If the two highest priority groups (left and right side of double bond) are on the same side of the double bond (top or bottom) then the double bond has the **cis configuration** and if they are on opposite sides the **trans configuration**.
C is a different structural isomer; A and B are the same structural isomer but different configurational isomers.
These three compounds are named: A: cis-2-butene, B: trans-2-butene, C: 2-methyl-1-propene

Alkynes

- hydrocarbons having at least one carbon-carbon triple bond

1) The nomenclature and numbering is the same as alkenes, except replace 'ene' with 'yne'.
2) They do not exhibit configurational isomerism due to the linear nature of the carbon triple bond.



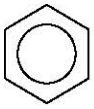
HC≡CH

ethyne (common name: acetylene)

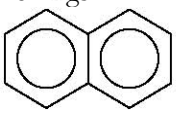
6,6-diethyl-3-octyne

Aromatic Hydrocarbons

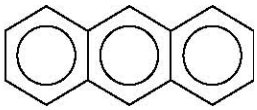
- based on the presence of benzene-like rings.



benzene

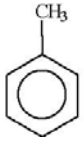


naphthalene

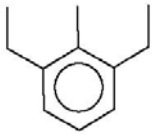


antracene

- substituents are treated as in cyclic alkanes.



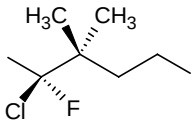
methylbenzene
(or toluene)



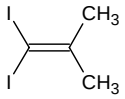
1,3-diethyl-2-methylbenzene

Alkyl halides

These are important compounds in organic synthesis reactions. For the purposes of nomenclature the halogens F, Cl, Br, I are treated as fluoro (not flouro), chloro, bromo and iodo side groups.



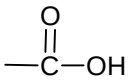
2-chloro-2-fluoro-3,3-dimethylhexane



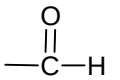
1,1-diiodo-2-methylprop-1-ene

Functional Groups

Having covered alkanes, alkenes and alkynes it is now time to consider other classes of organic compounds, in particular the common classes that contain oxygen and nitrogen. A summary of these functional groups is tabulated below.



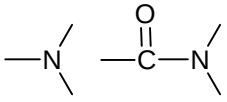
carboxylic acid



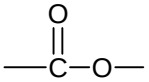
aldehyde

ketone

alcohol



amine amide



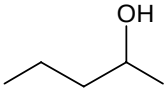
ester

ether

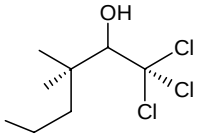
- a compound is thus classified by the presence of one or more of these functional groups.

Alcohols —OH

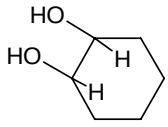
- contain the hydroxyl group (-OH) bonded to a carbon atom.
  1) Select as the parent structure the longest continuous carbon chain that contains the carbon attached to the alcohol group. Replace 'ane' with 'anol'.
  2) Number the chain from the end such that the -OH is attached to the carbon with the lowest number. Prefix the name with this number.
  3) Treat side groups as before.



pentan-2-ol



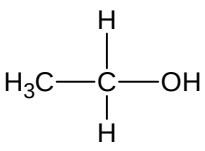
1,1,1-trichloro-3,3-dimethylhexan-2-ol



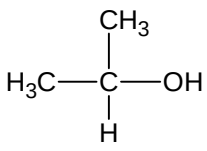
cis-1,2-cyclohexanediol

- compounds such as alcohols may be classified as being primary (1°), secondary (2°) or tertiary (3°) depending on the number of alkyl groups bonded to the carbon attached to the -OH group.

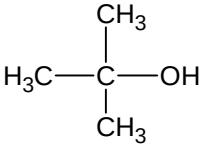
1 alkyl group → primary



2 alkyl groups → secondary

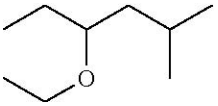


3 alkyl groups → tertiary



Ethers —O—

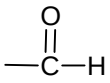
- contain an oxygen bridge (R-O-R')
- treat the shortest (R-O-) group as an alkoxy side group on the longest carbon chain



CH_3-O-CH_2-CH_3

1-methoxyethane O (common name ethyl methyl ether)

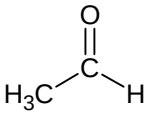
4-ethoxy-2-methylhexane

Aldehydes 

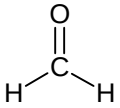
- contain a carbonyl group at the end of a carbon chain

1) Select as the parent structure the longest continuous carbon chain containing the terminal aldehyde group. Replace 'ane' with 'anal'
2) Number the chain such that the aldehyde carbon is atom number one.
3) Treat side groups as before.

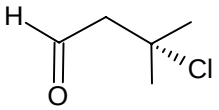
** The number '1' for the 'al' group need not be included in the name.



ethanal



methanal

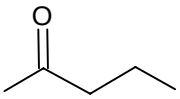


3-chloro-3-methylbutanal(formaldehyde)

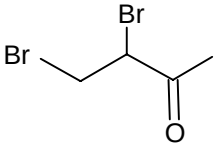
Ketones 

- contain a non-terminal carbonyl group

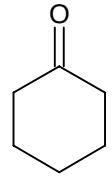
1) Select as the parent structure the longest continuous carbon chain containing the carbonyl group carbon atom. Replace 'ane' with 'anone'
2) Number the chain such that the carbonyl carbon has the lowest number. Prefix the name with this number.
3) Treat side groups as before.



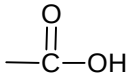
2-pentanone



3,4-dibromobutan-2-one



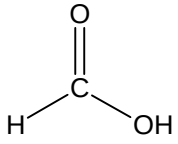
cyclohexanone

Carboxylic acids 

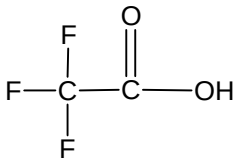
- contain the carboxylic acid group

1) Select as the parent structure the longest continuous carbon chain containing the carboxylic acid group. Replace 'ane' with 'anoic acid'
2) Number the chain such that the carboxylic acid carbon is atom number one.
3) Treat side groups as before.

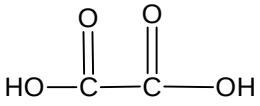
** The number '1' for the acid group need not be included in the name.



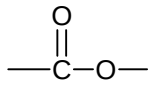
methanoic acid (formic acid)



2,2,2-trifluoroethanoic acid

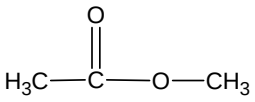


1,2-ethanedioic acid (oxalic acid)

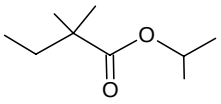
Esters 

- may be regarded as a carboxylic acid derivative
- contain R and R' being alkyl or aryl (benzene-like) groups

1) Locate the carboxylic acid portion of the molecule and name as the parent carboxylic acid. Replace 'anoic acid' with 'oate'. Name the rest of the molecule (alcohol portion) as a radical, placed in front of the parent name (not a prefix).
2) Carbon atom number '1' is the ester carbonyl.



methyl ethanoate



isopropyl 2,2-dimethylbutanoate

Amines 

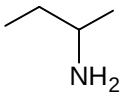
- contain nitrogen attached to sp^3 carbon atoms
- I.U.P.A.C. nomenclature is still in a state of flux (alias confusion)

1) Primary Amines Simple primary amines are named either by

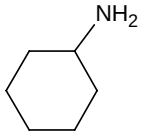
a) adding the suffix amine to the name of the alkyl group bonded to the nitrogen atom of the amine. The name of the amine in written as one word.

b) or by replacing the final e of the IUPAC name of the parent alkane with amine.

isopropylamine
2-methyl-2-ethanamine



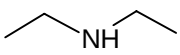
2-butylamine
2-butanamine



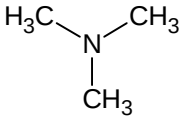
cyclohexylamine
cyclohexanamine

2) Secondary and Tertiary Amines

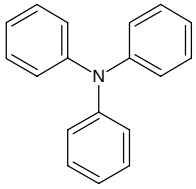
a) **Symmetrical secondary and tertiary amines** are named by adding the prefix di or tri to the name of the alkyl group.



diethylamine

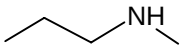


trimethylamine

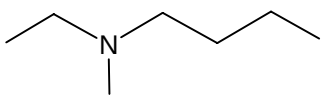


triphenylamine

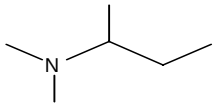
b) **Unsymmetrically substituted secondary and tertiary amines** are named as N-substituted primary amines. The largest of the alkyl substituents is chosen as the parent chain. The use of the letter N indicates that the alkyl groups are attached to the nitrogen atom and not to a carbon atom of the parent alkyl chain. The names of the alkyl groups bonded to the nitrogen atom are listed alphabetically.



N-methylpropan-1-amine

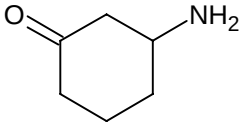


N-ethyl-N-methylbutan-1-amine

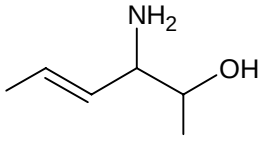


N,N-dimethylbutan-2-amine

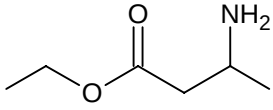
c) The –NH2 group whose structures are more complicated is called an amino group and is treated as any other substituents.



3-aminocyclohexanone

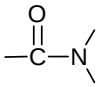


(4-trans)-3-aminohex-4-en-2-ol

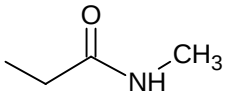


ethyl 3-aminobutanoate

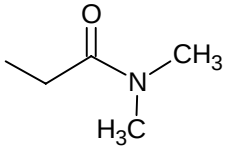
Amides



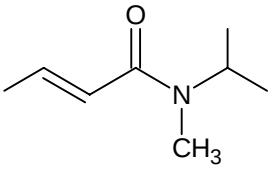
- contain the group
- named like esters, treat as a carboxylic acid derivative and use 'amide' ending (instead of oic acid). Name the amine portion of the molecule as a radical placed in front of the parent name (same as the alcohol portion in esters). There is no space between the alkyl group attached to the nitrogen and the parent name. The N-alkyl groups are listed alphabetically



N-methylpropanamide



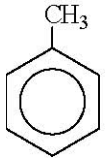
N,N-dimethylpropanamide



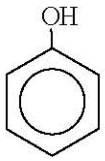
(2-trans)-N-isopropyl-N-methylbut-2-enamide

Aromatics

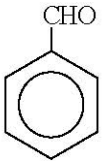
- the various functional groups that we have encountered may also be present in aromatic compounds. In many instances common names are still used.



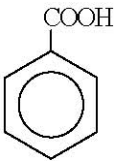
toluene



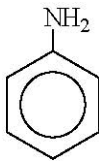
phenol



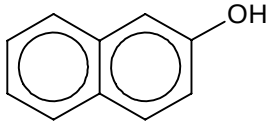
benzaldehyde



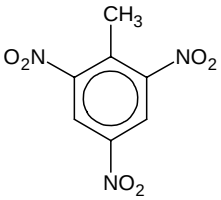
benzoic acid



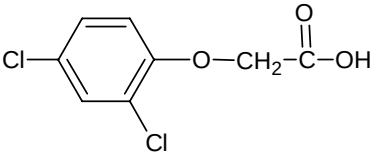
aniline



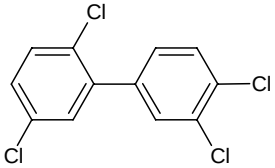
2-naphthol



2,4,6-trinitrotoluene
(T.N.T.)



2,4-dichlorophenoxyacetic acid
(2,4-D)



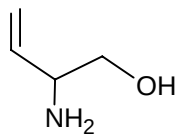
a polychlorinated biphenyl
(PCB)

Compounds with more than one functional group.

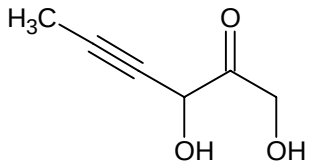
Compounds of this type are classified by the principle group (the main functional group) that is highest on the following hierarchy scale. The parent name is derived from the principle group.

carboxylic acid > aldehyde > ketone > alcohol > amine > alkyne = alkene > alkane

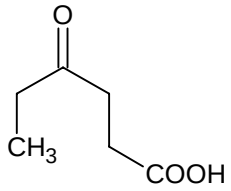
- A compound containing an alcohol and an aldehyde functional group is named as an aldehyde with an alcohol side group.
- A compound containing an alcohol, ketone and an acid is named as an acid with alcohol and ketone side groups.
- The numbering system is that for the principle group.
- An alcohol is regarded as a hydroxy-side group, an amine as an amino-side group and a carbonyl as an oxo-side group.



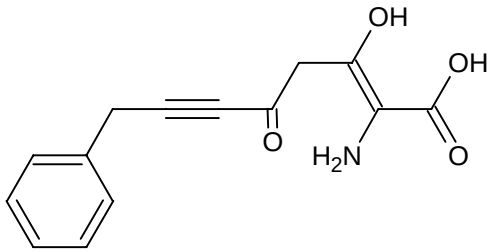
2-amino-3-buten-1-ol



1,3-dihydroxypent-4-yn-2-one



4-oxohexanoic acid

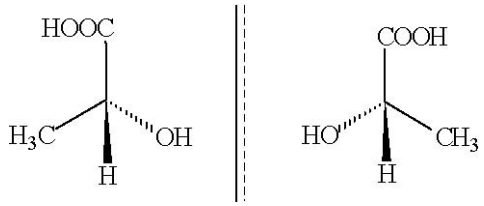


(2-trans)-2-amino-3-hydroxy-5-oxo-8-phenyloct-2-en-6-ynoic acid

Configurational Isomerism revisited - optical isomerism

An sp^3 carbon atom that is asymmetric, that is a carbon atom bonded to four different groups, shows two different ways of arranging the four groups in space and hence displays configurational isomerism.

- Such carbon atoms are called chiral.
- In compounds of this type, the molecule and its mirror image (isomer) are non-superimposable.
- As an analogy, your right hand when viewed in a mirror becomes a left hand. Your two hands are not superimposable on each other (at least when both palms are facing up). Each hand is chiral.



An isomer of this type is found to twist a beam of monochromatic polarized light either to the right or left, the other isomer twisting the light in the opposite direction. The Latin names being 'dextro' (to the right) and 'laevo' (to the left), were originally applied to these compounds. i.e., d-lactic acid and l-lactic acid.