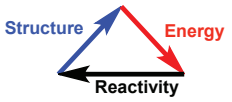


Functional Groups and an Introduction to Nomenclature

"Methane by any other name would still be tetrahedral."
– RTP

3-1. Introduction:

As you might guess from the quote above, I am not fascinated by nomenclature. However, that said, I also realize that we still need to be able to communicate structural information about a molecule, in whole or in part, without having to use some type of graphic representation for that molecule. We'll begin this this learning unit by first examining some commonly encountered types of functional groups, and also some general structural motifs that frequently occur in Organic Chemistry. This will be followed by an introduction into the basics of nomenclature for organic molecules.

3-2. What will be presented:

1. The concept of a functional group will be introduced and defined.

2. Those functional groups of particular importance to Organic Chemistry will be introduced and named.

3. Different types of carbon skeletons will be identified.

4. Types of carbon centers observed in organic molecules also will be defined and named.

5. Types of unsaturation will be identified (e.g. alkenes and alkynes) described and named.

6. A general approach to the nomenclature of Organic Compounds will be presented.

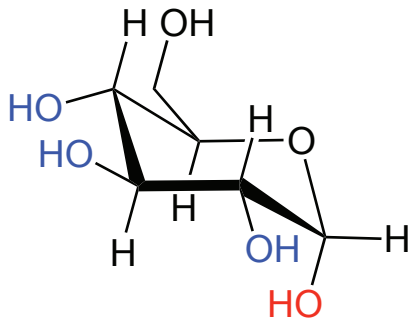
3-3. A General Approach for Construction of Organic Molecules:

Constructing and interpreting complex molecules often involves partitioning a molecule into its *Skeleton (R)* and *Functional Group (FG)* components. For example, consider a simple monofunctional molecule, e.g. R-FG:

Figure 3-1. Structural components of a monofonctional molecule:

R typically is a carbon-based skeleton or molecular platform onto which one or more functional groups like FG is/are attached. This carbon skeleton does not have to be either chemically or physically inert. However, these attached carbon-based skeletons often attenuate or modulate the chemical and physical properties created by the attachment of a functional group like FG.

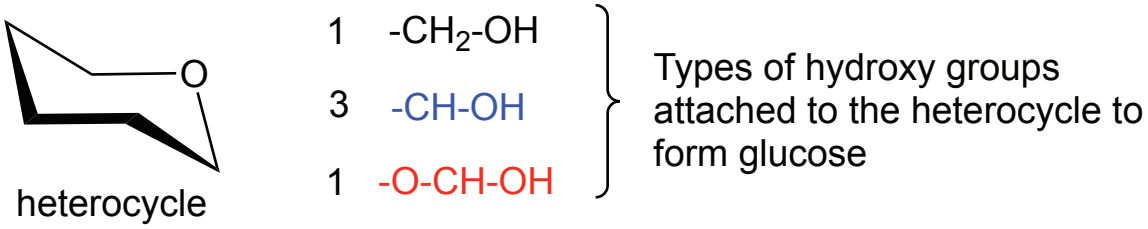
Molecules also can be polyfunctional. Molecules are polyfunctional when they have two or even more functional groups (e.g. FG_1 and FG_2) attached onto a skeleton (R). An important example of a polyfunctional molecule is the carbohydrate glucose (3-1). This biologically important molecule has the structure shown below:



3-1

Glucose is constructed from a six membered heterocyclic ring containing an oxygen atom with five attached hydroxyl groups of three different types:

Figure 3-2. Different structural components of a glucose molecule:



What is a functional group?
A functional group (-FG) is a sub-molecular fragment or even atom, other than H, that displays a characteristic set of chemical, physical, and spectral properties when attached to a carbon skeleton. A functional group like -FG usually determines the essential or primary chemical properties associated with an FG-R molecule containing that type of functional group (FG). Finally, FG groups are usually the source of a functional group or family name for a molecule [e.g. Generic FG family names include alcohols for an –OH group, or amines for $-NR_2$), halides (-Br, -Cl, -F), and nitro [$-NO_2$] groups.

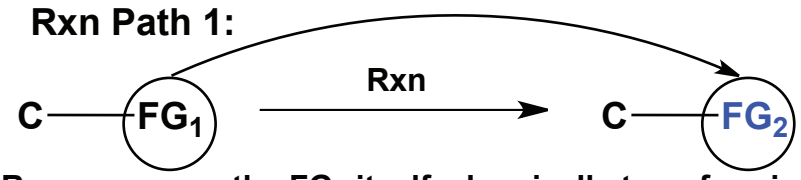
Thus each functional group (FG) has its own unique electronic geometry that imparts both chemical and physical properties onto its attached R-FG molecular platform. Thus, no matter where in the Universe we encounter this functional group, say on a new R'-FG, we expect this new R'-FG to possess chemical and physical properties similar to R-FG. If this new R'-FG doesn't behave as expected, then we'll want to know why it doesn't.

Organizing the study of Organic Chemistry around molecules that share a similar functionality (-FG) offers an efficient way to examine both the chemical and physical properties associated with that type of functional group (-FG). This is the primary reason for the traditional approach to both the organization and presentation of Organic Chemistry. For the reader, functional groups provide a practical way to both organize and also retrieve large amounts of chemically related information.

Although a functional group modifies the properties of a skeleton, the point of attachment of a functional group onto a skeleton (R) often also affects both chemical reactivity and physical properties of its attached functional group (FG). The chemical impact of a skeleton (R) not only involves its size, but also its shape and stereochemistry around its point of attachment to a functional group (FG). The skeleton is the yin to a functional group's yang.

Functional groups (FG) undergo two basic types of chemical transformations. One type of reaction directly transforms a reactant's "old" functional group (FG_1) into another "new" product functional group (FG_2). A second type of transformation attacks a reactant's "old" R-FG_1 bond and replaces or substitutes the entire "old" functional group (C-FG_1) by a new functional group (C-FG_2):

Figure 3-3. Typical chemistry of functional groups (FG):

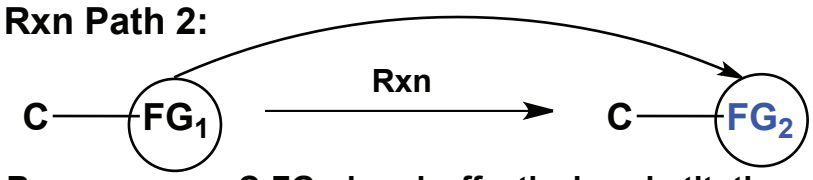


Rxn occurs on the FG_1 itself, chemically transforming FG_1 into a new FG_2.

Example:

$$CH_3 - NO_2 \longrightarrow CH_3 - NH_2$$

Bond between C and N remains intact



Rxn occurs on C-FG_1 bond, effectively substituting a new functional group (i.e.) FG_2 for the "old" FG_1 .

Example:

$$CH_3 - Br \xrightarrow{Na^+ {}^-CN} CH_3 - CN + Na^+ {}^-Br$$

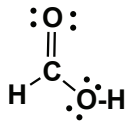
Bond between C and Br is broken and replaced by a C-C bond

As a more practical commercial matter, we also may have certain desired features that we want in a target molecule. These features may be physical properties (mp, bp, or solubility) or they also may be a desired chemical reactivity or perhaps even a lack of reactivity. Material scientists typically begin a design of their target molecules by first considering whether the desired properties can be generated by one or more of these different types of functional groups.

Typical functional groups presented in most introductory studies of organic chemistry are shown below in Table 3-1:

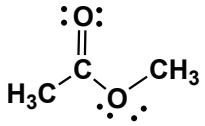
Table 3-1. Common Functional groups (-FG) are:

Carboxylic acids



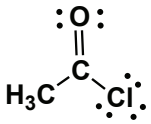
methanoic acid
"formic acid"

Ester



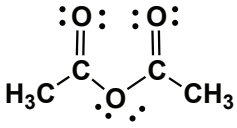
methyl acetate

Acid Chloride



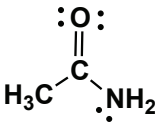
ethanoyl chloride

Anhydride



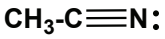
ethanoic anhydride
"acetic anhydride"

Amides



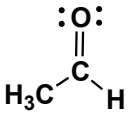
acetamide

Nitriles



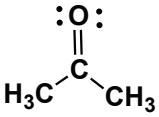
acetonitrile

Aldehydes



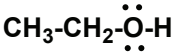
ethanal
"acetylaldehyde"

Ketones



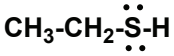
2-propanone
"acetone"

Alcohols



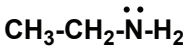
ethanol

Thiols



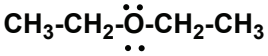
ethanethiol

Amines



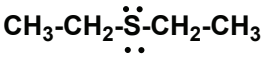
ethylamine

Ethers



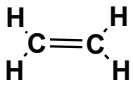
ethoxyethane
"diethyl ether"

Thioethers



1,1-thiobisethane
"ethylsulfide"
"diethyl thioether"

Alkenes

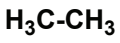


ethene
"ethylene"

Alkynes

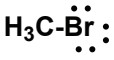
ethyne
"acetylene"

Alkanes



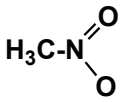
ethane

Haloalkanes



bromomethane
"methyl bromide"

Nitro alkanes



nitromethane

Nitroso alkanes

nitrosomethane

In Table 3-2 these same common functional groups are reorganized by their valences. Some of these functional groups can connect two or even more carbon skeletons, while monovalent groups can either be attached to a carbon skeleton or terminate a chain just like the tail on a rat.

Table 3-2. Valences of common Functional Groups (-FG):

Monovalent R-FG	Divalent R-FG-R^1	Trivalent R^2 R-FG-R^1	Tetravalent R^2 R-FG-R^1 R^3
-X (-F,-Cl,-Br,-I)	-O-	-C(O)-N<	>C=C<
-C(O)-Z ; Z = -OH, -X	-S-	-N<	
-C≡N	-C≡C-		
-NO_2	-C(O)-		
	-C(O)-O-		
	-SO_2-O-		

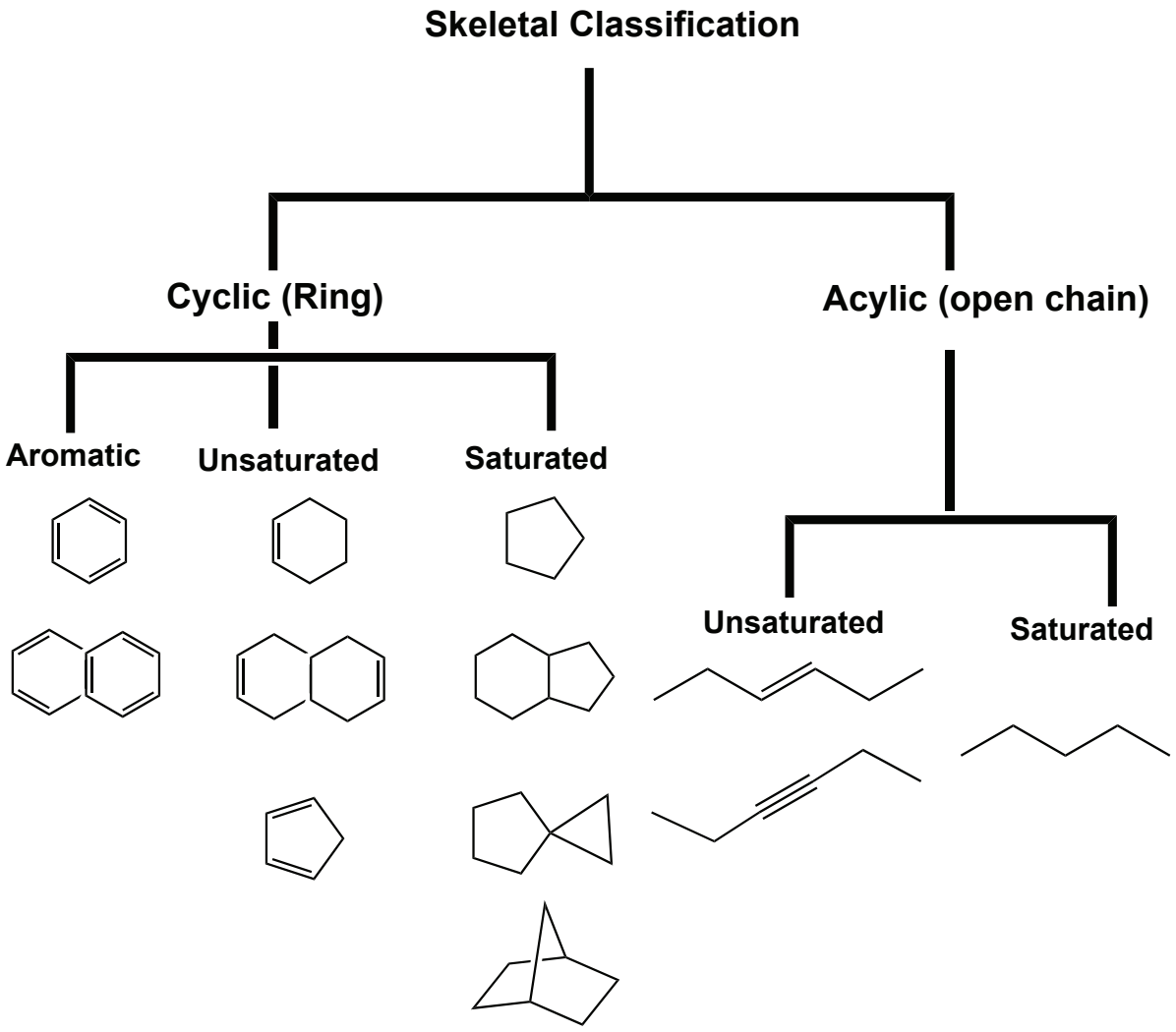
By coupling carbon skeletons (R) to functional groups (FG) one can create an enormous variety of different organic molecules (R-FG_n) containing one or even more of these different functional groups with a variety of skeleton combinations.

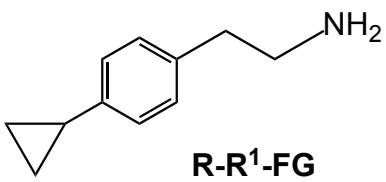
3-4. Generic skeletal motifs (R-) attached to functional groups:

So, what types of carbon skeletons are available to form bonds to different types of FG? One of the more remarkable features of carbon is that C-C covalent bonds can be formed in an almost unlimited variety to other carbon atoms (i.e. technically referred to as catenation). Those carbon-based skeletons also can contain a variety of electronic geometries for their constituent carbon components. Even this almost infinite variety of carbon skeletons or platforms can be organized. Many of those types of carbon skeletons most likely to be encountered in our discussion of Organic Chemistry are shown below in Table 3-4:

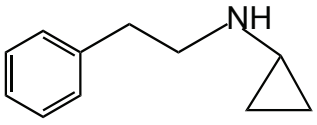
Figure 3-4. Types of hydrocarbon based skeletons or motifs found in Organic Chemistry:

Scheme 1: Skeleton Classifications:





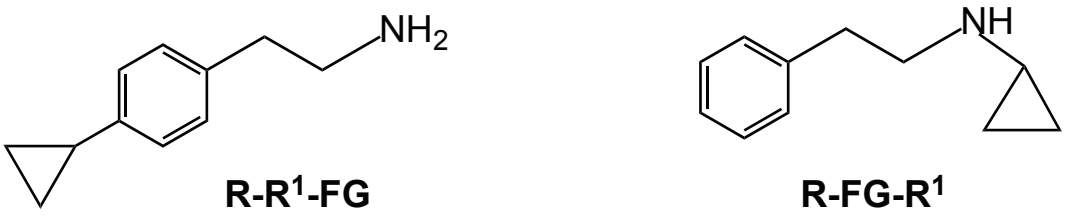
R-R^1-FG



R-FG-R^1

Although this skeletal classification shown in Figure 3-4 is essentially complete, it also is a huge over simplification of what types of skeletal structures are possible. There are numerous examples of complex structures containing several of these skeletal motifs coupled-up within a single molecular structure. For example, suppose I want a molecule that consists of a saturated ring, an aromatic ring that also contains an amine group. Just two of many possible examples of such structures that fulfill these general requirements can be easily constructed and are shown in Figure 3-5:

Figure 3-5. Constructing complex molecules from common functional group and skeletal motifs:



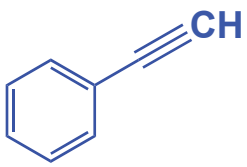
Constructing complex structures is achieved by simply coupling-up these carbon skeletal motifs along with any desired functional groups. For example, one can expand upon a carbon skeleton by creating a molecule using an R-R^1-FG type of motif or, as in this Fig. 3-5 example, one also can use a divalent or trivalent amine functional group to couple up these different carbon motifs to form an R-FG-R^1 type of structures.

Q: Draw a specific example of a molecule (i.e. R-FG) that contains those specific functional groups requested in each question:

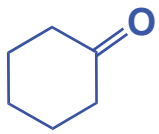
a) Draw a molecule that contains a saturated acyclic (i.e. chain) type of skeleton bonded to a chlorine atom:
An acceptable answer could look like this:

CH_3-CH_2-CH_2-Cl

b) Draw an aromatic benzene skeleton that is bonded to an alkyne group:
An acceptable answer could look like this:



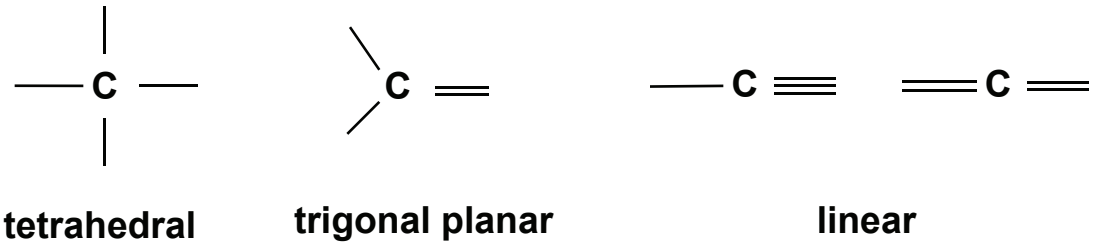
c) Draw a saturated ring that also contains a ketone:
An acceptable answer could look like this:



3-5. Types of Electronic Geometries for Carbon atoms:

Frequently, chemists will refer to types of carbon atoms based on their electronic geometry and also by their degrees of substitution. Several commonly encountered types of electronic geometries for carbon are shown below in Figure 3-6:

Figure 3-6. Important electronic geometries for various types of carbon atoms:

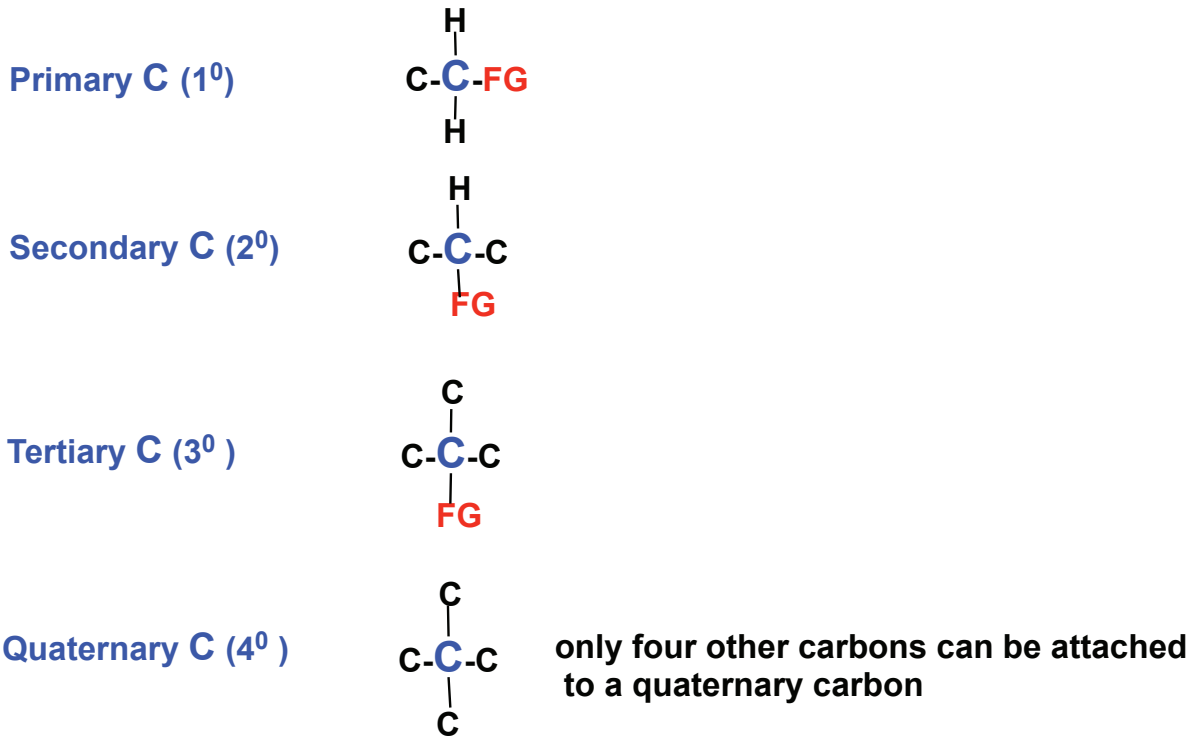


Notice that all of these different electronic geometries for a carbon have a formal charge on carbon equal to zero (i.e. FC(C) = 0), but each type of carbon has both a different electronic geometry and molecular shape.

3-6. Types of Tetrahedral Carbon Centers:

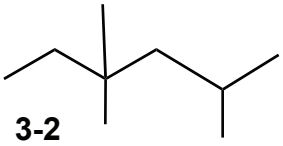
In addition to identifying the electronic geometry of carbon atoms, chemists also will refer to specific types of structural features within a carbon skeleton (R). One of the more important structural features concerns the carbon connectivity between different types of tetrahedral carbon centers:

Figure 3-7. Types of tetrahedral carbons (C) found in carbon-based skeletons:



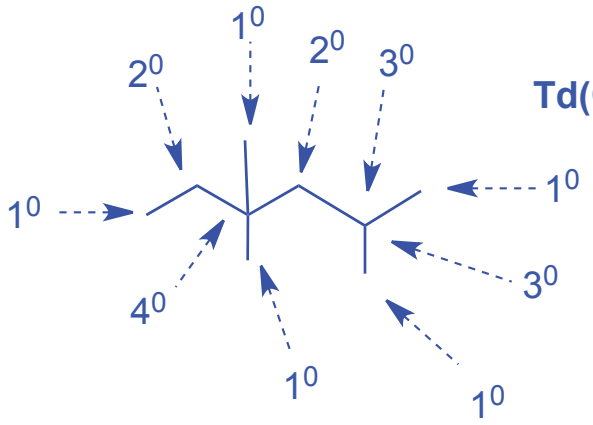
Notice that one can determine the type of carbon (1° , 2° , 3° , 4°) by simply counting the number of carbons attached to a selected carbon center (C).

For example, consider structure **3-2:**



3-2

Q: Identify the number and type of carbon atoms within this 3-2 structure



Td(C) type and number

5 x 1^0

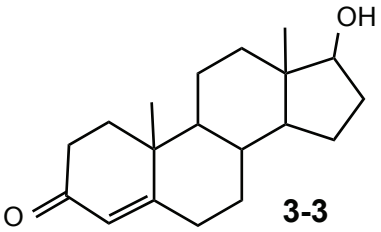
2 x 2^0

1 x 3^0

1 x 4^0

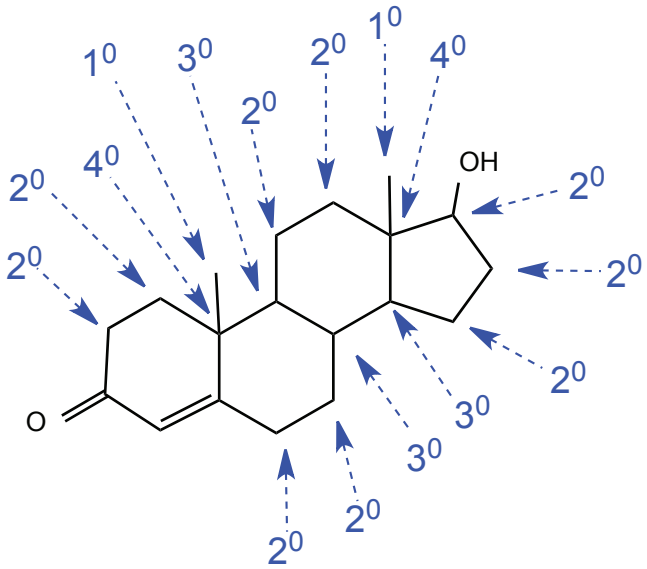
9 Td Catoms

Q: Consider the skeletal representation (3-3) for hormone testosterone:



3-3

Q: Identify the all the types of tetrahedral carbon atoms within this molecule of testosterone:



Td(C) type and number

2 x 1^0

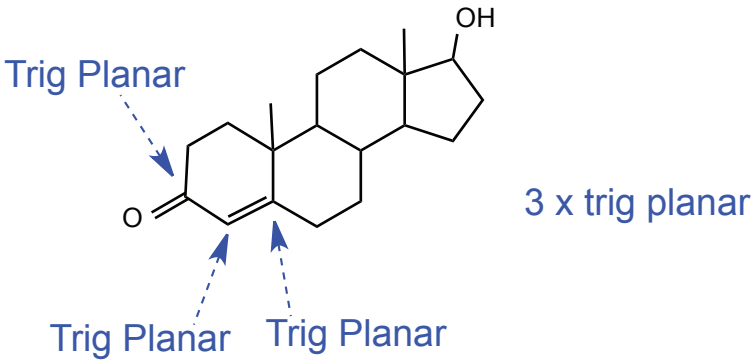
9 x 2^0

3 x 3^0

2 x 4^0

16 Td Catoms

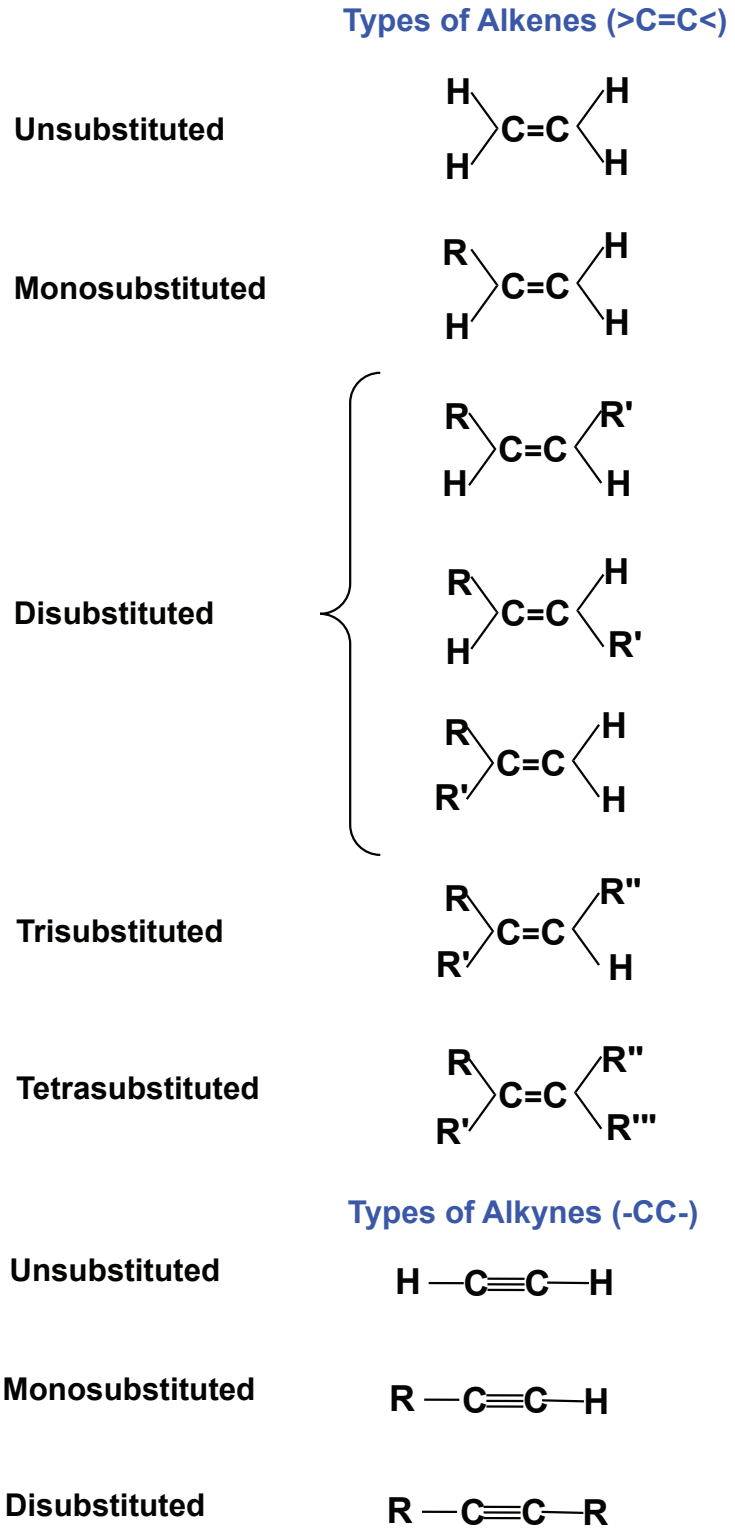
Q: For the testosterone structure above also determine the number of trigonal planar carbons:



3-7. Types of C-C unsaturation (i.e. Alkenes and Alkynes):

Alkenes and alkynes are important functional groups for Organic Chemistry. Chemists often differentiate types of alkenes by the number of carbons attached to an alkene's trigonal planar carbon atoms or to an alkyne's linear carbon atoms:

Table 3-3. Carbon-based functional groups containing π-bonds between two carbon atoms:



As we examine the chemistry of these unsaturated compounds in more detail, we also will learn that that both the number and types of substituents (R) on these unsaturated structural units affects their chemical reactivity.

3-8. Polyunsaturation Structural Motifs:

For carbon-carbon unsaturation there also are several combined structural forms or *motifs* that can occur within polyunsaturated molecules (i.e. molecules with two or more units of unsaturation). Dienes are carbon skeletons containing two alkene (i.e. C=C) groups). Common diene structural motifs or types include conjugated, cumulated, or isolated dienes:

Figure 3-8. Types of polyunsaturated alkene motifs:

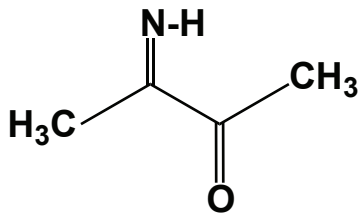
Conjugated	Cumulated	Isolated
$H_2C=CH-CH=CH_2$	$H_2C=C=CH_2$	$H_2C=CH-CH_2-CH=CH_2$
adjacent unsaturation	unsaturation connected to a shared atom	unsaturation separated by at least one Td carbon atom

A conjugative motif is not limited to just alkenes, or by extension, to alkyne functional groups. Conjugated structures (i.e. structures with adjacent functional groups) can be found between other types of functional groups in addition to just unsaturated carbon groups:

Figure 3-9. Examples of both carbon and non-carbon forms of conjugation:

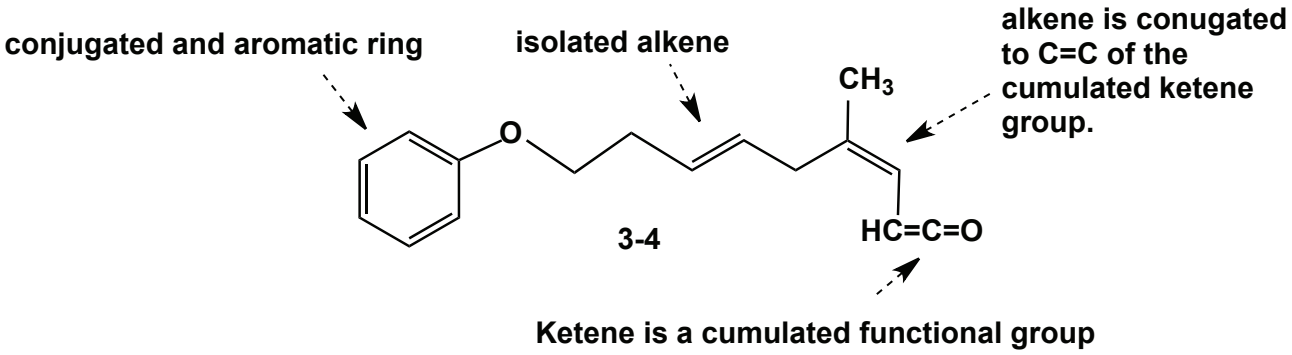
$H_2C=CH-CH=CH-C=O-R$

2 alkenes adjacent to each other and also to this -CO keto group



Imine (C=N-) and ketone -C(O)-

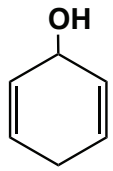
Below is an example that combines several types of these unsaturated groups into a single polyfunctional polyfunctional molecule like structure **3-4.** Arrows are used to identify the unsaturation motif(s) present in this example:



3-4

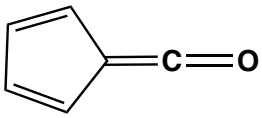
Cumulenes, like the ketene FG in structure **3-4,** are interesting because this type of alkene π-bond is perpendicular to its carbonyl (C=O) π-bond. As a result these two π-bonds do not conjugate (i.e. overlap) with each other. Thus these types of cumulated π-bonds are more or less isolated from each other even though they share a carbon atom and might appear to be bonded to each other.

Q: Specifically identify and then name the types of unsaturation motif(s) present in the following molecules:



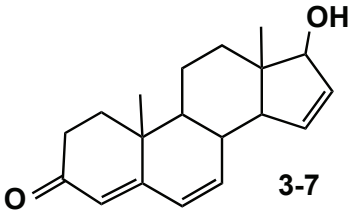
isolated alkenes

3-5



conjugated alkenes;
C=O of ketene is isolated

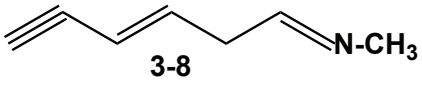
3-6



isolated alkene

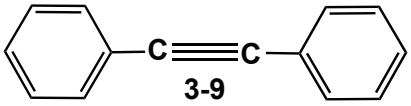
3-7

conjugated C=C AND C=O (ketone)



3-8

conjugated C=C AND -CC- but isolated from C=N- (imine)



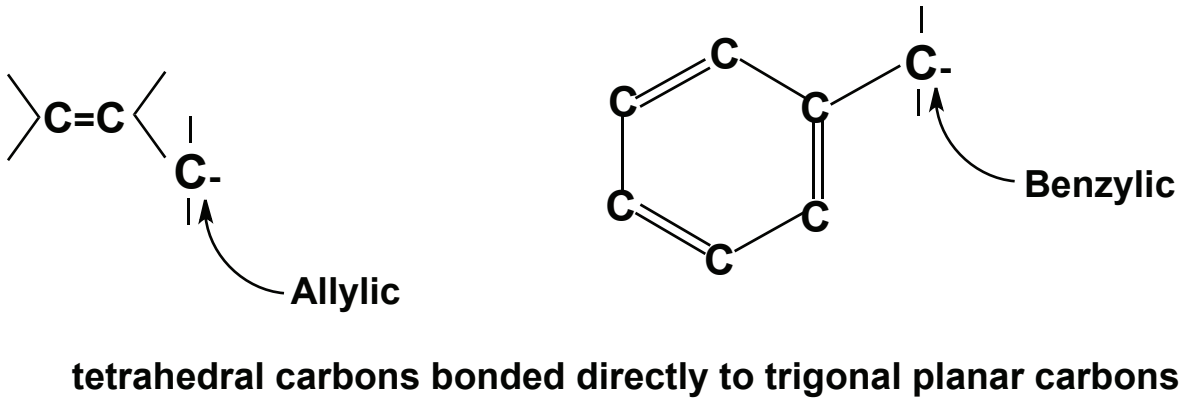
3-9

-CC- conjugated to both conjugated aromatic benzene rings

3-9. Tetrahedral carbon attachments adjacent to unsaturated skeletons:

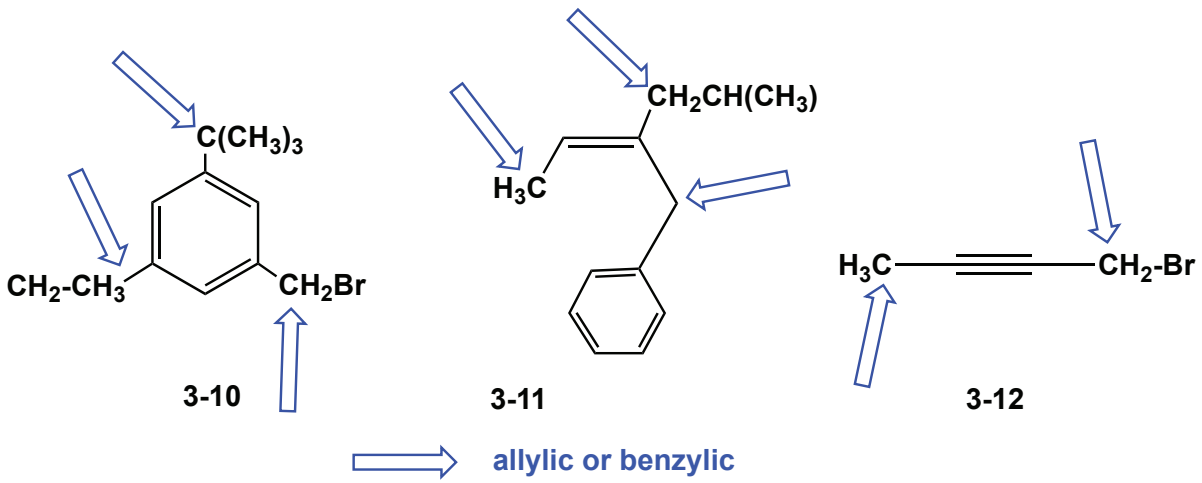
Tetrahedral (saturated) carbon atoms attached directly to unsaturated skeletons exhibit special chemical properties. These positions are identified as allylic if a saturated carbon is bonded to an alkene, and benzylic if the tetrahedral carbon is attached to an aromatic skeleton.

Figure 3-10. Allylic and benzylic types of tetrahedral carbons:



These allylic or benzylic carbons also may be of the 1^0, 2^0, 3^0 types. All of these allylic or benzylic carbons carbons must be tetrahedral in their electronic geometries. It also is possible to have more than one allylic or benzylic carbon adjacent in an unsaturated carbon group:

Figure 3-11. Multiple allylic and benzylic carbons on a single unsaturated molecule:



3-10. Introduction to the basics of Organic Nomenclature:

From the web:

$NaC_2H_3O_2$

Sodium X Acetate

Nacho.....

I apologize, but I also will say in my defense that there is not a lot of humor to be found in the subject of nomenclature.

So far structural features and functional groups along with some generic names for functional groups have been identified. Such terms are used, along with common names for many types of molecules, typically in conversation, and especially when we have a given molecular structure in front of us. However a formal system of naming organic molecules is necessary to both store and retrieve complete structural information about a given molecule that is independent of a graphical molecular representation. This formal naming system is referred to as nomenclature and was codified through the International Union of Pure and Applied Chemistry (IUPAC) and agreed to by most chemists and especially the journals that publish chemical research. A proper name for a molecule should permit a knowledgeable reader, like you or even me, to unambiguously construct a suitable graphical representation for that molecule with both the correct connectivity and stereochemistry. In theory, going from a name to a structure should be the easier problem, but to do this you'll need to have some general idea about how structures are named.

Basic Nomenclature Rules and Syntax:
For this introduction to nomenclature, a proper name for a structure has been broken down into four parts that when joined together, in a correct order, will provide a proper name:

Position number or locant: This refers to the position or location on a structure where this particular type of substituent (i.e. FG) is located.
Prefix: This part of a name identifies specific FG[1] type and also how many of these FG there are in our particular structure (e.g. dichloro, trimethyl, tetranitro, etc.).
Parent: This is the basic carbon platform or skeleton onto which these FG are attached. As noted in Fig. 3-4, this skeleton is either a ring or chain onto which these substituents (i.e. –FG) and, its highest priority group (i.e. PFG) are attached (i.e. our **R**- skeleton).
Suffix: This is the part of a name that identifies the highest priority group or primary functional group (**PFG**). **Identification of a PFG also determines the family name** for that structure. **Location of a PFG** within our structure **also will determine the parent skeleton.** For a simple structure, one puts all of these pieces together **in order to generate a proper name for that structure:**

(Locant + Prefix) + Parent + Suffix.

Parsing a more complicated polyfunctional molecule containing say three different substituents (A,B,C) and also a PFG will look something like this:

$$\textbf{(Locant + Prefix)}_{A} + \textbf{(Locant + Prefix)}_{B} + \textbf{(Locant + Prefix)}_{C} + \textbf{Parent} + \textbf{(Suffix)}_{D}\ .$$

An organic molecule is named as a member of a particular functional group or family formally identifed by a suffix attached to its platform name. For polyfunctional molecules, one particular functional group attached to a given carbon skeleton (i.e. parent) often will have priority over all of the other functional groups within that molecule and that #1 priority functional group (i.e. PFG) will form the family or group name for that structure and often determine the parent carbon skeleton (R) for that structure.

Quick Summary:
Identification of a PFG will determine the suffix for any **R-** skeleton onto which the PFG is attached. A proper name for **a structure has only one type of suffix.** The limitation of one suffix does not mean that one cannot have multiple PFG, such as 1,3-pentanedione (e.g. has two C=O groups), or cyclopropan-1,2,3-trioic acid (e.g. has three –CO2H groups). Any other functional groups **will become prefix parts of the name** for that structure. There also are several other types of FG that belong to the 2nd tier of names. These 2nd tier groups only have prefix names because they never can become a PFG (i.e. become a family name). Several common 2nd tier functional groups also are shown in the red section at the bottom of Table 3-4:

Table 3-4. Priority of common functional groups found in alphatic derivatives:

Priority & Group		Functional group	if Priority group (PFG), then suffix	prefix If not priority group
1	-CO-OH	Carboxylic acid	-oic	carboxy
2	-CO-OR	Ester	-oate	alkoxycarbonyl
3	-CO-X	Acyl halide	-oyl halide	haloformyl
4	$-CO-NH_2$	Amide	-amide[1]	amidol
5	-CHO	Aldehyde	-al	formal
6	-CN	Nitrile	-nitrile[2]	cyano
7	R^1R^2CO	Ketone	-one	oxo
8	-OH	Alcohol	-ol	hydroxyl
9	$-NH_2$	Amine	-amine	amino
10	C=C	Alkene	-ene	-enyl
11	-CC-	Alkyne	-yne	-ynyl
12	$-CH_2-CH_2-$	Alkane	-ane	-yl
13	C-O-C	Ether[3]	**none**	alkoxy
14	-X and $-NO_2$	Halide[3,4], Nitro[3]	**none**	nitro

1) also known as carboxamide 2) also known as carbonitrile

3) Never used as a suffix in a name, only as a prefix: Ether prefix is alkoxy; halide prefix is halo e.g. bromo; Nitro prefix is nitro-

4) for the halogens become halo: fluoro, chloro, bromo, iodo,

****Of these two broad categories of functional groups, only those 1st tier functional groups may become become a primary functional group (i.e. PFG) and thus a suffix to a parent chain or ring. Those 2nd tier groups can only become prefixes.**

After identifying a PFG, the next step is to determine whether that priority group is part of an alicyclic chain, a ring, or an aromatic skeleton. To begin this discussion let's first considering proper names for just carbon chains of different lengths and then show how to name rings of carbon atoms.

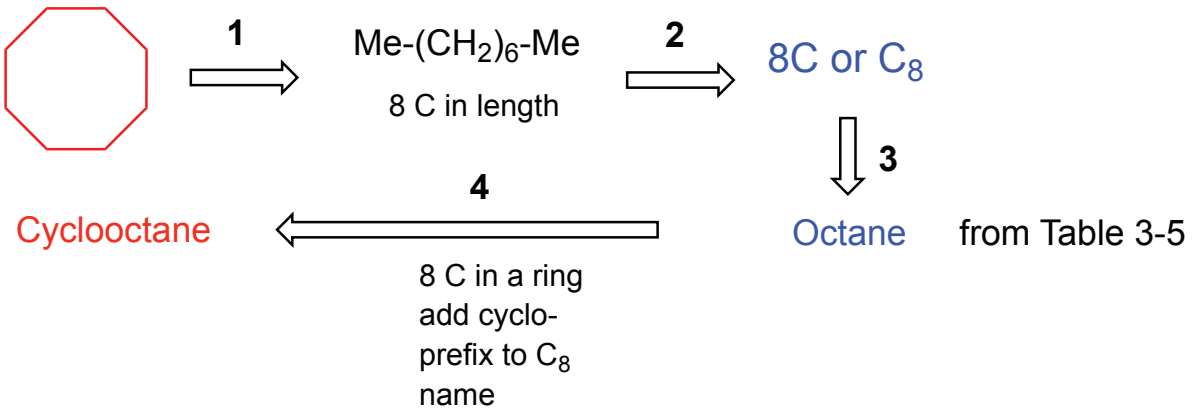
Proper IUPAC names for various lengths of carbon chains are collected below. This is only a partial list of chain names. You should know, from memory, the names of carbon chains from 1 to 10 carbon atoms in length.

Table 3-5. Proper IUPAC names for simple alkane chains:

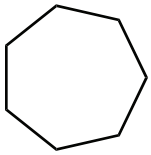
No. C	C_nH_{2n+2}	If Side Chain	If Chain is Parent
1	methane	methyl-	meth-
2	ethane	ethyl-	eth-
3	propane	propyl-	prop-
4	butane	butyl-	but-
5	pentane	pentyl-	pent-
6	hexane	hexyl-	hex-
7	heptane	heptyl-	hept-
8	octane	octyl-	oct-
9	nonane	nonyl-	non-
10	decane	decyl-	dec-
18	octadecane	octadecyl-	octadec-
20	eicosane	eicosyl-	eicos-

From these chain names, one also can form ring names by simply adding the prefix cyclo to a chain name that contains an equivalent number of C-atoms. For example consider a ring formed from eight carbon atoms, From Table 3-5, 8 carbon atoms in a chain is identified as octane. Then the prefix cyclo is added to this octane stem to form the name cyclooctane. Moving from a structural representation for cyclooctane to a proper parent name looks something like this:

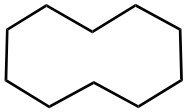
Figure 3-12. The logic behind naming rings of carbon atoms:



Q: Name the following alkanes:

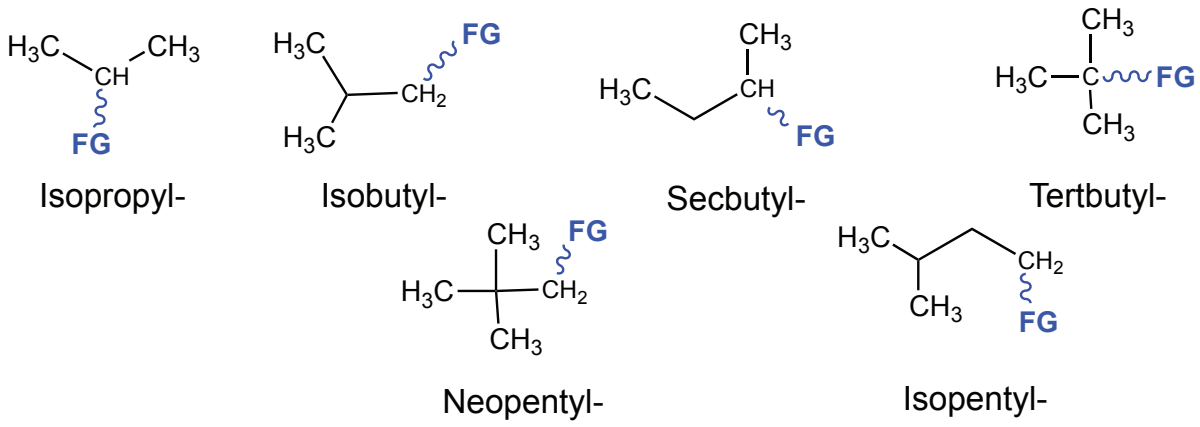
3-13  **cycloheptane**

3-14  **cyclopropane**

3-15  **cyclodecane**

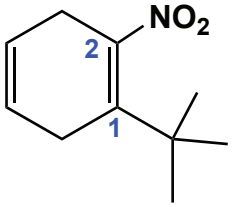
3-16  **nonane**

Figure 3-13. IUPAC acceptable short-cut names for simple branched C3-C5 alkanes (i.e. possible alkyl) or side chain names:



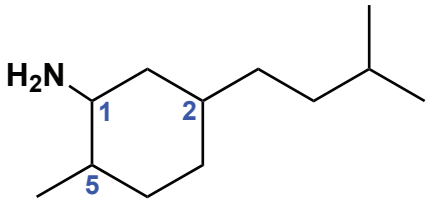
Below are some examples that use this abbreviated "short-cut" substituent notation:

3-17



2-nitro-1-tertbutyl-1,4-cyclohexadiene

3-18



2-isopentyl-5-methylcyclohexylamine

Don't worry right now about how one determines position numbers (i.e. locant positions) for these substituents. In a later section, you'll learn how to derive locant positions for both structures **3-17** and **3-18**.

3-11. Some commonly used nomenclature or trivial names (not IUPAC approved):

Common nomenclature is an older system of naming organic compounds. Instead of using the prefixes for the carbon skeleton above, another informal system(s) is/are used to assign a chain-functional group name.

Table 3-6. Some common or trivial names for some simple alphatic molecules:

Total Number of C-atoms	Parent-IUPAC for R-	Common Name for an R-OH	Common Name for an R-CHO	Common Name for an R-CO-OH
1	Meth-	Methyl alcohol	formaldehyde	Formic acid
2	Eth-	Ethyl alcohol	acetaldehyde	Acetic acid
3	Prop-	Propyl alcohol	propionaldehyde	Propionic acid
4	But-	Butyl alcohol	butyraldehyde	Butyric acid
5	Pent-	Amyl alcohol	valeraldehyde	Valeric acid
6	Hex-	None	caproaldehyde	Caproic acid
7	Hept-	Enanthyl alcohol	enanthaldehyde	Enanthoic acid
8	Oct-	Capryl alcohol	caprylaldehyde	Caprylic acid
9	Non-	None	pelargonaldehyde	Pelargonic acid
10	Dec-	Capric alcohol	capraldehyde	Capric acid

The reader is more likely to encounter these common names in the older literature, in other non-specialized literature and often also in informal conversations.

At this time it also is worth noting that there are some shortcuts that often are used in structural representations of complex molecules in order to help keep molecular representations "clean" and reduce visual clutter. Some commonly used abbreviations are collected in Table 3-7:

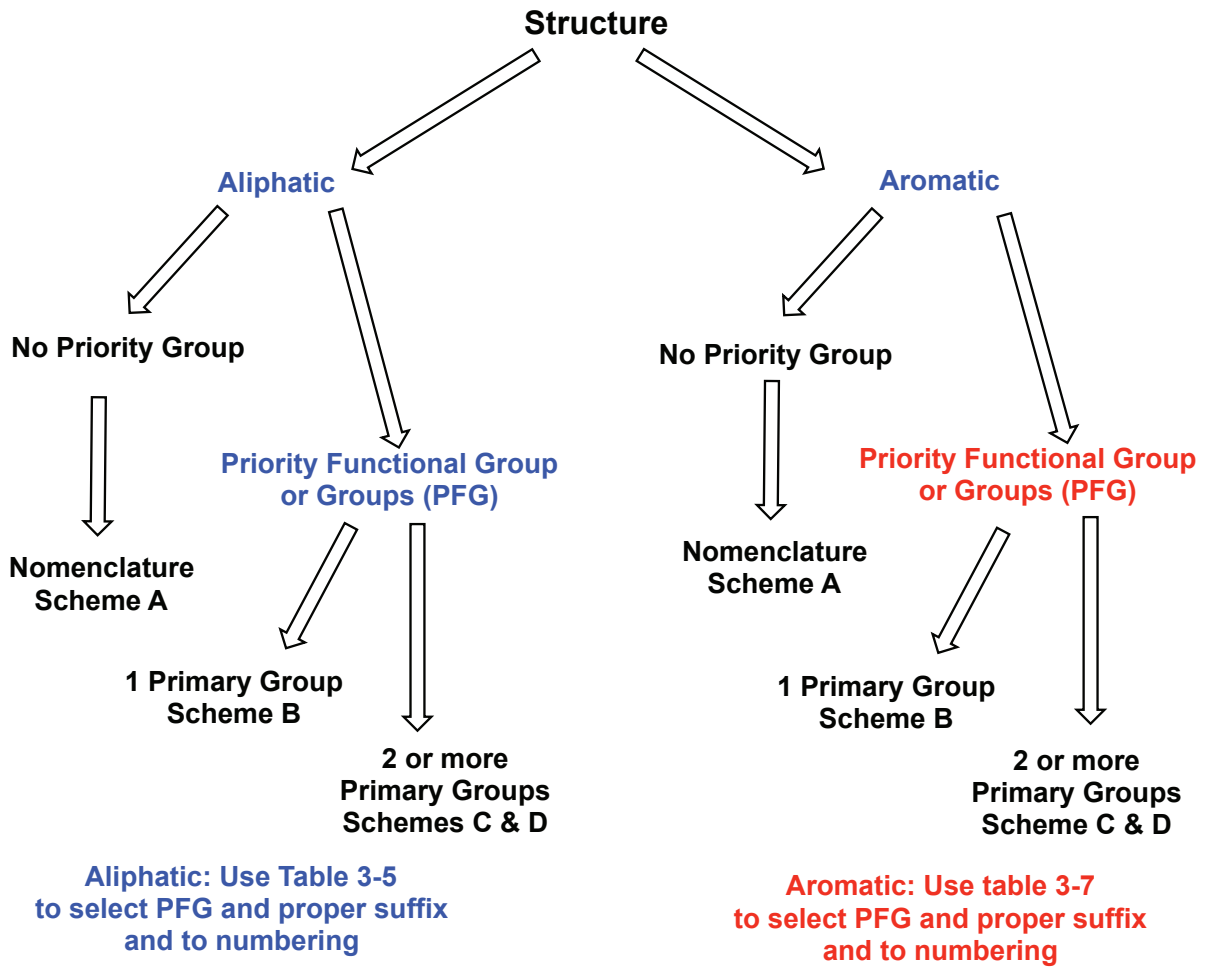
Table 3-7. Some common structural abbreviations used in molecular representations:

Total Number of C-atoms In fragment	Parent-IUPAC name for R-	Common Structural Representation Abbreviation	Examples:	IUPAC example
1	Methyl-	Me-	Me-OH	methanol
2	Ethyl-	Et-	Et-Br	bromoethane
3	Propyl-	Pro-	Pro-NO_2	nitropropane
3	Isopropyl-	i-Pro	i-Pro-OH	Isopropanol
4	Butyl- (chain)	n-Bu-	n-Bu-Cl	chlorobutane
4	IsoButyl-	i-Bu-	i-Bu-OH	isobutanol
4	SecButyl	Sec-Bu-	Sec-Bu-OH	secbutanol
4	TertButyl	t-Bu-	t-Bu-OH	tertbutanol
5	Pentyl- (chain)	n-C_5-	n-C_5-Cl	chloropentane
6	Hexyl- (chain)	n-C_6-	n-C_6-OH	hexanol
Benzene	phenyl	Ph-	Ph-OH	phenol
Benzyl	benzyl	Bn	Ph-CH_2-OH	benzyl alcohol

3-12. Introduction to IUPAC rules for nomenclature:

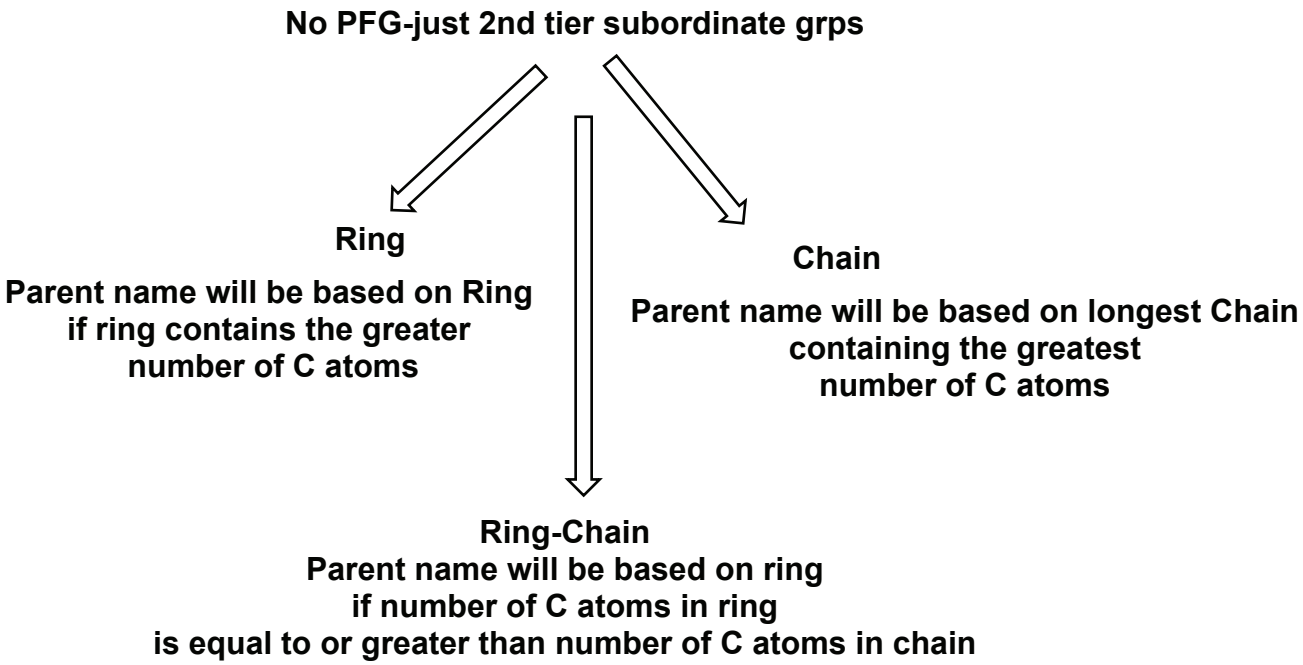
Applying the rules for nomenclature is a lot like reading your cell phone agreement. What follows is an approach to break this problem down into a set of decision trees that help dissect a structure into its various structural components. This approach breaks down the nomenclature problem into several basic situations or motifs likely to be encountered in an introduction to Organic Chemistry. This process, shown here, in not intended to be comprehensive. A "decision tree" like Figure 3-14 is just a useful tool for visualizing a process used to assign a proper name:

Figure 3-14. An overview of the organization of structures used to obtain a proper IUPAC name:



For the moment, let's just focus on the left side of Fig. 3-14, this is the non-aromatic side of this flow chart. We'll start here and learn how to properly assign names to simple basic alkane structures containing only 2nd tier FG. Then we'll move on to molecules with one primary functional group (PFG), and finally segue into a consideration of how to assign names for di- and other polyfunctional groups containing two or even more PFG.

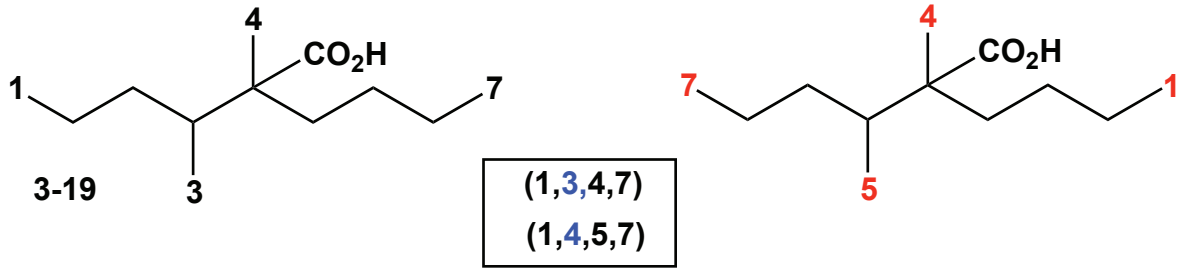
Scheme A. No Primary Functional Group (PFG), and none or only 2nd tier Functional Groups as substituents:



For molecules whose primary structure is that of an alkane with structural components consisting of combinations of rings and chains, their family or group name will be assigned to an alkane family name using the following rules. Start and then satisfy the requirements of Rule 1, then move through in the sequence at needed to form a proper name:

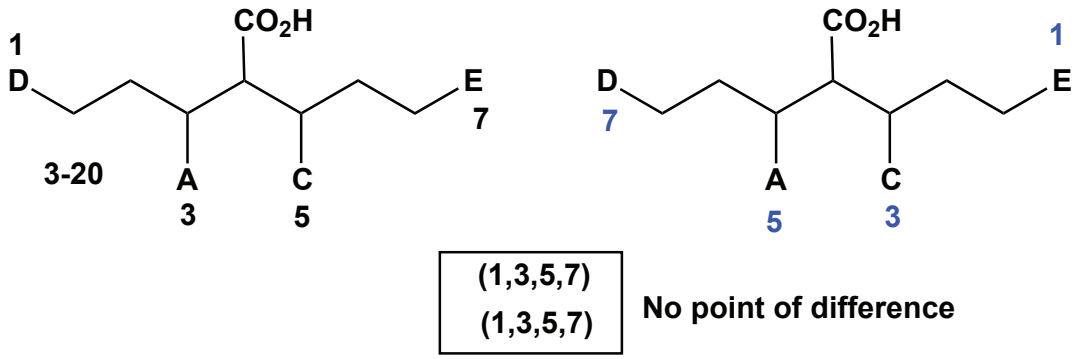
Rule 1: Determine the longest continuous number of carbons in a chain, or ring. The fragment with the greater number of carbons will determine the root name for the parent chain. For cyclic structures, a ring is usually considered the parent "chain", **unless** it is attached to **a longer chain of carbons**. One identifies a ring with the prefix "cyclo" before its parent chain name. If the two longest chains or rings in a structure are of **equal length**, then designate the chain or ring with the greater number of substituents as the parent or main chain.

Rule 2 (numbering direction-I): Number the parent chain or ring in a direction such that the position numbers (i.e. locants) of the first substituent has the smaller number. If the first substituents numbered from either end have the same locant or position number, then number the remaining substituents so that the second substituent has the smaller number, etc. In order to attack this problem efficiently, number longest chains or rings in both directions (R-L and L-R), and place its locant values into an array that is sequenced from lowest position number to highest. As an example consider structure **3-19**. Then compares these different arrays and looks for a "point of first difference" between these them. For example, consider structure 3-**19** [numbered L-R (left to right): 1,**3**,4,7)] vs **3-19** [numbered R-L: 1,**4**,5,7)]. The Point of first difference for these two arrays is at the second position L-R has a 3 and R-L has a 4. Since 3 < 4, the **correct numbering should be 1,3,4,7** and **NOT** 1,4,5,7.



At this step in this procedure, one can associate a locant number with each particular substituent: e.g. 1-C, 3-B, 4-E, 7-D. This identifies substituents with both a prefix (type) and a locant number for each substituent within this structure.

Rule 3 (numbering direction-II): If one cannot differentiate substituents based on position numbers [e.g. if R-L: (1,3,5,7) is same as L-R: (1,3,5,7)], then one selects a numbering system for that end of the chain closest to the substituent which comes first in an **alphabetic order of all substituent prefix names** (e.g. A before E):



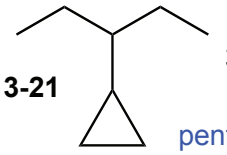
correct numbering: 3-A, 5-C, 1-D, 7-E, with Parent chain: heptane chain; Suffix: 4-oic acid

For structure **3-20**, the problem of no point of first difference is resolved by numbering its substituents alphabetically. Thus A's locant comes before E's locant:

3-A, 5-C, 1-D, 7-E followed by Parent name (heptane) and finally a suffix for $-CO_2H$.

Rule 4 (numbering multiple FG): If there are a number of identical functional groups, they will be grouped together and identified using additional prefixes such as; di, tri, tetra, etc for a substituent as needed, e.g. 1,2,3-trimethyl, or perhaps 1,1,2,12-tetrachloro, etc. Also notice the use of commas to separate locants for multiples of a group. These substituent prefixes (i.e. di-, tri-, tetra-) for the number of a particular FG are ignored when alphabetizing substituent prefix names. For example, consider di**m**ethyl- and tri**c**hloro-; its still C(chloro) before M(methyl). Thus, if no point of first difference, then trichloro or one of these chloro substituents will have the lower locant (i.e. position number) than any of the dimethyl groups.

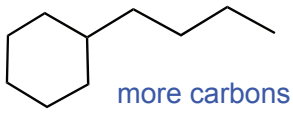
Figure 3-15. Examples of structures named using Scheme A: No primary FG:



3-21

3-cyclopropylpentane

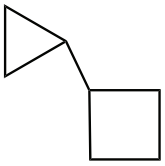
pentane longer chain(C_5) than
number of carbons in cyclopropane-pentane is parent



3-22

1-butylclohexane

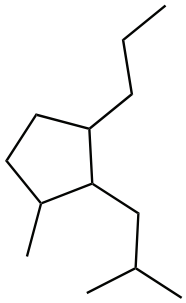
more carbons in (C_6) ring than (C_4) chain



3-23

cyclopropylcyclobutane

(C_4) ring is parent name



3-24

1-butyl-2-isobutyl-3-methylcyclopentane

C_5 ring > C_4 chains

substituents are: Methyl, isobutyl and butyl

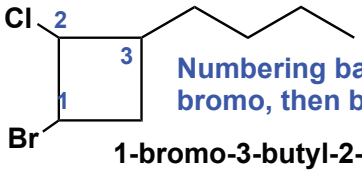
alphabetize subst: **b**utyl, **i**sobuty and **m**ethyl , b before i

Numbering substituents: starting from Methyl: 1,2,3 or
starting from butyl: 1,2,3
either direction : locants are equivalent
Then base numbering decision on alphabetized prefixes: B before M

Rule 5: In order to assemble a proper name, one places these locant-names of the substituent groups in alphabetical order, before the parent chain or ring name. In alphabetizing, **ignore prefixes like sec-, neo-, tert-, di, tri, etc.**, but **do alphabetize** prefixes like **iso-** and **cyclo-**. Always include a locant or position number for each substituent, regardless of any redundancies.

The only other types of substituents that also fit into Scheme A are those FG from the 2nd tier of functional groups. These are functional groups that can ONLY be named as substituent prefixes. These 2nd tier functional groups include the halogens (F, Cl , Br, I) and the nitro, nitroso (-NO) functional groups. Below are more examples of some frequently encountered numbering situations that also are described by Scheme A:

Figure 3-16. Examples. Possible numbering examples of other aliphatic rings or chains with just 2nd tier FG:

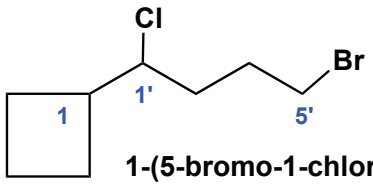


3-25

4C ring = 4C chain

Numbering based on alphabetized order:
bromo, then butyl, then chloro: Br is at #1C

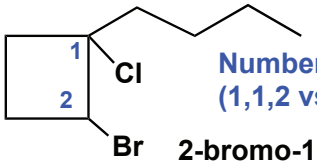
1-bromo-3-butyl-2-chlorocyclobutane



3-26

Numbering based on first difference:
(1,1',5' vs 1',5',5)

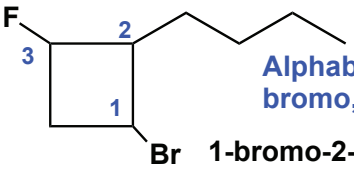
1-(5-bromo-1-chlorobutyl)cyclobutane



3-27

Numbering based on first difference:
(1,1,2 vs 1,2,2)

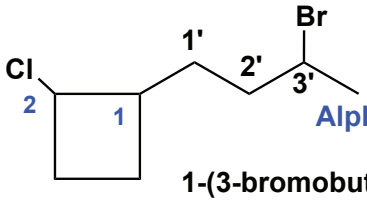
2-bromo-1-butyl-1-chlorocyclobutane



3-28

Alphabetized order:
bromo, then butyl, then fluoro ; Br is at #1C

1-bromo-2-butyl-4-fluorocyclobutane



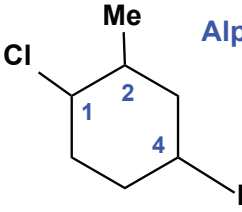
3-29

Alphabetized order: butyl, then chloro: butyl is at #1C

1-(3-bromobutyl)-2-chlorocyclobutane

C6 vs C1-cyclohexane

Alphabetized order: bromo, then chloro, then methyl: Br is at #1C



3-30

1, 3, 4
1, 2, 4

2 < 3

4-Br , 1-Cl , 2-Me

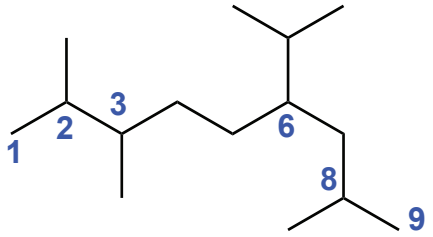
NOT 1-Br , 4-Cl, 3-Me

4-bromo-1-chloro-2-methylcyclohexane

Notice for this series of butylcyclobutanes (**3-26** to **3-29**) where the various halogen substituents are located does NOT alter the parent name of the alkane or cycloalkane.

Q. Name the following structures:

3-31



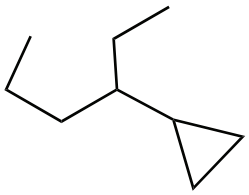
C_9 -longest chain. From Fig. 3-5
parent is nonane

L-R: groups at 2,3,6, 8
R-L: groups at 2,4, 7,8
first difference is 3<4. numbering is L-R

2,3,8--trimethyl, 6-isopropyl (fig. 3-13,
alphabet: i before m, tri is ignored

6-isopropyl-2,3,8-trimethylnonane

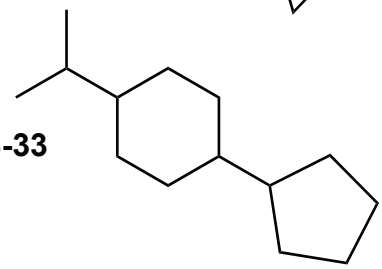
3-32



Chain C_6 ring C_3 : parent is hexane

3-cyclopropylhexane

3-33



Chain C_3 rings C_6 and C_5 : C_6 ring is parent

Positions 1 and 4 in either direction

groups: cyclopentyl - c
isopropyl -i
alphabet : c before i

1-cyclopentyl-4-isopropylcyclohexane

Schemes B and C will be used to build and elaborate on those 5 rules used to assign names for Scheme A structures. For both Schemes B and C we now will consider naming structures with at least one or even more 1st tier functional groups within a particular structure. Recall that 1st tier groups can function either as substituents (prefix name) and may become the PFG for our structure and then used to generate a family name (i.e. suffix name). Scheme B, considers structures with ONLY one 1st tier functional group, and then those structures that contain just one 1st tier group with one or more 2nd tier groups. Thus the rules for both Scheme B and Scheme C are summarized below:

Basic IUPAC nomenclature Rules for structures containing PFG : (Refer to the Priority of Functional Groups shown in Table 3-4 for help).

Rule 1a: Ring or Main chain is "longest chain", **or it must contain the highest priority group (PFG)**.
Rule 1b: If the PFG is on a chain or ring, then this **main chain or ring also must contain** the maximum number of substituent groups; or

b) This PFG-main chain must have maximum number of multiple bonds; or
c) This PFG-main chain must have maximum number of double bonds; or
d) This PFG-main chain must contain the maximum number (i.e. length) of carbon atoms.

Rules 1a and 1b are just more elaborate versions of the Rule 1 (Scheme A) that have been adjusted to accommodate the nomenclature for structures containing PFG. Applications of Rules 2-5 remain the same as they are for the Scheme A structures. Remember to satisfy these rules in their properly ordered sequence (1,2,3,4,5, etc). That is step through and address Rules 1a and 1b first before moving on to Rules 2, etc.

Also take notice of the importance of the relationship between chain length or ring and where the primary functional group (PFG) is located. Application of **Rule 1a** is relatively easy to apply and it is the main focus of Scheme B. However, as we'll see in Scheme C and D, it is the application of **rules 1b-d** that can create difficulties if one gets careless. By focusing on naming a structure with only one primary (1st tier) functional group we can begin dealing with the application of these rules to more interesting and complicated structures.

Scheme B. Only One Primary Functional Group (PFG), none or other subordinate groups

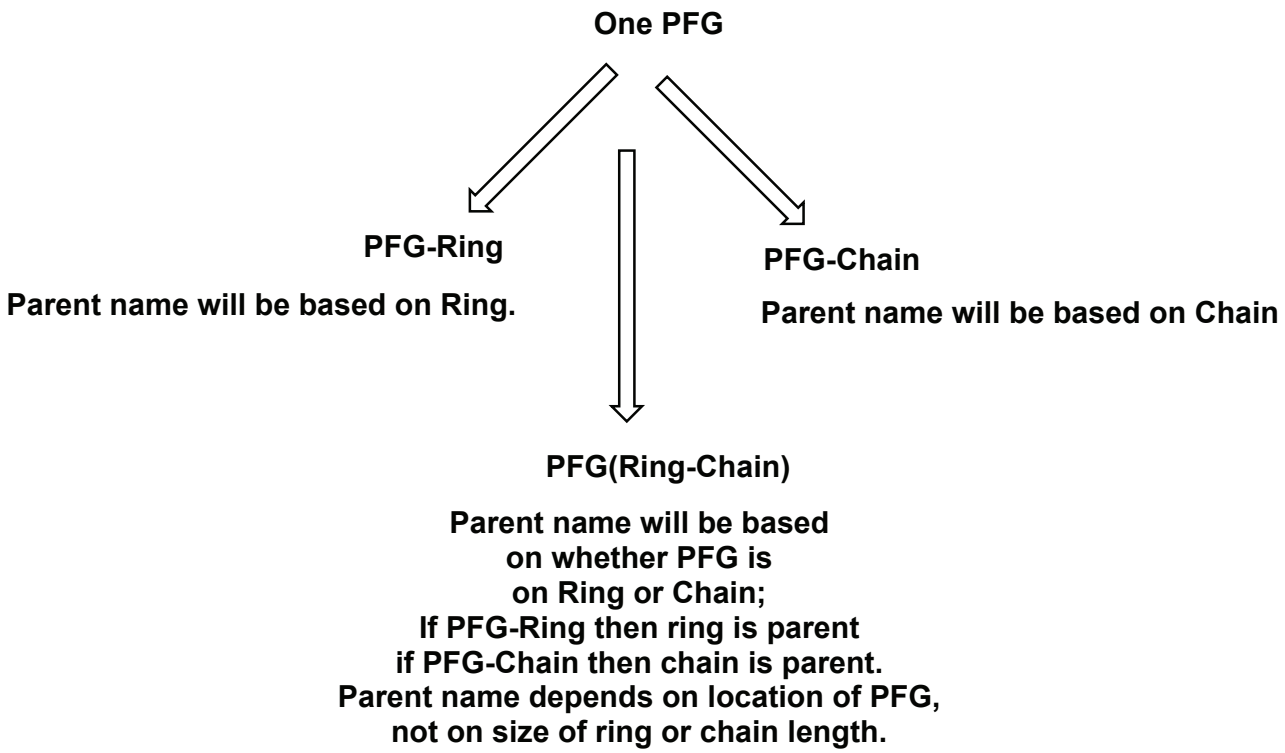
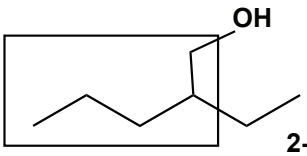


Figure 3-17. Examples of naming structures that belong to Scheme B are shown below:

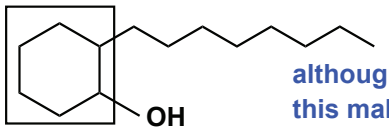
3-34



-OH, is Primary FG (PFG)
$C_5 > C_4$ pentane is parent

2-ethylpentan-1-ol

3-35

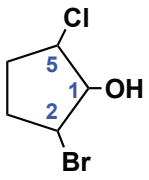


-OH, is PFG

although $C_6 < C_8$, the C_6 ring contains the PFG, this makes cyclohexane the parent name

2-octylcyclohexanol

3-36



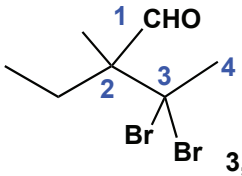
-OH, is PFG

numbering is either 1,2,5 or it's 1,2,5

If no positional difference then alphebetical: Br before Cl

2-bromo-5-chlorocyclopentanol

3-37

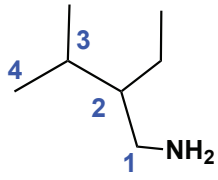


-CHO is PFG

C_4 chain contains most of the substituents along the longest chain.

3,3-dibromo-2-ethyl-2-methylbutanal

3-38

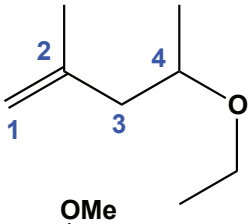


-NH_2, is PFG

C_4 chain contains most of the substituents along the longest chain.

2-ethyl-3,4-dimethylbutanamine

3-39

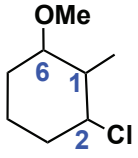


C=C, is PFG

C_5 chain contains most of the substituents along the longest chain.

4-ethoxy-2-methylpentene

3-40



-Me (alkane) is PFG

numbering is either 1,2,6 or it's 1,2,6

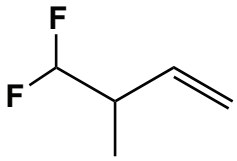
If no positional difference then alphebetical: C before M

2-chloro-6-methoxymethylchclohexane

Notice that location of the PFG determines the parent structure, and sometimes it also often determines, either directly based on its point of attachment, or indirectly, the location of carbon #1 within a structure because a PFG always has the lowest locant position in a proper name.

Q. Name the following structures:

3-41

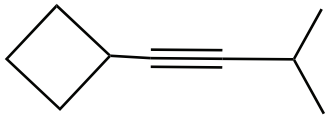


Alkene is PFG and determines C#1

3-methyl and 4,4-difluoro, F before m

4,4-difluoro-3-methylbutene

3-42



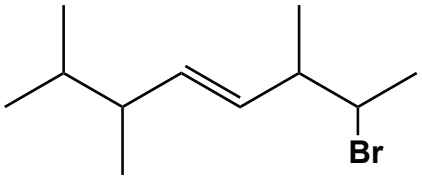
Alkyne is PFG, and determines C#1

longest chain with PFG is butane

1-cyclobutyl 3-methyl

1-cyclobuty;-3-methyl-3-butyne

3-43



Alkene is PFG, and determines

longest chain with PFG is octane

numbering from either end gives position #4 for alkene

Look at subst patterns:

L-R: 2,3,6,7

R-L: 2,3,6,7 same

2-bromo-3,6,7-trimethyl-4-octene

alphabetize: Bromo and triMethyl, B before M

Notice that the main distinction between Scheme A and Scheme B is the importance of a primary functional group (PFG). Location of a PFG, by default, determines a main chain or ring. After determining the main chain or ring, one then can move on to determine locant and then substitution patterns: Is there more than one direction to number from a #1C? One then can look at arrays of different possible position numbers to search for any point of first difference. If there is no point of first difference, then you'll need to alphabetize substituents in order to decide which position to assign as C#1.

Finally, let's move on to the last category of structures, those with two or more primary functional groups and examine how this additional functionality impacts naming. Possible structural patterns of multiple PFG frequently encountered are shown below in Scheme C:

Scheme C. Two or more Primary Functional Groups (PFG), possibly with additional 2nd tier functional groups:

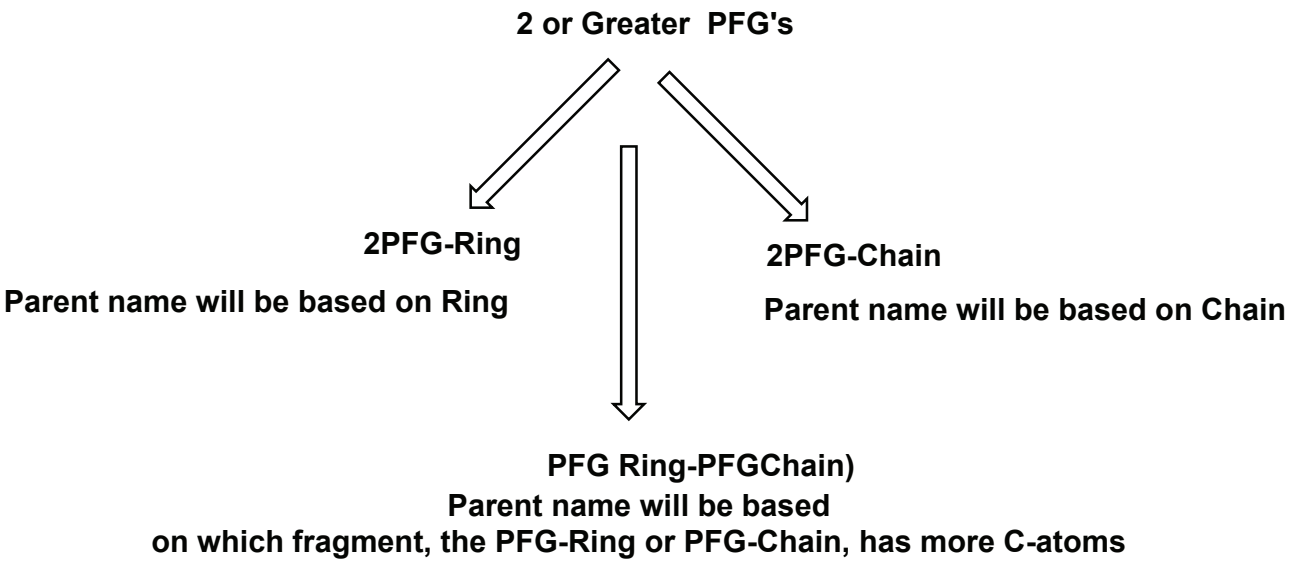
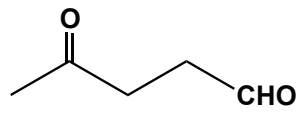


Figure 3-18. Examples of structures containing two or more FG:

3-44

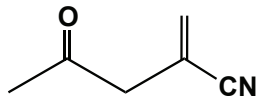


4-oxopentanal

-CHO (Aldehyde) is #1 PFG; and also on C#1

C_5 Chain -pentan, parent name is pentamal with 4-oxo (ketone grp)

3-45



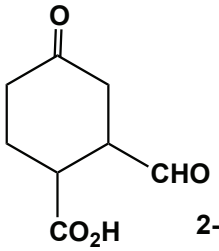
4-oxopentene-2-nitrile

-CN (Nitrile) # 1 PFG: and at C#2

C_5 Chain -pentan

lowest locant position for CN is 2-CN Parent name is 2-pentenenitrile then substituents are 1-C=C and 4-oxo

3-46



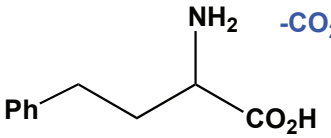
2-formyl-4-oxocyclohexanoic acid

-CO_2H (Carboxilic acid) is #1 PFG; and at C#1

C_6 Ring -cyclohexane

-CO_2H at locant #1, lowest numbering gives 2-formal, 4-oxo

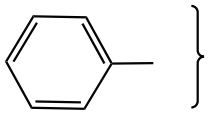
3-47



2-amino-4-phenylbutanoic acid

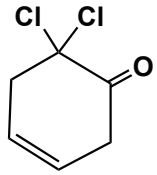
-CO_2H (Carboxilic acid) is #1 PFG, suffix -oic acid and IS C#1

C_4 Chain -butan: parent name is butanoic acid then substituents are 2-amino and 4-phenyl



Ph-, phenyl

3-48

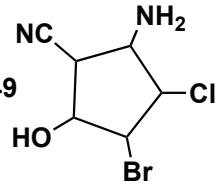


2,2-dichloro-2-cyclohexenone

$R_2C=O$ (ketone) is #1 PFG: suffix is -one; and at C#1

C_6 Ring -cyclohexane : parent name is cyclohexanone numbering of substituents: CW is 3,6,6 or CC: 2,2,4 , point of first difference at positions: 2 and 3 thus numbering is 2,2-dichloro and 4-ene

3-49



2-amino-4-bromo-3-chloro-5-hydroxycyclopentanitrile

-CN (Nitrile) # 1 PFG: and is at C#1

C_5 Ring: -cyclopentan: Parent is cyclopentanitrile

No direction difference between positions: ring atoms both are 1,2,3,4,5. if alphabetize substituents: Amino, Bromo, Chloro, Hydroxy. place Aminio at locant with lowest number: C#2

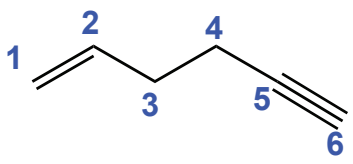
Structures containing multiple units of unsaturation:
A special sub category of Scheme C structures concerns the nomenclature when both alkene and alkyne functional groups are present and **also part of a main chain**. If an alkene is the PFG in a molecular structure, then a parent name for a mixed alkene alkyne structure becomes -en-yne:

alk-# locant-en-# locant-yne.

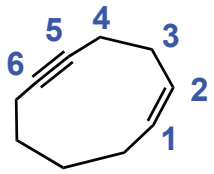
Proper "syntax" requires that an alk**e**ne fragment always gets listed before an alk**y**ne segment (i.e. its e before y). Syntax also requires modification to the "*ene*" suffix of an alkene. Since "*yne*" begins with a vowel (y), the final "e" of *ene* is dropped to form -en. For molecules containing multiple alkene and/or alkyne segments di, tri and tetra, etc., for example, -dien-triyne and **not** diene-triyne.

This next section requires close attention, because the rules become more complex. If both an alkene and alkyne occupy terminal positions in a main chain, or if they happen to be part of a ring, then **the alkene occupies either the #1C or the lower locant or position number:**

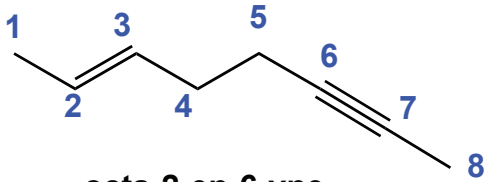
Figure 3-19. Numbering for en-yne symmetrically located within a main chain or ring e.g. symmetric array: (R-L en-yne same as L-R en-yne locant positions):



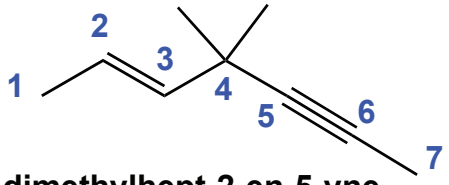
hexa-1-en-5-yne



cyclodec-1-en-5-yne



octa-2-en-6-yne

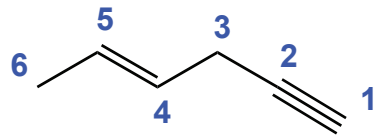


4,4-dimethylhept-2-en-5-yne

Notice that for **these examples in Fig. 3-33 all have their en and yne functional groups symmetrically located** from each other within a chain or ring.

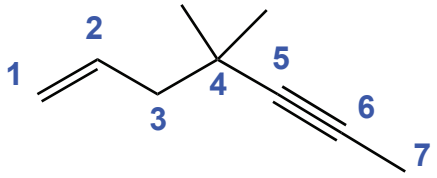
For **unsymmetrically located en-yne functionality**, priority locant **numbering will be from that end of a chain** that is **nearest to the first multiple bond**-regardless of bond type (i.e. en or yne):

Figure 3-20. Numbering for en-yne unsymmetrically located within a main chain or ring e.g. array (R-L en-yne NOT as L-R en-yne locant positions):



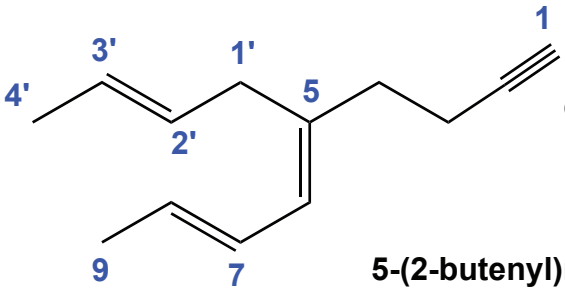
hexa-4-en-1-yne

1,4 vs 2,5



4,4-dimethylhept-1-en-5-yne

2,4,4,6 vs 1,4,4,5



chain 1-9 contains 3 of the 4 FG

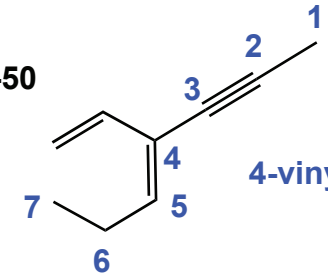
numbering 1,5,7 vs 2,4,8

side chain is: (2-butenyl)

5-(2-butenyl)nona-5,7-dien-1-yne

Q. Name the following structures:

3-50



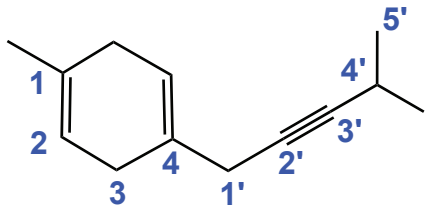
$C_7 > C_6$: hept

numbering: 2, 4 vs 3, 5; 2 < 3: 2-yne, 4-en

4-vinyl or 4-ethenyl

4-vinylhept-4-en-2-yne

3-51



$C_6 > C_5$: cyclohex

ring numbering for substituents: 1,4 vs 2,5;
b/c Methyl before Pentyne

1-,4-cyclohexadiene

1-methyl

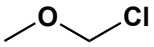
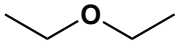
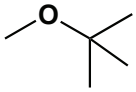
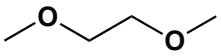
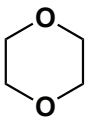
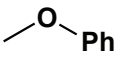
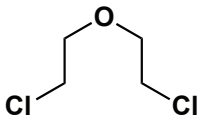
4-(4-methyl-2-pentyne)

1-methyl-4-(4-methyl-2-pentyne)-1,4-cyclohexadiene

This complication of alkenes and alkynes functional groups within the same structure generally follows the procedure already established for polyfunctional structures in schemes B and C. The major issue with these types of en-yne structures is the direction of numbering. You'll notice that there are three basic pattern of en-yne structures: en-yne structures that are symmetrically located around a chain or ring, or the en is internal and the yne is located at the terminus of a chain, and finally, when both the en and yne are buried within a molecular structure at different distances from their chain termini.

Ether nomenclature:
The nomenclature of ethers also is confusing and requires close attention. Should one identify a C-O-C ether group as an alkoxy group or alternatively with the **prefix oxa.** A common name for "simple" ether derivatives identifies those carbon chains or rings on either side of a -O- linkage:

Figure 3-21. Common ether names and their equivalent IUPAC designations:

	Common Names:	IUPAC
	dimethyl ether methyl ether	methoxymethane
	chlorodimethyl ether	chloro(methoxy)methane
	ethyl ether ether diethyl ether 3-oxapentane	ethoxyethane
	MTBE methyl tert-butyl ether tert-butyl methyl ether	2-methoxy-2-methylpropane
	mono-glyme DME glyme dimethylcellulosive dimethylglycol	1,2-dimethoxy ethane
	THF cyclotetramethylene oxide oxacyclopentane	IUPAC prefers to name as heterocycle: Oxolane The IUPAC systematic name is: Oxacyclopentane
	dioxane dioxan	1,4-dioxane 1,4-dioxacyclohexane
	methyl phenyl ether Anisole	methoxybenzene
	oxygen mustard bis(2-chloroethyl) ether	1-chloro-2-(2-chloroethoxy)ethane(m

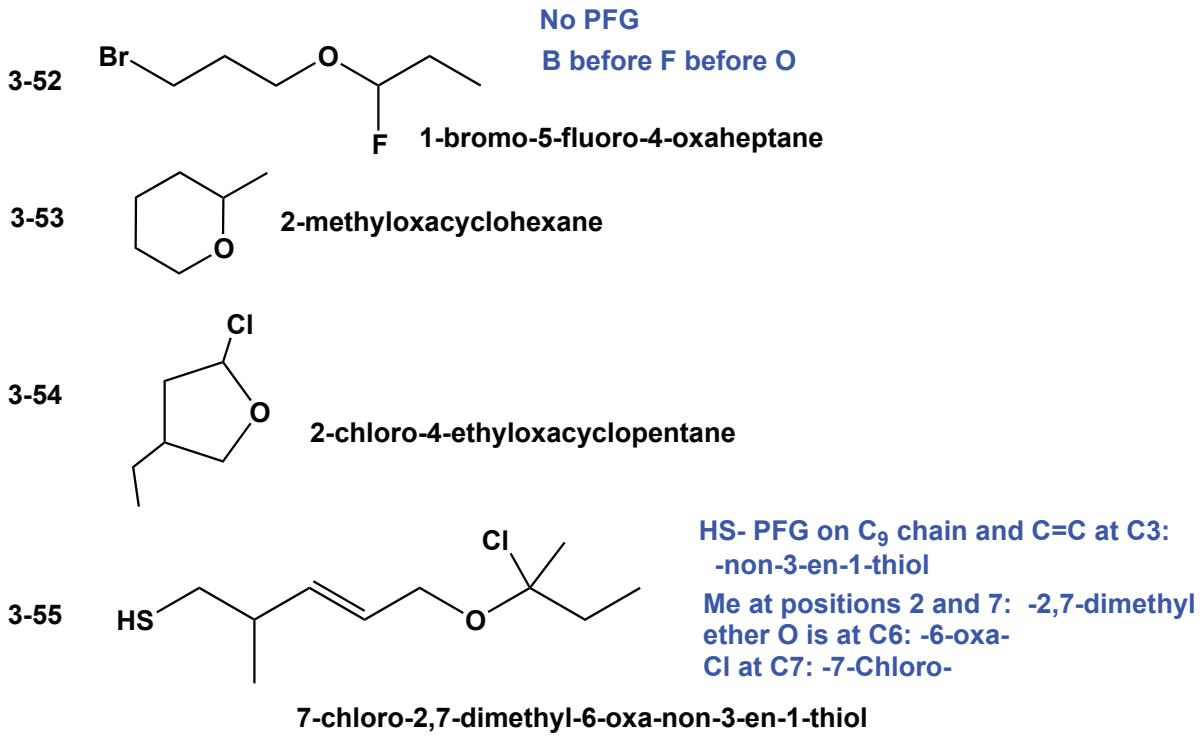
The simple IUPAC notation identifies the shorter of the two alkyl chains by modifying the shorter chain suffix and replacing its -ane with an –oxy suffix, while letting the longer alkane chain become the parent chain and retain its -ane suffix. The ordering of these pieces is –oxyalkane (e.g.

ethoxypropane). Thus CH_3-O-CH_3 is methoxymethane, and $CH_3OCH_2CH_3$ is methoxyethane (**not** ethoxymethane), and $CH_3OCH(CH_3)_2$ is named as 2-methoxy-2-methylpropane.

However, as a practical matter, once substituent chains on either side of the ether linkage get beyond C5 in length (e.g. pentoxy) it is probably best to consider such ether structures as a complex rather than as simple ethers. IUPAC says that if an ether is complex (e.g. highly substituted, or part of a long main chain or ring) then one should use the **–oxa**-notation.

In this "oxa" notation one counts oxygen as part of an alkane ring or chain. Within the rules already established, determine the lowest possible locant position of that "ether" oxygen atom. Then add the prefix #-oxa- to specify the locant position of that ether oxygen linker. Examples of this type of notation are shown below:

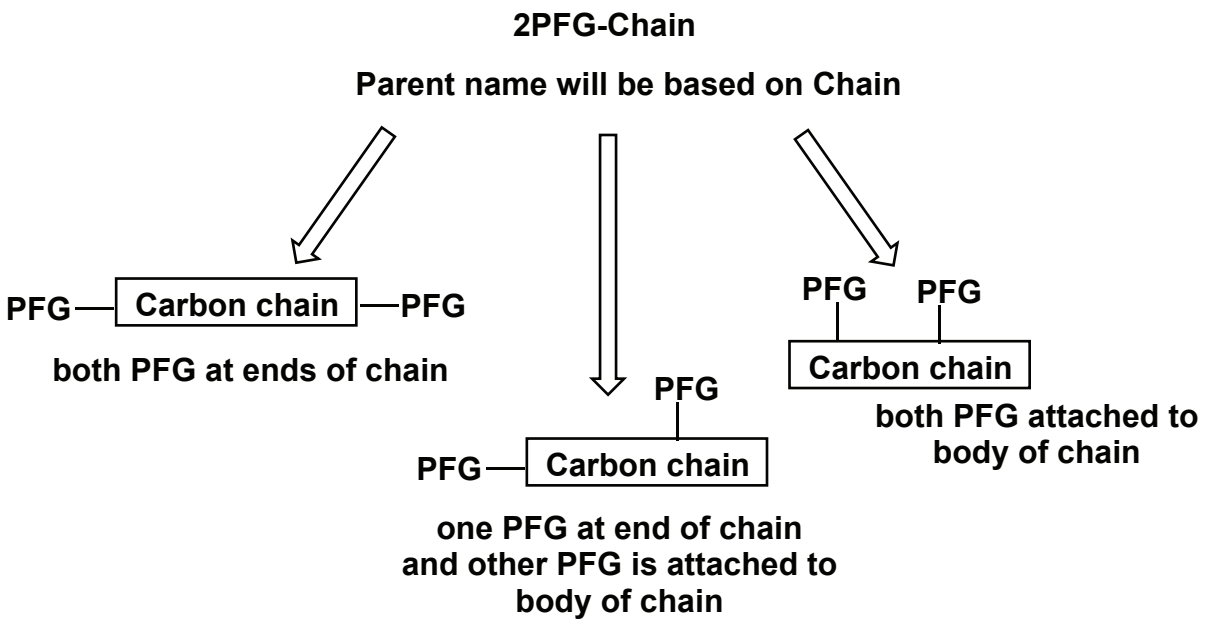
Figure 3-22. Examples of complex ethers named using the –oxa notation:



***Note: DO NOT Confuse oxa (an ether prefix) with oxo (a keto prefix)**

Scheme D is a special extension of Scheme C and is used here to name structures with two or more identical PFG's within same molecular structure. Although the competition between ring and chain priorities may be a bit different, most of the numbering issues have already been presented and resolved in the discussions of Schemes B and C examples.

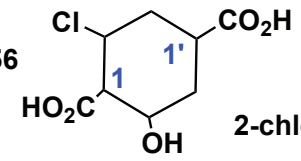
Scheme D. Structural patterns for chains containing two or more primary functional groups (PFG), containing none or other subordinate groups:



Scheme D elaborates several common di-PFG substitution patterns observed for chains. Below are some of the more common situations encountered with having two or even more PFG attached to the same structure.

Figure 3-23. Nomenclature examples of ring-chain structures containing two or more polyfunctional groups (PFG):

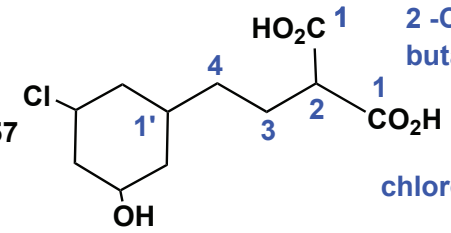
3-56



2 -CO_2H PFG on C_6 ring: cyclohexane; -dioic acid
numbering: 1,2,4,6; 1,2,4,6 vs 1',3',4',5'; 1',3',4',5'
chloro vs hydroxy: C before H: 2-Chloro, 6-Hydroxy

2-chloro-5-hydroxy-1,4-cyclohexandioic acid

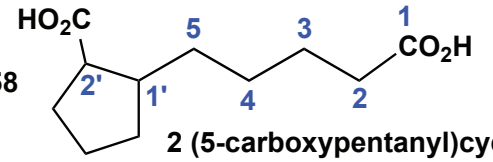
3-57



2 -CO_2H PFG on C_4 chain and a C_6 ring:
butan; 1,1-dioic acid
numbering: 4-cyclohexyl
numbering on cyclohexane: 1',3',5' or 1',3',5'
chloro , hydroxy: C before H: 3-Cl, 5-Hydroxy

4-(3-chloro-5-hydroxycyclohexanyl)-1,1-butandioic acid

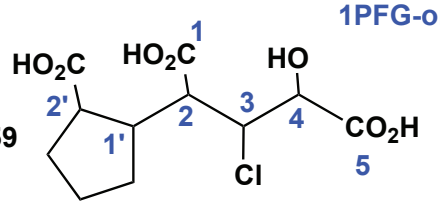
3-58



C_5 ring vs C_5 chain: cyclopent
but 1PFG-Ring AND 1PFG-chain = -oic CO_2H
so parent is cyclopentanoic acid

2 (5-carboxypentanyl)cyclopentanoic acid

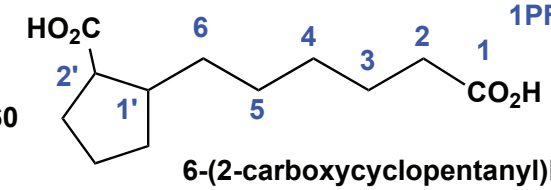
3-59



1PFG-on C_5 ring AND 2PFG- on C_4 chain pentandioic CO_2H
pentandioic: L-R: 2,3,4 and R-L: 2,3,4
chloro, cyclopentyl, hydroxy
3-chloro, either direction, next cyclopentyl :
2-cyclopentyl, 3-Chloro, 4-hydroxy

3-chloro-2-(2-carboxycyclopentanyl)-4-hydroxy-1,5-pentandioic acid

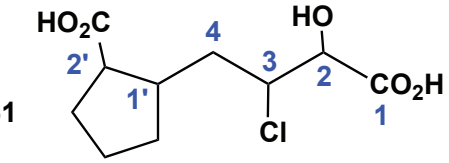
3-60



1PFG- C_5 Ring AND 1PFG- C_6 chain = -oic CO_2H
hexanoic acid

6-(2-carboxycyclopentanyl)hexanoic acid

3-61



1PFG-Ring AND 1PFG-chain = -oic CO_2H
chain has more substituents: parent butanoic
based chain with nore substituents: 2,3,4

3-chloro-5-(2-crboxycyclopentanyl)-2-hydroxypentanoic acid

From what you know now, you should be able to write a proper name for even these highly functionalized alphatic structures shown below. Don't panic, simply step through the rules by first identifying any PFG and then moving through the rest of the rules as might be required and you should be able to arrive at a proper name, even for some rather overly complex structures like those below. When you are done, you should be capable of correctly naming most of the simple structures used in this text.

Summary of nomenclature rules for non-aromatic chains and rings:

Rule 1a: Ring or Main chain is "longest chain", or it must contain the highest priority group (PFG).
Rule 1b: If the PFG is on a chain or ring, then this main chain or ring also must contain the maximum number of substituent groups; or

b) This PFG-main chain must have maximum number of multiple bonds; or
c) This PFG-main chain must have maximum number of double bonds; or
d) This PFG-main chain must contain the maximum number (i.e. length) of carbon atoms.

Once a PFG has been determined from Table 3-4, the priority numbers have no additional impact on this nomenclature process. Table 3-4 does remain a useful and valid reference for prefix and suffix names.

Rule 2: Number the parent chain or ring in a direction such that the position numbers (i.e. locants) of the first substituent has the smaller number. If the first substituents numbered from either end have the same locant or position number, then number the remaining substituents so that the second substituent has the smaller number, etc. To attack this problem efficiently, number longest chains or rings in both directions (R-L and L-R), and place those locant values into an array that is sequenced from lowest position number to highest (e.g. for **3-19**). Then compare these different arrays and look for a "point of first difference" between these arrays.

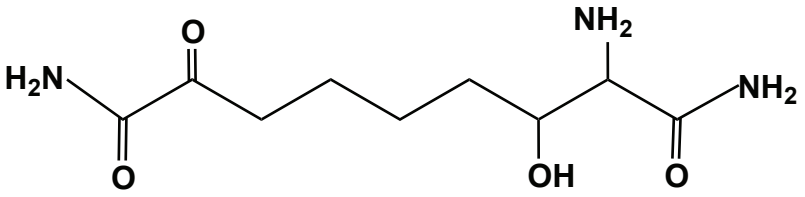
Rule 3: If one cannot differentiate substituents based on position numbers [e.g. if R-L: (1,3,5,7) is same as L-R: (1,3,5,7)], then one selects a numbering system for that end of the chain closest to the substituent which comes first in an alphabetic order of all substituent prefix names (e.g. A before E).

Rule 4: If a there are a number of identical groups, they will be grouped together and identified using additional prefixes di, tri, tetra, etc for a substituent as needed, e.g. 1,2,3-trimethyl, or perhaps 1,1,2,4-tetrachloro, etc

Rule 5: Place names of the substituent groups in alphabetical order, before the parent chain or ring name. In alphabetizing, **ignore the prefixes** sec-, neo-, tert-, di, tri, etc., but **do alphabetize** prefixes like **i**so and cyclo (e.g. **i**sopropyl, **c**yclopropyl). Always include a position number for each substituent, regardless of any redundancies.

Q: Name this structure:

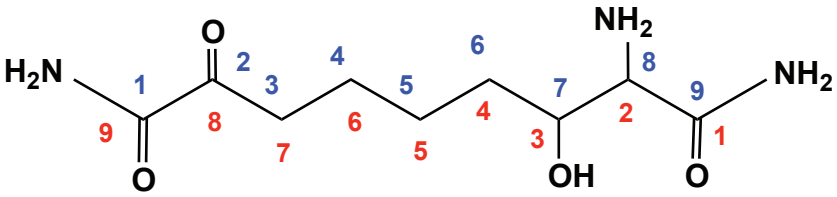
3-62



Start here:

1. Structure has two PFG, these are the amide groups located at both ends of a 9C chain.
2. Parent structure is a continuous carbon chain of 9 atoms, nonane:

3-62b



3. Q: is numbering from right end (L-R) is 1,2,7,8,9 or from left end (R-L) is 1,2,3,8,9?
To decide this issue number substituents alson this 9C chain:
a. No functional groups are part of the 9C carbon chain, thus look at substituent locant positions:
L-R subst at: (1,2,7,8,9); arrayed: lowest to highest
vs
or R-L subst at (1,2,3,8,9) arrayed lowest to highest
Point of first difference is at third position in these two arrays (with 3 < 7)
This means that chain should be numbered from R-L.

Putting it together:

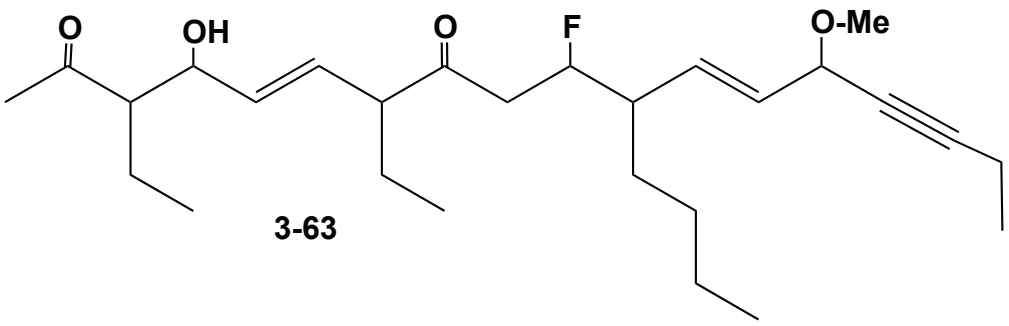
4. There are 2 amides (PFG's) at either end of a nonane carbon Chain: **-1,9-nonanediamide**

5. Now number and name all subordinate functional groups:
2-amino ,3-hydroxyl , 8-oxo

6. Alphabetize and group subordinate substituents:
Subordinate Substituents attached to 9C carbon chain are: **2-amino , 3-hydroxy, 8-oxo;**

Proper name is: 2-amino-3-hydroxy-8-oxo-1,9-nonanediamide

Q: Name this structure:



3-63

1. (What is PFG?). Priority group is ketone group (C=O) closest to left-end of carbon chain suffix will be based on suffix -one. There are two keto groups, which requires the proper suffix: -**dione**

2. (Ring or chain? How many carbons in that parent unit?). This dione functionality is attached to an 18-carbon chain is assigned the name: **octadecane** (see Table 3-5)

3. (How should the parent be numbered?). Chain numbering is based on position of ketone groups: Carbonyl groups at positions 2 and 8, are identified as: **-2,8-dione** because ketone positions from L-R at 2 and 8 are at lower locant position numbers than those from R-L at 11 and 17 **(lowest positional numbers not lowest sum of position numbers**).

4. (Any side chains?). Alkyl side chains are from L-R: 3-ethyl, 7-ethyl and 11-butyl. Putting this together one arrives at:
11-butyl-, 3,7-diethyl-

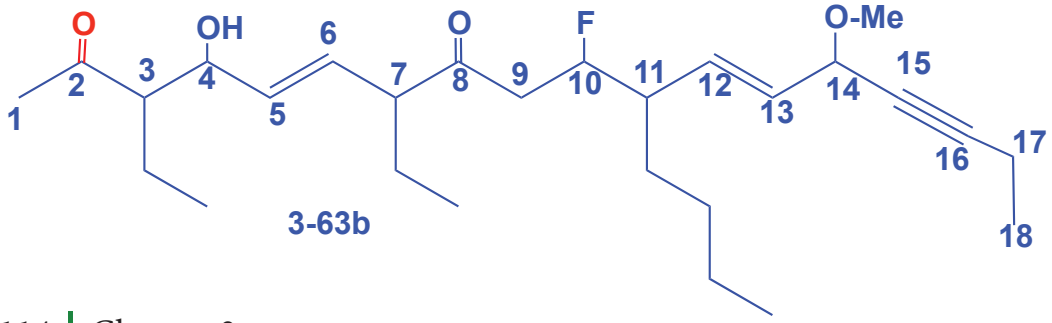
5. (Any other substituents?). Other secondary substituents are: **10-fluoro-, 4-hydroxy, 14-methoxy-**

6. (Any unsaturation in ring or chain?). There also are two double bonds at positions: 5- and 12-, and one triple bond at 15-. For these structural units one then writes: **-5,12-dien and -15-yne**

7. Place these assigned substituents and locant positions in their proper alphabetical order. These are: **11-butyl , 3,7-diethyl, 10-fluoro, 4-hydroxy, 14-methoxy ,-5,12-diene, and -15-yne**

8. Assemble the final name: Putting all of these structural units together we arrive at a final name of:

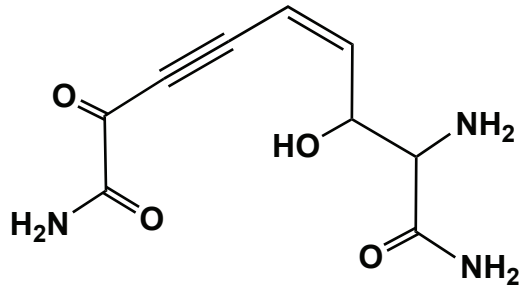
11-butyl-3,7-diethyl-10-fluoro-4-hydroxy-14-methoxy-octadec- 5,12-dien-15-yne-2,8-dione



3-63b

Q: Name this structure:
Notice that this is molecule contains two or more Primary Functional Groups (PFG) and other subordinate groups

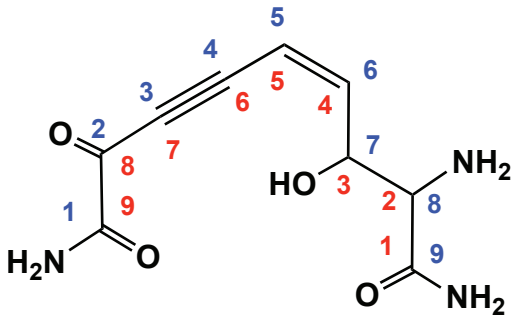
3-64



Start here:
1. (What are PFG?). Structure has two PFG, which are the amides (-C(O)-NH_2 located at both ends of chain: -diamide
2. (Ring or chain?). How many carbons in that parent unit?). Structure is a continuous carbon chain of 9 atoms: nonane

Now number chain: R-L and L-R

3-64b



3. (Number Chain R-L and L-R). Substituent numbering generates arrays: (L-R) is 1,2,3,**5**,7,8,9 from left end or (R-L) is 1,2,3,**4**,6,8,9

Since amides are at both ends of this C_9 chain. In order to decide which direction is proper, look for unsaturation along this C_9 chain:

Numbering of chain will be based on locations of en-yne unsaturation.

IUPAC Rule says: if numbering R-L or L-R is same for PFG is to then determine locations of alkene and alkyne. If the alkene-alkyne locant positions are different then go with **lowest** locant position for **either the alkene or alkyne**:

R-L C#3 and C#5; place in sequence array lowest to highest locant number: (3,5)
vs
L-R C#4 and C#6; place in sequence array lowest to highest locant number: (4,6);
Position of first difference: 3 vs 4 and because 3 < 4.
this chain should be numbered from L-R.

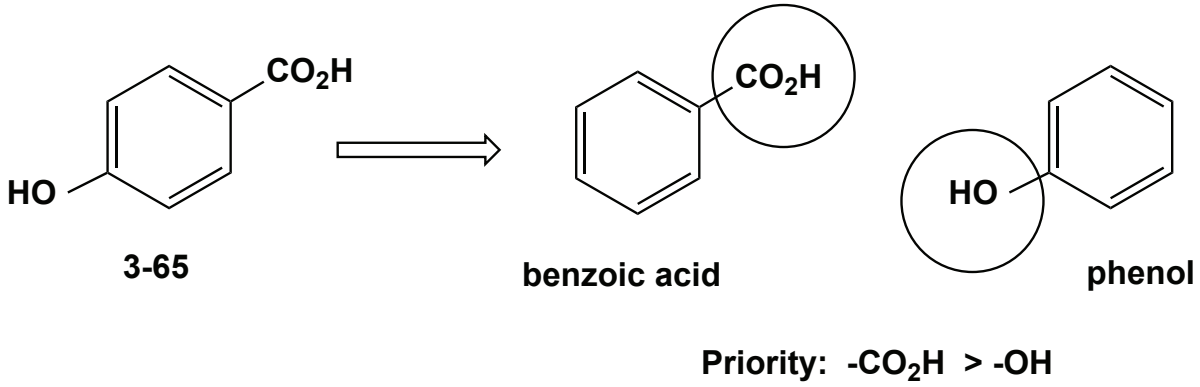
4. Thus number and also name all subordinate functional groups are:
2-oxo , 5-en-3-yne, 7-hydroxyl , 8-amino

5. Put it all together:
8-amino-7-hydroxyl-2-oxonon-5-en-3-yne-1,9-diamide

3-13. Naming Aromatic compounds:

Suffix priorities for Aromatic derivatives also are the same as those shown in Table 3-5 that were used to prioritize functional groups attached to aliphatic skeletons. However, many of the **suffix endings** for aromatic PFG are bit different. However, here too, generation of a name for an aromatic compound begins by identifying the priority group attached to an aromatic skeleton. Once a parent aromatic structure has been determined, one then considers the locant positions of any secondary groups (i.e. substituents) using the same method that was applied to the aliphatic structures. Since benzene is the most frequently encountered aromatic ring in this text, it will be benzene derivatives that will be emphasized in this section on aromatic ring nomenclature. For example consider the following benzene derivative:

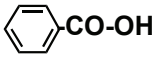
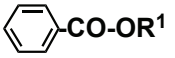
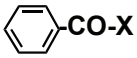
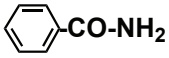
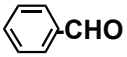
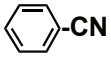
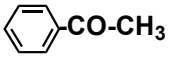
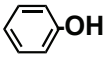
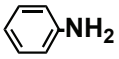
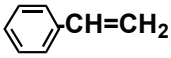
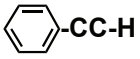
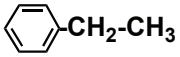
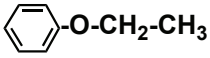
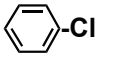
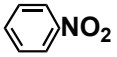
Figure 3-24. Naming Benzene derivatives:



As a result of Table 3-8 (below); structure 3-65 is named as derivative of benzoic acid (i.e. hydroxybenzoic acid) and NOT as a derivative of phenol.

Aromatic ring functional group priorities in Table 3-8 (see below) are identical to those for aliphatic carbon chains and rings in Table 3-5. Although many suffix names in Table 3-8 are slightly different, the prefix names for those 2nd tier functional groups are identical to those listed in Table 3-4 for aliphatic molecules.

Table 3-8. Aromatic family suffix names:

	Group Priority	Functional group type	Priority group then suffix	Examples:	
1	-CO-OH	Carboxylic acid	-oic		benzoic acid
2	-CO-OR	Ester	-oate		alkyl benzoate
3	-CO-X	Acyl halide	-oyl halide		benzoyl halide
4	$-CO-NH_2$	Amide	-amide[1]		benzamide
5	-CHO	Aldehyde	-al		benzaldehyde
6	-CN	Nitrile	-nitrile[2]		benzonitrile
7	$-CO-R^1$	Ketone	-one		phenylethan-1-one
8	-OH	Alcohol	-ol		Phenol
9	$-NH_2$	Amine	-ine		aniline
10	C=C	Alkene	-ene		Phenylethene
11	-CC-	Alkyne	-yne		Phenylethyne
12	$-CH_2-CH_2-$	Alkane	-ane		ethylbenzene
13	C-O-C	Ether[3]	none		ethoxybenzene
14	$-X^4$ and $-NO_2$	Halide[3], Nitro[3]	none		chlorobenzene
					nitrobenzene

1) also known as carboxamide

2) also known as carbonitrile

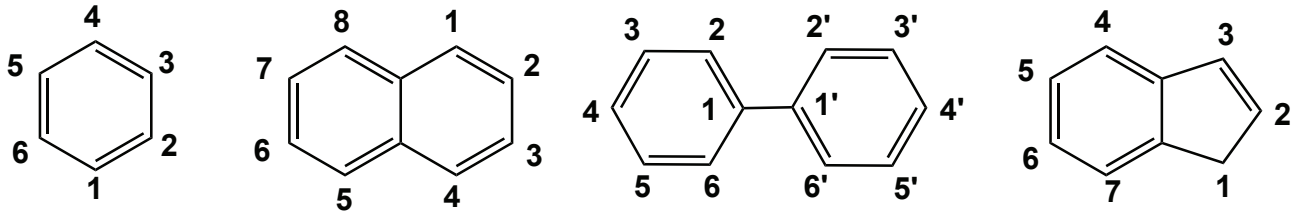
3) Never used as a suffix in an aromatic name, used only as a prefix: e.g. Ether prefix is alkoxy; halide prefix is halo; Nitro prefix is nitro-

4) for the halogens: fluoro, chloro, bromo, iodo,

Another slightly different issue for naming aromatic compounds concerns the numbering patterns around aromatic rings. Unlike for benzene, position numbering for many other polycyclic aromatic rings is fixed. However, positional numbering for benzene is determined in a fashion similar to that used for cyclic aliphatic rings. For benzene, like that for many alphatic structures, it is the PFG that is attached to #1C.

Examples of the IUPAC numbering system for some common aromatic structures is illustrated below:

Figure 3-25. General ring position numbers for some commonly encountered aromatic rings.



Benzene
3-66

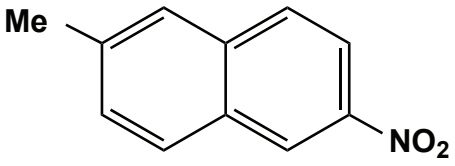
Naphthalene
3-67

Biphenyl
3-68

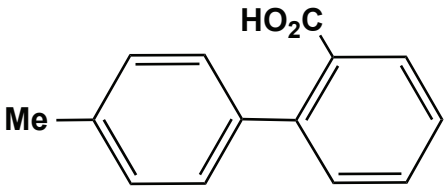
1-H-Indene
3-69

For the benzene structure 3-65, its position-1 or carbon-1 gets assigned to that carbon bearing the PFG on that substituted benzene ring. For aromatic ring skeletons **3-67**, **3-68** and **3-69**, their relative position numbering is fixed. However, even within these fixed numbering schemes for these other aromatic structures, priority groups (PFG) still are given the lowest position numbers possible within these condensed aromatic ring structures with their fixed locant numbering:

Figure 3-26. Examples of fixed position numbering for aromatic rings B and C:



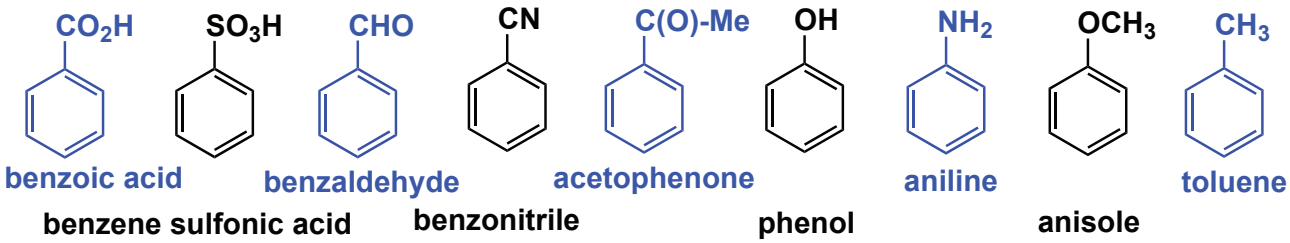
2-methyl-6-nitronaphthalene
methyl has priority
3-70



4'-methylbiphenyl-2-carboxylic acid
-CO_2H has priority
3-71

Although there are some slight differences in suffixes, both aromatic and aliphatic structures share a similar approach to nomenclature. One big difference between benzene and alphatic nomenclature is that IUPAC recognizes several common root (i.e. parent) names for certain benzene derivatives and those commonly encountered are shown below in descending priority (Lft-to-Rt) in accordance with those priorities in Table 3-8:

Root benzene names: parent-PFG



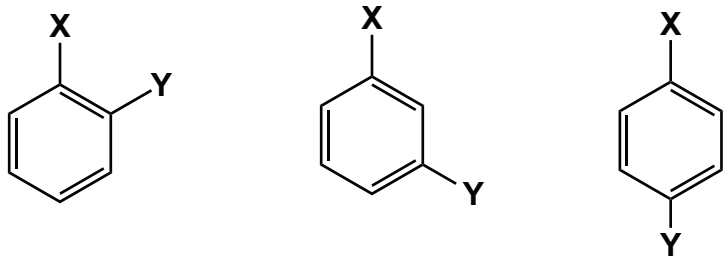
Priority (Lft-Rt): ⟹ **decrease, just like that in Table 3-8**

These root names are treated as if they are special types of super parent names that incorporate the (PFG) functional group names with parent aromatic benzene to form one super parent structural name. Application of this principle is illustrated first for some disubstituted benzene names and then also applied to some other examples of polysubstituted benzene derivatives.

If only one group is attached to a benzene ring then no numbering is necessary. For example see the examples shown in the far right column of Table 3-7 (e.g. phenyl or -Ph). However, disubstitution on a benzene ring can give rise to three different patterns of substituent attachment:

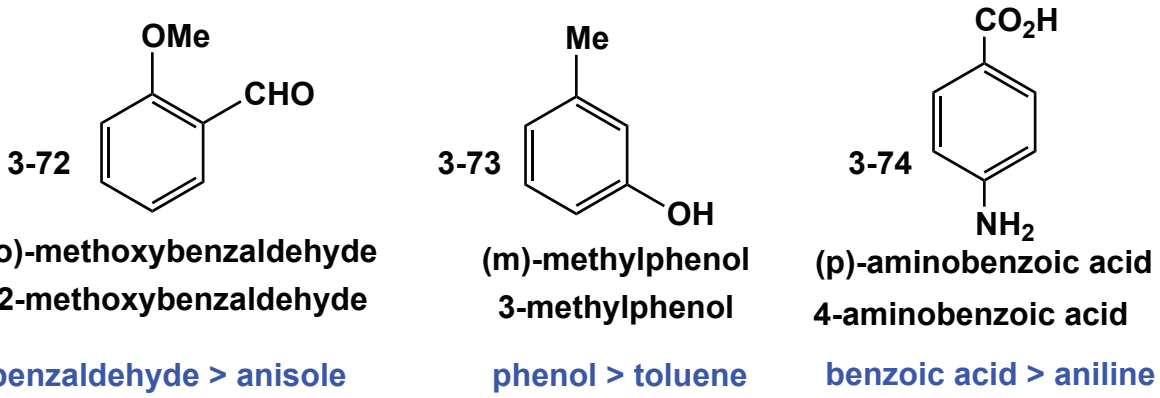
Figure 3-27. The three possible structural variations of disubstituted benzene derivatives

Disubstitution on benzene: Only three possible structural variations:



common nomenclature:	**ortho-**	**meta-**	**para-**
IUPAC:	**1,2-**	**1,3-**	**1,4-**

Figure 3-28. Examples of root nomenclature applied to disubstituted benzene derivatives:



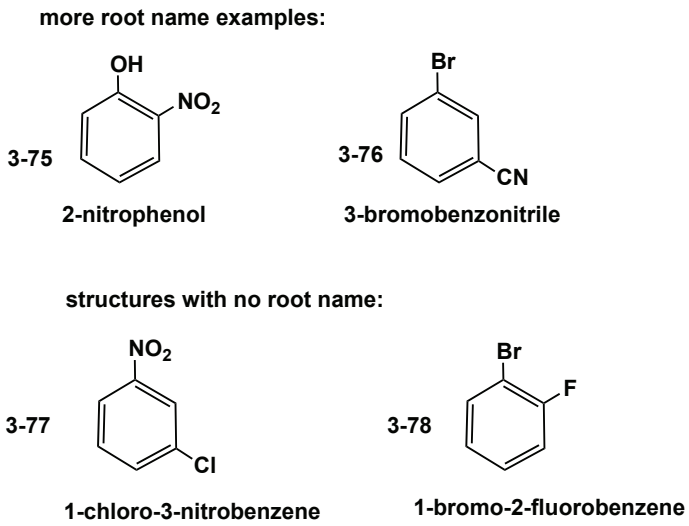
Parent name is formed from highest priority root name when more than one root name is possible.

Nomenclature rules for benzene derivatives:
Nomenclature for disubstituted benzene derivatives follows three, now familiar, types of rules:

Rule 1: If the PFG imparts a root name to the molecule, then the other substituent is treated as a derivative of that root benzene name.

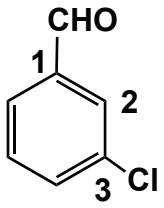
Rule 2: If the two groups on a benzene ring do not have root names, then identify the PFG and use that suffix.

Figure 3-29. Example applications of disubstituted benzene rules:



Q: Name the following molecular structures:

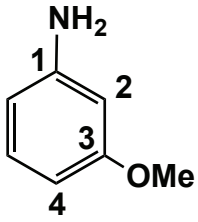
3-79



root is benzaldehyde, CHO at #1C

3-chlorobenzaldehyde

3-80



root is aniline

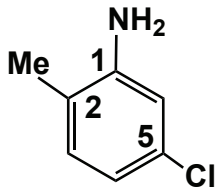
3-methoxyaniline

Situations for which the resulting numbering system may not be uniquely determined by a root name, or if there are no root names then determine the lowest possible locant positions for those substituents around the benzene ring. Then Rule 3 is applicable:

Rule 3: If the two groups are from the 2nd tier then FG_1 attached to #1C is that group which comes first in an alphabetic ordering of these substituent names. If numbering R-L is the same as L-R, then this numbering direction will be determined by which substituent comes second in this alphabetized set of substituents names.

Figure 3-30. Examples of benzene ring numbering with or without a root name:

3-81

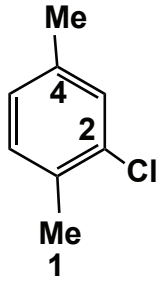


root is aniline (aniline > toluene), -NH_2 at #1C

numbering: 1,2,5 or 1,3,6 ; 2 < 3

5-chloro-2-methylaniline

3-82



no root name b/c 2 Me groups

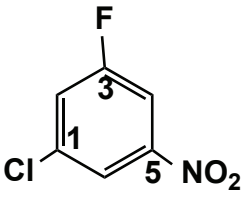
lowest position numbering:

1,2,4 vs 1,3,4 ; 2 < 3

alphabetize chloro, methyl, C before M

2-chloro-1,4-dimethylbenzene

3-83



No root name

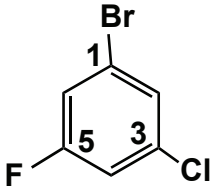
lowest position numbering:

1,3,5 vs 1,3,5; no preferred numbering

alphabetize chloro, fluoro, nitro; C before F before N

1-chloro-3-fluoro-5-nitrobenzene

3-84



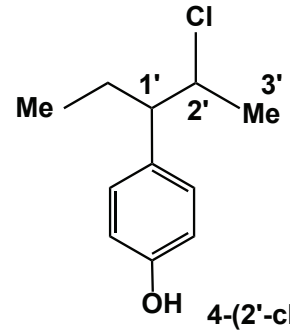
No root name : alphabetize bromo, chloro, fluoro:

B before C and F. This sets Br at #1C

C before F sets Cl at #2C

1-Bromo-3-Chloro-5- Fluorobenzene

Figure 3-31. Naming examples for some complex benzene derivatives:



3-85

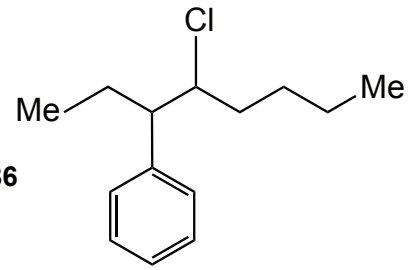
Root name is phenol

-OH at position #1C then alkyl chain attached to #4C

side chain: propyl with 2'-chloro-1'ethyl substituents

since Bz ring has priority; where Bz is attached to the side chain becomes position #1' on that side chain.

4-(2'-chloro-1'ethylpropane)phenol



3-86

3-chloro-2-phenyloctane

C_6 ring (Bz) vs C_8 chain, thus C_8 is parent chain

Chain numbering is 2,3 vs 5,6

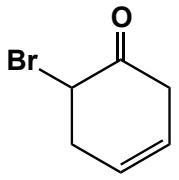
This benzene ring has no attached substituents. Benzene is a substituent and it has the prefix: phenyl

Phenyl, abbreviated as Ph- or even by the greek letter phi, $(-\Phi)$

substituent groups on chain are chloro and phenyl

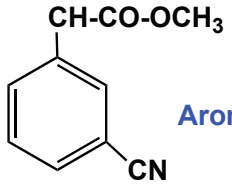
C is before P

Q: Identify the priority group in the following structures and whether or not they will be named according to the aliphatic or aromatic nomenclature schemes:



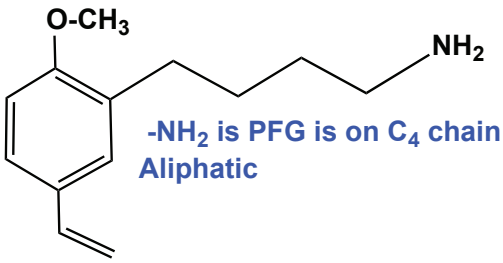
Alphatic C_6 Ring with C=O is PFG

3-87



Arom, -CN is PFG

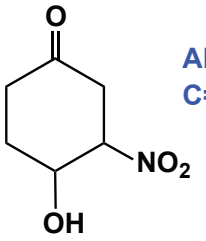
3-88



-NH_2 is PFG is on C_4 chain

Aliphatic

3-89



Alphatic C_6 Ring

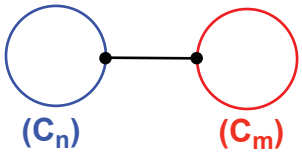
C=O is PFG

3-90

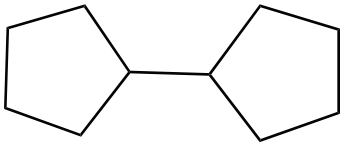
You now have the rules necessary to write proper names for about 85-90% of the organic compounds that will be discussed in this text. Any other nomenclature that might be required will be illustrated and explained, as it may be needed.

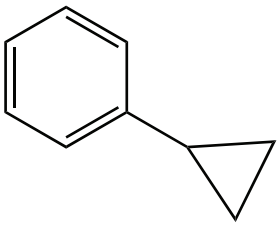
There are several other types of polycyclic structures that were not discussed in this introduction to nomenclature, but these types of structures will be encountered even in an introduction to Organic Chemistry. What follows below is a basic description for those molecules containing multiple rings and a brief summary of multi-ring types and how to identify them:

1. Substituent rings-no common atoms and 1 common bond connecting rings:



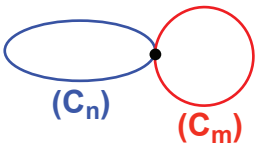
Examples:



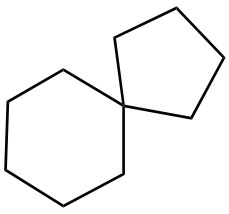


These types of substituent rings have already been discussed here in Ch. 3.

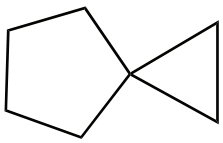
2. Spirocyclic rings just share 1 atom:



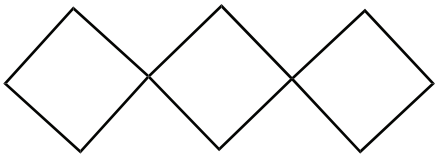
Examples:



spiro[5.4]decane

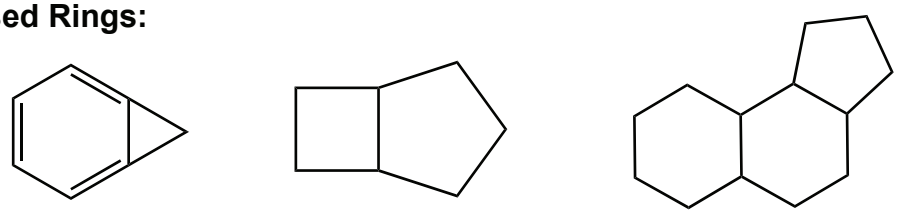


spiro[4.2]hexane



3. Fused rings share 2 atoms and 1 bond that also connects these two atoms . Fused rings share both ends of that 1 bond between two rings:

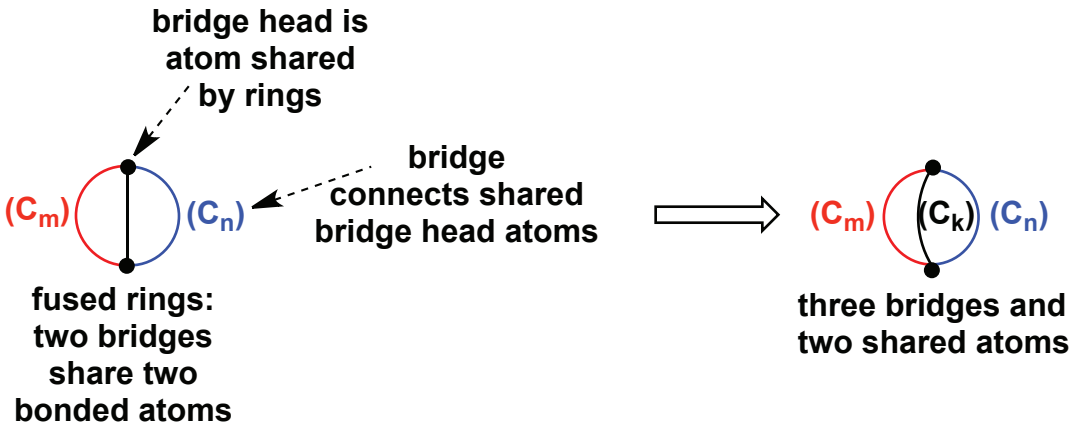
Fused Rings:



This fused ring terminology is used descriptively to highlight a structural relationship between two rings. This term is not used in formal nomenclature. Instead, fused rings are formally treated as if they are large rings that are bridged by a bond between two atoms.

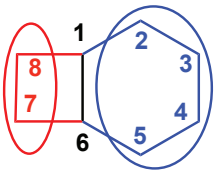
4. Bridged rings share ≥ 2 atoms and often more than one bond:
Rather than get into the weeds, here is some introductory guidance on at least identifying these types of more complex carbon skeletons:

Types of bicyclic rings share two bridgehead atoms:

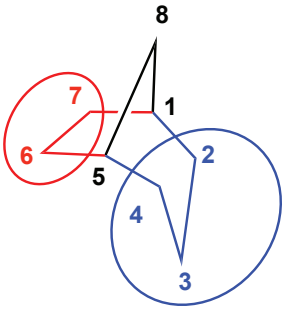


The number of bridging atoms defines basic ring structure, and if necessary for more complex structures also the locant positions of attachment (i.e. positions of attached by a bridging bond) for these bonds:

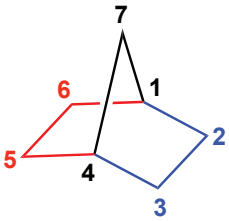
Examples:



[4.2.0] bicyclooctane

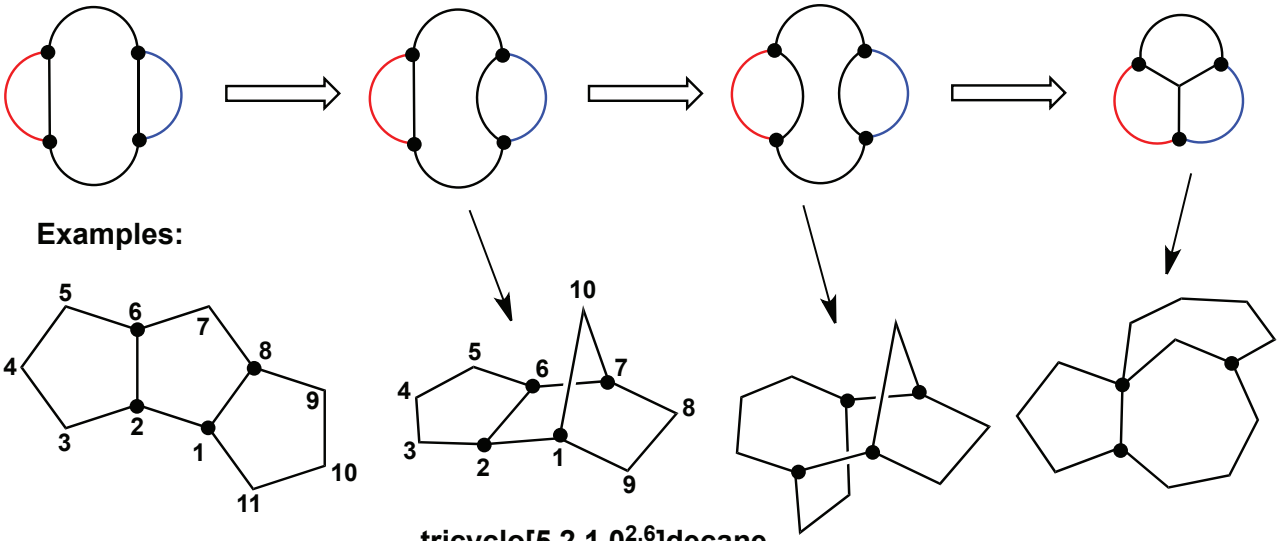


[3.2.1] bicyclooctane



[2.2.1] bicycloheptane

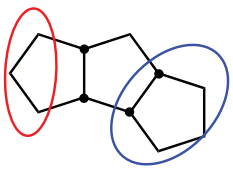
Tricyclic rings share three or four bridgehead atoms:

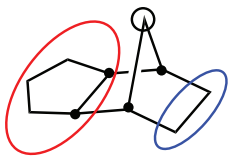


Examples:

tricyclo[6.3.0.0^{2,6}]undecene

tricyclo[5.2.1.0^{2,6}]decane





3-14. Conclusion:

One of the things that you might have noticed in this chapter is how we have moved from a description of structure into a discussion of how one parses a molecule's structure into its important structural components of carbon types and functional groups. In a way, this chapter also introduces a process for how to "read" a structure. Interpreting the fine points of molecular structure will become even more important when the reactions of functional groups are discussed in subsequent chapters. You'll find this skill will assist you in deciding not only whether or not a reaction can occur but also where on the structure this particular reaction is likely to occur.

In this chapter you also have been introduced to the formal process for naming organic structures. What was presented here illustrates the basic syntax of the nomenclature process. At the heart of this process is identifying the presence of a primary functional group (PFG) and the ring or chain onto which it is attached. These rules are summarized at the end of Section 3-12 for alphatic structures and modified for benzene derivatives in Section 3-13.

3-15. What you should be able to do and know:

1. Identify both the names and structures of those common functional groups as shown in Table 3-1 and 3-2.

2. Identify the four types of tetrahedral carbons (1^0, 2^0, 3^0, 4^0).

3. Identify types of alkenes (mono-, di-, tri-, or tetrasubstituted)

4. Identify the various types of polyunsaturated motifs (conjugated, cumulated and isolated).

5. Know the proper chain names from 1 to 10 carbon atoms in length.

6. Name molecules with carbon chains or rings of 10C or less, and also benzene derivatives.

7. Be able to draw a suitable structure from a given structural name

3-16. Problems:

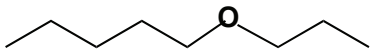
1. Draw an example of a molecule R-FG that containing the following combinations of functional groups:

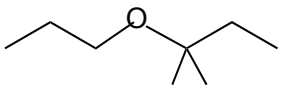
a) A molecule containing a cycloalkane, an unsaturated chain, and a nitro group:

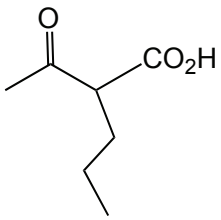
b) A molecule containing an aromatic ring, along with both chlorine and nitrile groups:

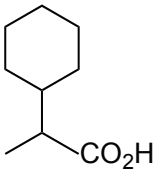
c) An unsaturated cyclic ring with an amide group:

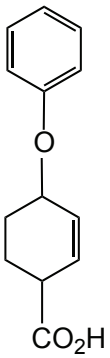
2. Determine the priority group and "main" chain for the following compounds, and briefly explain your selection:

a) 

b) 

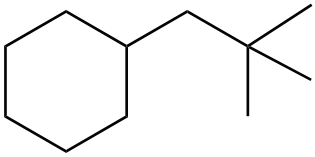
c) 

d) 

e) 

3. Identify the parent alkanes:

a)



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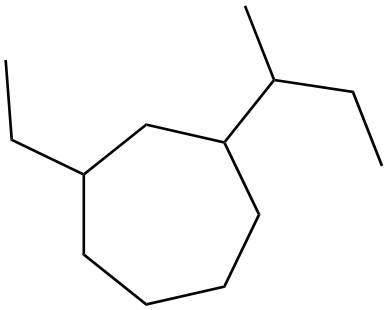

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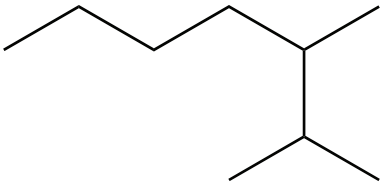


4. Go back to the structures in Q3 and identify the substituents by name and locant position. Make sure that you use a proper prefix for each substituent.

a.

b.

c.

5. For Q3 structures: b, c, and d now write a complete name:

a.

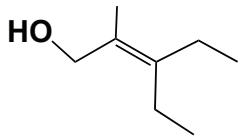
b.

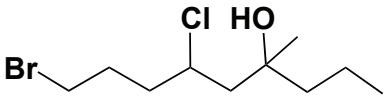
c.

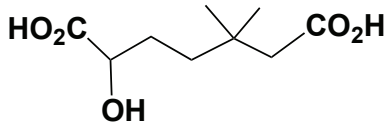
6. Draw a proper structural representation from the provided names:

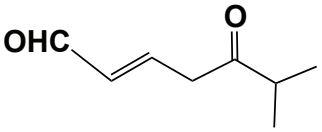
a) 2,5-dimethylheptane	**b) 3-methyl-1,3-cyclohexadienenitrile**
c) 1-isopentyl-3,4-dimethylcyclohexylamine	**d) 5-oxopentanoic acid**
e) 5-hydroxyheptanoic acid	**f) 4-phenylbutanoic acid**
g) 3-hydroxy-4-methyloctanedioic acid	**h) 2-isobutyl-55-dimethylhexanoic acid**
i) 4-(1-bromoethyl)heptanoic acid	**j) 4-methyl-8-oxo-3-nonenoic acid**

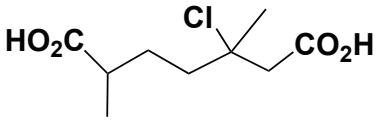
7. Name the following aliphatic structures:

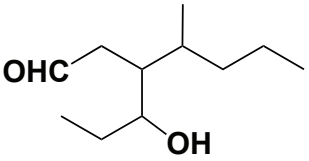
a) 

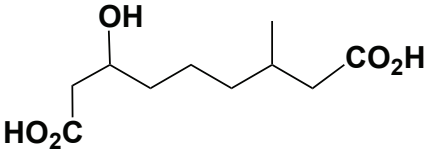
b) 

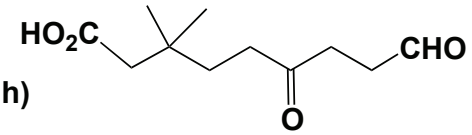
c) 

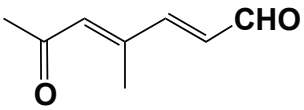
d) 

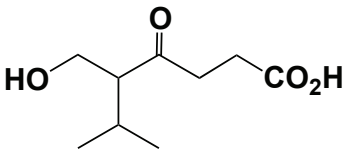
e) 

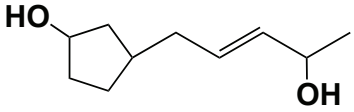
f) 

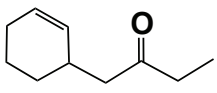
g) 

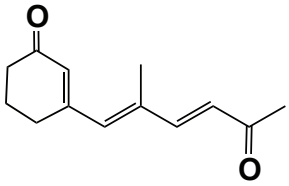
h) 

i) 

j) 

k) 

l) 

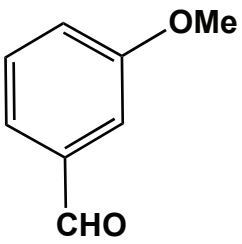
m) 

8. Draw a proper structure from its given name:

a) 3-methoxy-5-methylbenzoic acid	**b) 2,5-dimethylphenylacetate**
c) 1,3,5-benzenetricarboxylic acid	**d) 3-bromo-2-iodobenzoic acid**
e) 2,6-dimethylbenzonitrile	**f) 2-methoxy-6-nitrobenzoic acid**
g) 2-ethyltoluene	**h) 4-chloro-2-nitroacetophenone**
i) 3-bromo-4-methoxy-5-methylaniline	**j) 2-ethyl-5-methylbenzenesulfonic acid**
k) 1,2-benzenediamine	**l) 4-bromo-3-iodophenylacetate**
m) 3-methoxy-2-methyl-6-iodobenzonitrile	**n) 2-chloro-5-nitrobenzoic acid**
o) 4-tertbutyl-2-ethyltoluene	**p) 2,4-dinitroacetophenone**

9. Name the following benzene derivatives:

a)



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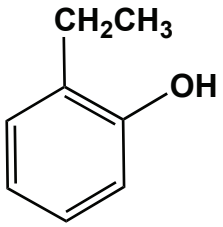

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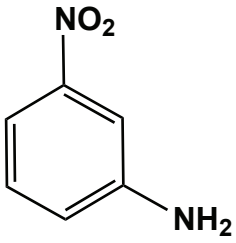
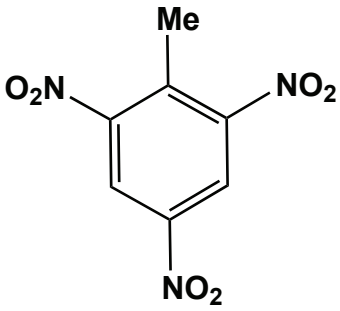


d)



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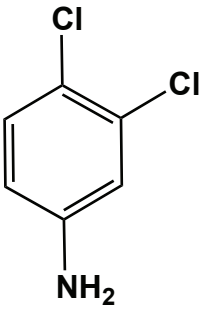

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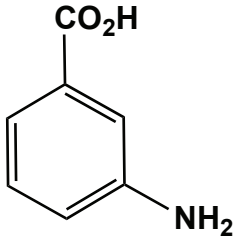

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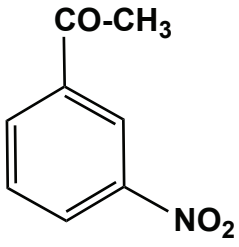

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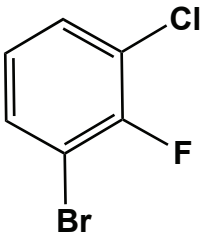
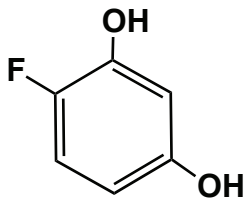
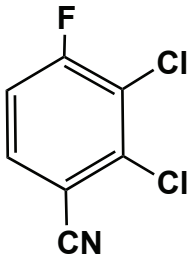
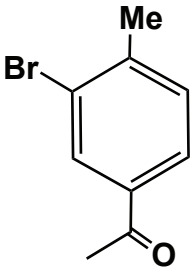
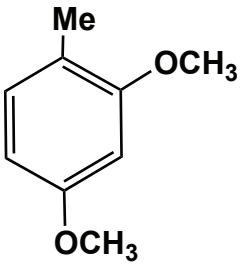
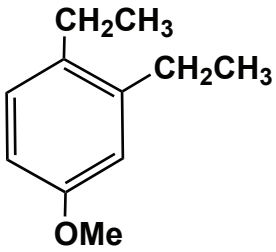


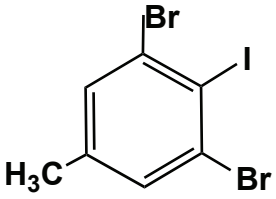
i) 

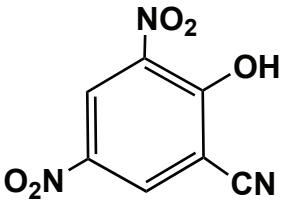
j) 

k) 

l) 

m) 

n) 

o) 

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