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Organic chemistry requires a language that is precise, concise and systematic. Not only do we have to communicate in the written and oral manner, but we must catalogue and store our information in a manner that allows us to retrieve it when searching through the literature. With the explosion of information that is occurring in our time, this becomes more important with each passing day. As a foreign language, organic is relatively simple. But as a scientific language, organic is probably more complicated than in any other science (I'm considering organic and biochemistry as a part of the same language). To our benefit, organic is also probably more organized than any other scientific language.

Our nomenclature topic covers about 20 functional groups of organic chemistry. A few more are listed for reference purposes and we will not cover many additional, but less frequently used functional groups. While common names are not stressed in these topics, there are a few that any student of organic chemistry should be familiar with. These will be given in the relevant sections. Don't be intimidated by these trivial names. They are included so you have a list of the more common examples (for consultation, not for memorization). A few aromatic derivatives (substituted benzene derivatives, etc.) are also included in the relevant functional group sections and at the end. If you have questions as you work through this chapter, visit an office hour for clarification. My hope is that you will be able to speak "basic organic" after finishing these pages. This nomenclature topic has been written with the goal that you can teach yourself too.

The following sequences of rules should usually produce an acceptable name for commonly encountered organic compounds. Accessible guidelines to a more complete strategy of nomenclature are provided in Section C of the CRC "Handbook of Physics and Chemistry". An even more complete compilation of rules of organic nomenclature is provided in "A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations, 1993", (IUPAC = International Union of Pure and Applied Chemistry).

As we proceed through organic chemistry we will often focus our interest on a limited portion of a structure when the remainder of the structure is not important to the topic of discussion. Symbolic representations for generic portions of a structure are given below and are commonly used. We will often use these representations in this and the coming chapters.

R = any general carbon group (it sometimes includes hydrogen too)

Ar = any general aromatic group, (when more specificity than 'just' R is desired)

The foundation of organic nomenclature requires an ability to name alkanes, alkenes and alkynes. Learning the rules for these groups will be your biggest nomenclature challenge. Many functional group patterns have a prefix (if lower priority) and a suffix (if higher priority) to specify their presence. Numbers on the longest specified chain will identify their locations. It's all very organized, but it does require practice. As usual in school, you are the only one who can do that. Pencil, paper and your hard work provides the most reliable path to success.

I. Nomenclature Rules For Alkanes and Cycloalkanes

The following list provides the names for carbon straight chains of various lengths. They must be memorized (through C_{19} for problems in this book, $C_{11} - C_{19}$ is easier than you think).

CH_4	methane (C_1)	C15H32	pentadecane (C_{15})	$C_{20}H_{40}$	nonaicosane (C ₂₀)
C_2H_6	ethane (C_2)	$C_{16}H_{24}$	hexadecane (C_{16})	$C_{29} H_{c2}$	triacontane (C_{20})
C ₃ H ₈	propane (C ₃)	$C_{17}H_{26}$	heptadecane (C_{17})	$C_{21}H_{c4}$	hentriacontane (C_{21})
$C_{4}H_{10}$	butane (C_4)	$C_{10}H_{20}$	octadecane (C_{18})	$C_{22}H_{cc}$	dotriacontane (C_{22})
$C_{5}H_{12}$	pentane (C_5)	$C_{10}H_{40}$	nonadecane (C_{10})	$C_{22}H_{40}$	tritriacontane (C_{22})
$C_{6}H_{14}$	hexane (C_6)	$C_{20}H_{42}$	icosane (C_{20})	$C_{24}H_{70}$	tetratriacontane (C_{24})
$C_{7}H_{16}$	heptane (C_7)	$C_{21}H_{44}$	henicosane (C_{21})	$C_{25}H_{70}$	pentatriacontane (C_{25})
$C_{8}H_{18}$	octane (C_8)	$C_{22}H_{46}$	doicosane (C_{22})	C_{2} H_{74}	hexatriacontane (C_{26})
$C_{9}H_{20}$	nonane (C_9)	$C_{22}H_{49}$	tricosane (C_{22})	$C_{27}H_{74}$	heptatriacontane (C_{27})
$C_{10}H_{22}$	decane (C_{10})	$C_{24}H_{50}$	tetraicosane (C_{24})	$C_{20}H_{70}$	octatriacontane (C_{29})
$C_{11}H_{24}$	undecane (C_{11})	$C_{25}H_{52}$	pentaicosane (C_{25})	$C_{20}H_{00}$	nonatriacontane (C_{20})
$C_{12}H_{26}$	dodecane (C_{12})	$C_{24}H_{54}$	hexaicosane (C_{26})	C40He2	tetracontane (C_{40})
$C_{13}H_{28}$	tridecane (C_{13})	$C_{20} - 34$	heptaicosane (C_{20})	0401182	(040)
$C_{14}H_{30}$	tetradecane (C_{14})	$C_{28}H_{58}$	octaicosane (C_{28})		
		4 M M M M M M M M M M M M M M M M M M M	. 40%		

Basic Steps to Name an Alkane

1. Locate the longest carbon chain present. This becomes the parent name. Make sure to check at each branch point for the longest chain path. (Unless it is obvious, count at each branch point through all possible paths.)



If there are several branches radiating out from a central carbon, you can count how long those branches are and use the longest two plus the central carbon and add them all together.



Number the longest chain from the end nearest a branch point or first point of difference. (The lowest first branch number decides which end of the chain you number from in an alkane.)



A lower number for the substituent branch, R, is preferred. C_4 is better than C_9 so number from the left end. The number will be used to specify the position of the alkyl branch

If additional branches are present, the lowest number of the first branch determines the numbering direction on the longest chain.



The direction of the numbering is reversed because the new branch would get a lower number, C_3 , at the first point of difference, than C_4 if the numbering occurred from the opposite direction.

When an alkane portion is present as a substituent or branch (i.e. it is not part of the longest carbon chain) one drops the -ane suffix of a similar length alkane and adds the suffix -yl. Alkane becomes alkyl when it is a substituent; (ethane → eth + -yl → ethyl.) These substituent names are placed in front of the parent name, as

prefixes, with their designating numbers immediately in front of them. Use the numbers obtained from rule 2 to show the location(s) of any substituent(s) or branch(es). Each substituent gets a number, even if it is identical to another substituent and on the same carbon. Hyphens are used to separate the numbers from the letters. Separate substituent position numbers from one another with commas (if the numbers are adjacent). The substituents are listed in alphabetical order. The numerical prefixes (see rule 3) do not count in deciding the alphabetical order (unless they are inside parentheses).



There are three one carbon branches on C3, C5 and C9 carbons and two two carbon branches, both on the C8 carbon. The first branch at C3 determines the direction of numbering because it generates the lowest possible number at the fist point of difference.

IC branch = methyl	C branch = hyptyl
2C branch = ethyl	8C branch = octyl
3C branch = propyl	9C branch = nonyl
4C branch = butyl	10C branch = decyl
5C branch = pentyl	11C branch = undecyl
6C branch = hexyl	12C branch = dodecyl

3. For identical substituents, use the prefixes di-, tri-, tetra-, penta-, hexa-, etc. to indicate 2, 3, 4, 5, 6, etc. of these substituents. These prefixes are not considered in deciding the alphabetical order of each substituent (unless inside parentheses).



4. With two or more possible longest chains of identical length, choose as the parent name the one with the greater number of substituents. This will produce simpler substituent names.



7-butyl-8,8-diethyl-2,5,10-trimethyl-9-propyldodecane

correct order, your structure will still be drawn correctly from the given name.

- 5. For complex substituents (substituents that have substituents on themselves), follow the above rules for alkanes except:
 - i. The -ane suffix of the subparent name is changed to -yl (see rule 2 above)

ii. The longest chain of the complex branch always uses the carbon directly attached to the parent chain as C_1 . Starting at this position one would count the longest substituent chain possible, as shown below.

iii. Parentheses are used to separate the entire complex substituent name, its numbers, its branches, and its subparent name, from the principle parent name. A number and a hyphen precede the entire complex substituent name in parentheses to indicate its location on the parent chain. If the complex branch has a common name, this can be used and no parentheses are necessary, but you have to memorize these.

iv. Prefixes do count in alphabetizing the branch names when part of a complex substituent name and inside parentheses. This is not true for simple substituents on the parent chain.



Outside the parentheses the numerical prefix does not count for alphabetical order, but inside the parentheses the numerical prefix does count for alphabetical order. If you do not write these prefix names in the correct order, your structure will still be drawn correctly from the given

8-(1,2-dimethylpropyl)-7-(1-ethylbutyl)-2,10-dimethyl-5-(2-methylpropyl)-9-propyldodecane

alphabetical = dimethylpropyl > ethylbutyl > dimethyl > methylpropyl > propyl "d" (parens) "m" (no parens) "m-p" "e" "p"

Examples





All of the above are: 3,3-diethylhexane



Rule 1 - The longest chain is six carbons. Rule 2 - Number from the end closer to the two two carbon branches, as C₃ positions instead of C₄ positions.

Rule 3 - Name two carbon branches as 3-ethyl and 3-ethyl.

Rule 4 - Use the di prefix since there are two ethyl substituents.

There are many ways to get this name in this particular compound.

In this example, the parent name would still be hexane (6 carbons long). This would be the only acceptable parent "hexane". The chain would have to be numbered this way because the methyl substituent gets a lower number than any other possibility, 2-methyl. The 3.3-diethyl would come alphbetically before 2-methyl, and would appear first in the name.



6-(1,2-dimethylbutyl)-5-methyl-4-(1-methylethyl)-6-pentyldodecane

<u>Problem 1</u> – Provide an acceptable name for the following structures.

/3' 4'





There are a number of specialized terms used to refer to the number of carbon structures and branches bonded to a specific atom (carbon or nitrogen below). For nomenclature purposes we will introduce them here, but you will also have to know some of them to predict patterns of reactivity when you start studying organic reactions later in the course. Learning these terms is memorization, just like learning a new friend's name. You have to use them to become familiar with them.

1. **Primary patterns** (1°) - If a carbon has only one other carbon attached to it, it is called a primary carbon (1°) , and if a nitrogen has only one carbon attached to it, it is called a primary amine (1°) . Similar terms are used with amides.



2. Secondary patterns (2°) - If a carbon has only two carbons attached to it, it is called a secondary carbon (2°), and if a nitrogen has only two carbons attached to it, it is called a secondary amine (2°). Similar terms are used with amides.



3. Tertiary patterns (3°) - If a carbon has three carbons attached to it, it is called a tertiary carbon (3°) , and if a nitrogen has three carbons attached to it, it is called a tertiary amine (3°) . Similar terms are used with amides.



4. Quaternary patterns (4°) - If a carbon has four carbons attached to it, it is called a quaternary carbon (4°), and if a nitrogen has four carbons attached to it, it is called a quaternary ammonium ion and has a positive formal charge.



There are also three special names for one carbon groups having different numbers of hydrogen atoms attached to them.



Frequently encountered common names for alkyl branches

1. The letter n (= normal) signifies a straight chain branch, with no subbranches on itself. If used, the "*n*" is not part of the alphabetical ordering, i.e. *n*-propyl is alphabetized under "p". Also the *n* is italicized in typing or underlined in writing. (We won't follow this rule.) It is generally assumed that if the *n* is not present, a straight chain branch is present. Its use is disappearing and we will rarely use it (common commercial product that we use: n-butyl lithium).

$$CH_{3}CH_{2}CH_{2}-X \qquad CH_{3}CH_{2}CH_{2}CH_{2}-X \qquad CH_{3}CH_{2}CH_{2}CH_{2}-X \qquad CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}-X \\ n-propyl "X" \qquad n-butyl "X" \qquad n-pentyl "X" \qquad n-hexyl \ n-hexyl \$$

2a. The "iso" pattern is a simple three carbon chain with only one branch or substituent on the middle carbon. The "iso" prefix <u>is</u> part of the name and <u>is</u> used in alphabetizing the substituent name. It is <u>not</u> italicized. If the "iso" pattern is present with additional carbons in a straight chain the <u>root</u> name includes the total number of carbons.



"iso" is part of the name and used to alphabetize

Note - This pattern can be written and twisted in a variety of ways, but all are still called "iso".

b. A substituent at a secondary carbon of the four carbon straight chain is sometimes designated with special notation. Such a substituent is prefaced with "*sec*", which stands for secondary. This designation is only unambiguous for the four carbon chain. With five carbons or more it becomes ambiguous and is not used. The "*sec*" portion is italicized when typed or underlined when written. (Again, we won't follow this rule.) Also "*sec*" is not used in alphabetizing the substituent.

3. The *tertiary* or "*tert*-" or "*t*-" pattern has three methyl groups attached to a central carbon with a fourth bond to a carbon or substituent group. The "*tert*-" or "*t*-" prefix is italicized (or underlined) and is not alphabetized in a manner similar to "*sec*". (Again, we won't follow this rule.) If the "*t*" pattern is present with additional carbons in a straight chain the <u>root</u> name includes the total number of carbons (like iso).



а

b.

c.

d.

e.

f.

4. "Neo" groups have three methyls and an additional fourth methylene carbon group around a central 4° carbon atom (a minimum of five carbons). The "neo-" prefix is part of the substituent name (just like iso) and is used to alphabetize the substituent. It is not italicized or underlined. The central carbon with four other carbons attached is a quaternary carbon. If the "neo" pattern is present with additional carbons in a straight chain the <u>root</u> name includes the total number of carbons (like iso).



"neo" is part of the name and used to alphabetize

If there is a choice (e.g. you are naming the compound), it is preferable to use systematic nomenclature and to not use the trivial names above. However, when familiar complex substituents are present as branches on larger parent chains, the temptation to use the simple common names is often overwhelming to avoid the complex names with their multiple numbers, branches and parentheses. Also, other people use the trivial names and you may need to interpret such nomenclature (*n*-butyl lithium, *sec*-butyl lithium, *t*-butyl lithium). Learning the above terms is memorization, just like learning a new friend's name. You have to use them to become familiar with them. Work your way around the following oval several times and you will know them.

<u>Problem 2</u> - Identify each of the substituent patterns below by its common name. Point out an example of a 1° , 2° , 3° and 4° carbon and nitrogen. Also, point out an example of a methyl, methylene and methine (methylidene) position.



Naming Cycloalkanes

A ring is formed when a chain of atoms connects back on itself. This is possible with as few as three atoms and can be of unlimited size. There are ring structures in the literature numbering in the hundreds. There are only minor differences in the nomenclature of cycloalkanes and acylic alkanes. Often a ring can be drawn in more than one way. You just have to count the carbons to know what the parent name will be.

1. Attach a prefix of cyclo- to the name of a cyclic alkane possessing the same number of carbons as the straight chain name. A cycloalkane has the carbons connected in a ring. The smallest possible ring has 3 carbons. The following are unsubstituted cycloalkanes up to C_{12} .



2. With only one alkyl branch, name the structure as an "alkylcycloalkane". No number is necessary since there is only one substituent present.



3. With two or more alkyl substituents, number about the ring so as to obtain the lowest number possible at the first point of difference. In cycloalkanes, alphabetic order is used to determine the number one position if the numbers are similar. In the second example below, numbering is based on lowest number, not alphabetically.



Priority based on lowest possible number at first point of difference (5 versus 7 for butyl). Alphbetical order is used for the branch names

4. If a chain component has more carbons than the ring, then the chain may become the parent name and the cyclic portion a branch (ends in "-yl"). However, if it is easier to name as a cycloalkane, that is acceptable.



3-cyclopentyloctane



1-methyl-3-(1-methylethyl)cyclopentane or 1-isopropyl-3-methylcyclopentane

priority based on alphbetical order of branch names



3-cyclohexyl-2,2,3,4,4-pentamethylpentane

5. If the ring is classified as the substituent, the C_1 carbon of the ring (for numbering purposes) is the carbon directly attached to the parent chain. Number around the ring in the direction to give the lowest number at the first point of difference (or the lowest number to the highest priority feature in the ring, once functional groups are included).



6. When two substituent groups are on the same side of a cyclic structure (both on top or both on bottom), the "*cis*" prefix is used. When two groups are on opposite sides (one on top, one on bottom) and on different carbons, the "*trans*" prefix is used. These terms go just before the designating number and are separated from the number by a hyphen. The terms "*cis*" and "*trans*" are italicized (or underlined, if written) and not used in alphabetizing. (We won't follow this rule.)



7. We won't use the cis/trans rule when more than two substituents are present in a ring at different carbons.

<u>Problem 3</u> – Provide an acceptable name for each of the following structures.



II. Nomenclature Rules For Alkenes

1. The parent name will be the longest carbon chain that contains both carbons of the double bond. Drop the -ane suffix of the alkane name and add the –ene suffix. Never name the double bond as a prefix. If a double bond is present, you have an alkene, not an alkane.

alkane + -ene = alkene

2. Begin numbering the chain at the end nearest the double bond. Always number through the double bond and identify its position in the longest chain with the <u>lower</u> number. In the older IUPAC rules (American system) the number for the double bond was placed in front of the stem name with a hyphen. Under the newer rules (European or British system), the number for the double bond is placed right in front of "ene", with hyphens. We will use the newer rules for specifying the location of pi bonds.

1 2 3 4 5 6H₃C-CH=CH-CH₂-CH₂-CH₃

hex-2-ene (newer rules)

2-hexene (older rules)

I

3. Indicate the position of any substituent group by the number of the carbon atom in the parent (longest) chain to which it is attached.

5,6-dimethylhept-3-ene (newer rules)

5,6-dimethyl-3-heptene (older rules)

Numbering is determined by the double bond, not the branches, because the double bond has higher priority than any alkyl branch.

4. Number cycloalkenes so that the double bond is 1,2 (number through the double bond). Number in the direction about the ring so that the lowest number is used at the first point of difference.



5. One method to designate the geometry about a carbon-carbon double bond having two different groups on each carbon is by using "*cis*" (if two similar groups are on the same side) or "*trans*" (if two similar groups are on opposite sides). The two sides referred to are determined by a plane running through the two, connected carbons of the double bond, parallel to the p orbitals of the pi bond. If *cis/trans* identifiers are used, the substituent groups are usually obvious. Note that if there are two identical groups attached to the same carbon of the double bond, then *cis/trans* structures do not exist (they are not possible). Cis/trans isomers can also be called "geometric isomers". They represent a special type of stereoisomer and can also be called diastereomers. We will study distereomers in the chapter on stereochemistry.



If four different groups are attached to the carbons of the double bond, you need to use the E/Z nomenclature convention (you can also use this system even if only two groups are present). In the E/Z system of classification the atoms attached to each carbon of a double bond are assigned a **priority** based on atomic number. Higher atomic number atoms are assigned a higher priority. In organic chemistry we are mostly concerned with the halogens, oxygen, nitrogen, hydrogen and occasionally sulfur and phosphorous. It would seem like nothing could be lower than a hydrogen, but a lone pair of electrons is the lowest of all (...so I > Br > Cl > S > P > F > O > N > C > H > lone pair of electrons). If the attached groups at carbon are different, but the directly attached atoms are identical, the highest priority path in each group must be followed until a distinction can be made.

The relative positions of the high priority groups at each carbon of the double bond are compared. If the two high priority groups (on different carbons) are on the same side of the double bond, they are classified as Z from the German word **zussammen**, meaning together (...notice "same" in the middle of zussamen?...or think "Z-BIG groups are on Z-SAME side", said with a French accent). If the high priority groups (on different carbons) are on opposite sides of the double bond, then the double bond is classified as E from the German word "**entegegan**", for opposite. To interconvert one geometric isomer to the other requires enough energy to break the pi bond (typically, over 60 kcal/mole). Background thermal energy is about 20 kcal/mole, so this interchange is very, very slow. Each carbon of the double bond with the two different groups is called a **stereogenic center** (**or atom**), because if the two groups are switched, a new stereoisomer is formed. The symbols E and Z specify the **configuration** of the double bond (configuration can be thought of as a relatively stable stereochemical arrangement of atoms in our world, not to be confused with conformation = single bond rotations).



The priority rules are quite extensive to cover all of the possibilities (to classify every E/Z scenario...and later, R/S configurations). We will not look at all such possibilities, but will focus on some that are more common. These rules arose from a state of confusion that existed up to about the middle 1950's, when three chemists cleared things up with a set of defining rules. Sidney Cahn, Christopher Ingold and Vladimir Prelog were the chemists and that has become the name of the defining rules ("CIP" for short).

Some basics rules of the CIP (Cahn-Ingold-Prelog) sequence rules for defining priorities are listed below (E/Z here and R/S in the stereochemistry topic). We will elaborate these rules in our chapter on stereochemistry.

- 1. Higher atomic number = higher priority (typical possibilities in organic chemistry: I > Br > Cl > S > P > F > O > N > C > H > lone pair)
- 2. If two (or more) directly attached atoms are the same, then compare the atoms attached to them in order of decreasing priority, (based on atomic number). Make a priority designation at the first point of difference. Always follow the highest priority path along each atom to make the designation. A single higher priority atom takes precedence over any number of lower priority atoms.
- 3. Double and triple bonds are treated as if they are bonded to the same atoms two or three times, respectively. However, those hypothetical atoms do not continue beyond that connection, as real atoms would.

Example



<u>Problem 4</u> - Classify the order of priorities among each group below (1 = highest). The "*" specifies attachment to a stereogenic center.



Problem 5 - Classify each alkene, below, as E, Z or no stereochemistry present.



All small rings are 'cis' inside the ring, but not all are Z. The E/Z terms are part of a classification system. If you change any atom in a structure you may alter the priorities and change the absolute configuration (E or Z).

6. Rings having a double bond and seven carbons (atoms) or less are only stable with a *cis* geometry (in the ring). The *cis* designation is almost never explicitly written in such rings, but understood to be required.



It is too difficult for trans groups to connect to one another until there are at least 8 atoms. Even in a cyclooctene, the trans stereoisomer is about 10 kcal/mole less stable than the cis isomer. However, if the ring gets big enough, the trans isomer becomes the more stable stereoisomer, as is our usual expectation.



7. If more than one double bond is present, the prefixes di-, tri-, tetra-, etc. are used for 2, 3, 4, etc. of the double bonds. An "a" is added between the "alk" stem and the "ene" suffix part for better phonetics (i.e., alkadiene, alkatriene, etc.) A number is required for each double bond present. Place any numbers right in front of the "ene" prefix. (Remember, one always uses the lower of the two numbers possible for each occurance of a double bond.) The *cis/trans* nomenclature should be indicated just previous to each number, when relevant. A hyphen separates the letters from the numbers. *Cis* and *trans* are italicized when typed or underlined when written, and they are not alphabetized when applicable. (We won't follow this rule.) If E/Z terms are used to specify the pi bond configuration, they can be written just after the number or all of the configurations can be placed in parentheses in the front of the name.

alk	+	а	+	diene =	alka-#,#-diene
alk	+	a	+	triene =	alka-#,#,#-triene
alk	+	a	+	tetraene =	alka-#,#,#,#-tetraene
					- 1



9. When double bonds are present in lower priority substituent branches, they are named as indicated above with the C_1 carbon being the point of attachment to the parent chain. As a substituent, the name will end in "yl" as in alkenyl, not alkene. Two common alkene branch names you should know are "vinyl" and "allyl".





The following are some examples of frequently encountered alkene substituent and compound "trivial" or "common" names. You should know "vinyl" and "allyl" substituents.



- a. 2-methylbut-2-ene (no E/Z or cis/trans possible with two identical groups on one carbon)
- b. 4-(2-methylcycloprop-2-enyl)-4,5-dimethylhex-2E-ene
- c. 1-ethyl-4-heptylcyclohexa-1,4-diene (numbers based on alphabetical order)
- d. 1,5,5-trimethylcyclohex-1-ene (numbers based on the first methyl group and number through C=C)
- e. 1-allyl-6-vinylcycloocta-1,3,5,7-tetraene or 1-ethenyl-6-(prop-2-enyl)cycloocta-1,3,5,7-tetraene

<u>Problem 6</u> – Provide an acceptable name for each of the following structures.



III. Nomenclature Rules For Alkynes

1. Pick the longest carbon chain which contains the triple bond as the parent name. Drop the -ane suffix of the alkane name and add -yne.

alkane + yne = alkyne

2. Begin numbering the chain at the end nearest the triple bond to assign it the lowest possible number. Write the number immediately preceding "yne" with hyphens on both sides. Triple bonds do not have E/Z stereoisomer possibilities, because of their linear shape, so these terms are not needed.

 $R-C\equiv C-R$ No E/Z stereoisomers possible

3. Indicate any substituent groups by the number of the carbon atom in the longest chain to which they are attached.



6-ethyl-7-methyloct-3-yne

4. Number cycloalkynes so that the triple bond is 1,2 (number through the triple bond). Number in the direction about the ring so that the lowest number is used at the first point of difference. Like the cycloalkenes, there are no stable cycloalkynes until there are at least 8 atoms in the ring (cyclooctyne). It takes that many atoms to reach around and attach the ends to one another. Even with eight atoms in the ring the linear shape of the triple bond is distorted, producing a higher potential energy state and more reactive triple bond. (Build a model and look at it.)



6. If more than one triple bond is present, a numerical prefix is used to indicate the appropriate number of triple bonds. Just as with alkenes, an "a" is added between the "alk" stem and the "yne" suffix part for better phonetics (i.e., alkadiyne, alkatriyne, etc.) A position number is provided for each occurrence. Hence, alka-#,#-diyne, alka-#,#,triyne, alka-#,#,#-tetrayne, etc. are used for 2, 3, 4, etc. of the triple bonds.

alk	+	a	+	diyne =	alka-#,#-diyne
alk	+	a	+	triyne =	alka-#,#,#-triyne
alk	+	а	+	tetrayne =	alka-#,#,#,#-tetrayne

9. When triple bonds are present in lower priority substituent branches, they are named as indicated above with the C_1 carbon being the point of attachment to the parent chain. As a substituent, the name will end in "yl" as in alkynyl, (not alkyne).



1-methyl-3-(4-methylpent-2-ynyl)cyclohexa-1,3-diene

The following are some examples of frequently encountered compounds and one alkynyl substituent "trivial" or "common" names. You should know "propargyl".

 $H-C\equiv C-CH_2$ $H-C\equiv C-H$ $R-C\equiv C-R$ $CH_3-C\equiv C-CH_2CH_3$ propargyl "X"common: acetylene
IUPAC: ethynecommon: dialkylacetylene
IUPAC: pent-2-ynecommon: ethylmethylacetylene
IUPAC: pent-2-yne

Examples You should know all of these.





c.

d.





- a. 4-ethyl-5-methylhex-2-yne
- b. 4-(2,2-dimethylcycloprop-1-enyl)-6-isopropylcyclooct-1-yne

b.

- c. 2,2,7-trimethylocta-3,5-diyne
- d. 1-cyclopentyl-3-ethyl-4,4-dimethylpent-1-yne
- e. 5-(1-methylpent-2-ynyl)-1-(2-methylprop-2-enyl)cyclohex-1-ene

<u>Problem 7</u> - Provide an acceptable name for each of the following structures. (Know how to do all of these.)



IV. Nomenclature Rules If Both Alkene(s) and Alkyne(s) Are Present

If both double and triple bonds are present, the parent name becomes alk-#-en-#-yne. The alkene part always comes before the alkyne part. Numbers are required for every pi bond. The numbers for any alkene(s) are placed directly in front of "ene" and separated from the name with hyphens and the number for any alkyne(s) are placed prior to "yne", also separated by hyphens. Because the trailing "yne" begins with a vowel (y), the final "e" of "ene" is dropped. If more than one double or triple bond is present, the appropriate numerical prefixes are also used (di-, tri-, etc.). If an alkene has stereogenic centers use the appropriate E/Z designation with its location number.

alk-#-en-#-yne

alka-#,#-dien-#,#,#-triyne

All other things being equal, the alkene is higher priority than the alkyne for numbering purposes. The structures below would all start with the #1 position at the first carbon of the alkene pi bond.



non-1-en-8-yne



hexa-1-*trans*-3-dien-5-yne (3E)-hexa-1,3-dien-5-yne

hexa-1,3E-dien-5-yne



cycloundec-*cis*-1-en-4-yne (1Z)-cycloundec-1-en-4-yne

cycloundec-1Z-en-4-yne

However, if a lower initial number can be used by assigning the triple bond a higher priority, then it takes precedence. Alternatively, if an alkene and an alkyne are equally positioned, a substituent can determine the direction of the numbering in order to assign it the lowest possible number. The following examples should clarify this point.



pent-3E-en-1-yne pent-*trans*-3-en-1-yne

The priority changes because a lower first number can be assigned to the triple bond.



4,4-dimethylnon-8-en-1-yne

The priority changes due to lower numbers for the methyls.



5-(but-2E-enyl)nona-5Z7D-dien-1-yne

The priority changes because a lower first number can be assigned to the triple bond. The nine carbon chain with two double bonds is chosen over the nine carbon chain with one double bond.

Examples of " ene " plus " yne " hydrocarbons (You should know all of these.)



5-ethenylocta-1,3Z-dien-6-yne

The 6,7 triple bond is chosen over the 6.7 double bond because it is a longer chain.



- a. nona-3E,7E-dien-1,5-diyne or (3E,7E)- nona-3,7-dien-1,5-diyne
- b. 5,5-dimethylhept-1-en-3-yne
- c. 2-(1-methylpropyl)pent-1-en-3-yne or 2-sec-butylpent-1-en-3-yne
- d. 3-(4,4-dimethylcyclobut-2-enyl)pent-1-en-4-yne (a tie goes to the alkene)





V. Functional Group Nomenclature

Many commonly encountered functional groups in organic chemistry are discussed below. Only a "bare bones" list is provided showing the functional groups in their relative priorities from top to bottom (highest priority = first on the list to lowest priority = last on the list). A very brief overview of their nomenclature is provided showing the prefix and suffix terms associated with each functional group. The highest priority group in a structure is indicated by a suffix and a designating number. (If the number can only be #1 it is usually left out.) In compounds where more than one functional group is present, lower priority functional groups are indicated with prefixes preceded by numbers identifying each substituent's position on the parent chain. Alkene and alkyne functionality is <u>always</u> indicated at the end of the name (as a suffix), even if both are present. This means there could be as many as three suffix components if an alkene, alkyne and a high priority functional group are all present.

To form the parent name, drop the -e ending if the suffix of the highest priority group begins with a vowel (most do) from the alkane, alk-#-ene, alk-#-yne or alk-#-ene#-yne name. If the suffix begins with a consonant, retain the final e of the parent name and simply append the suffix. In this book the only two functional group examples like this are nitrile and thiol.

Try to adopt a systematic (repetitive) strategy to approach each nomenclature problem. If you do this every time you work on a nomenclature problem, it won't take many efforts until nomenclature problems become a routine effort, devoid of any mystery.

Basic Strategy for Naming Structures - Approach every nomenclature problem the same way.

1. Identify the highest priority group and name the longest continuous chain of carbons containing the highest priority group so that it is assigned the lowest number possible. Lesser priority groups are still considered when secondary choices can be made at branches to decide what is the longest chain. Include these lesser priority groups in the longest chain when possible.

2. Use the numbers in the longest chain to indicate the position of all branches and substituents. Lower priority groups are indicated with prefixes at the beginning of the name, along with any necessary numbers to indicate their position(s). The prefixes should be placed in the name in alphabetical order for referencing purposes. If the prefixes are not in alphabetical order, a correct structure can still be drawn, however, you might have a problem looking up a structure in alphabetized lists in the literature.

3. Indicate any double bonds and triple bonds with suffixes, in addition to the high priority group suffix. Each occurrence of these will get a number preceding it to indicate its position on the parent chain. If more than one multiple bond or group is present, indicate this with the numerical prefix of the suffix name (i.e., two double bonds = -#,#-diene, three triple bonds = -#,#-triyne, four alcohol groups = -#,#,#-tetraol, etc.). If both a double and triple bond are present, the parent name is alk-#-en-#-yne. If two doubles, three triples and an alcohol group are present, the parent is alka-#,#-dien-#,#,#-triyn-#-ol). Stereochemical identifiers (E/Z and R/S) can be grouped together in parentheses in front of the name with their appropriate numbers.

In addition to several alkane, alkene and alkyne branch names listed earlier there are two commonly encountered aromatic branch names we use in our course.



Common Functional Groups

Most of the following functional groups have more details than is specified in the examples provided in this topic. More groups are provided in the priority list below than are emphasized in our course. Also, there are even more functional groups not discussed by us. Only the more commonly encountered groups are included here. The functional groups you are responsible for are listed in **bold**. There are 12 functional groups bolded, plus 5 lower priority substituents at the end. The first functional group you are responsible for in this list is the carboxylic acid functional group, number 4.

Order of Priorities of Organic Functional Groups (You are not responsible for all of these, only those in bold.)

1. Free Radicals- not	t covered by us.					
	Prefix Name	Suffix Name				
General Structure	<u>(if lower priority)</u>	(if higher priority)	<u>Example</u>			
R [/] C: R	none given	alkyl radical	2-methyl-2-butyl radical			
2. Cationic Compour	nds– not covered by us.					
a. carbon– not covere <u>General Structure</u>	ed by us. Prefix Name <u>(if lower priority)</u>	Suffix Name (if higher priority)	Example			
$R \sim C \oplus R$	none given	alkyl cation	2-methyl-2-butyl cation			
b. Nitrogen– not cov General Structure	ered by us. Prefix Name (if lower priority)	Suffix Name (if higher priority)	<u>Example</u>			
R R N⊕ R R	ammonio-	-ammonium	ethyltrimethylammonium			
c. Oxygen– not cove <u>General Structure</u> R	red by us. Prefix Name (if lower priority)	Suffix Name (if higher priority)	Example			
$R \xrightarrow{Q \oplus} R$	0x01110-	-oxonium	triethyloxonium			
3. Anionic Compoun	ds– not covered by us.					
a. Carbon– not covered by us.						
General Structure	Prefix Name (if lower priority)	Suffix Name (if higher priority)	Example			
$\mathbb{R}^{\stackrel{I}{} \Theta}_{\mathbb{R}}$	none given	alkyl anion -ide	2-methyl-2-butyl anion 2-methyl-2-butanide			



Drop the -e ending of the longest chain having the carboxylic acid functional group and add the -**oic acid** suffix. The acid functional group is usually at the #1 position of the longest chain and does not require a position number. Since it is our highest priority group we will never use the prefix name. Cover the right side, below, and try to name each structure on your own.





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5-phenylpent-2-ynoic acid





Drop the -e ending of the longest chain having the anhydride functional group and add the **-oic anhydride** suffix. Use just one name if the anhydride is symmetrical. If the anhydride is not symmetrical, name each part as –oic and then a single "anhydride" to finish the name. If the anhydride is the high priority group, each of the carbonyl carbons will be the #1 carbons of their respective chains and do not require a location number. The anhydride prefix (when it is a lower priority group) is too complicated for a first time course.



8. Ester– you need to know this group.



Drop the -e ending of the longest chain having the carbonyl portion (C=O) and add the -**oate** suffix. The other carbon chain, attached to oxygen with only a single bond, is <u>named at the very beginning of the name as an **alkyl** substituent and placed as a separate word. If the ester is the high priority group, the carbonyl carbon will be the #1 carbon and does not require a location number. If the ester is a lower priority group it is named as "alkoxycarbonyl" with a locator number.</u>

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9. Sulfonate Ester - not covered by us.



10. Acid Halide- you need to know this group.



Drop the -e ending of the longest chain having the functional group and add **-oyl chloride**. If the acid chloride is the high priority group, the carbonyl carbon will be the #1 carbon and does not require a location number. If the acid chloride is a lower priority group it is named as "chlorocarbonyl" with a locator number.



11. Sulfonyl Chloride - not covered by us.



12. Amide – you need to know this group. $(1^{\circ}, 2^{\circ}, 3^{\circ}$ are possible, refers to the number of carbons attached to the nitrogen atom)



Drop the -e ending of the longest chain having the C=O functional group and add **amide**. If nitrogen is substituted with an alkyl group indicate so with N- preceding the substituent name. If the nitrogen is substituted with two alkyl groups, use an N- before each of the substituents. An amide nitrogen with only the carbonyl carbon (C=O) attached is a primary amide (1°). If two carbons are attached to the nitrogen, it is a secondary amide (2°) and if three carbons are attached, it is a tertiary amide (3°). If the amide is the high priority group, the carbonyl carbon will be the #1 carbon and does not require a location number. If the amide is lower in priority it can be named using either the "carbamoyl" or "amido" prefix (with a locator number).



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3'

4'

2

2'

5' 0 6'

3 2

2

ÓН





3

О.

4

5

6



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Do <u>not</u> drop the -e ending. Since nitrile begins with a consonant the -e is retained in the root name and **nitrile** is added to this name. If the nitrile is the high priority group, the carbon with the nitrogen will be the #1 carbon and does not require a location number. If a higher priority group is present use the **cyano** prefix with a location number. Examples are provided.



15. Aldehyde- you need to know this group.



Drop the -e ending of the longest chain having the functional group and add -al. If the aldehyde is the high priority group, the carbonyl carbon will be the #1 carbon and does not require a location number. If a higher priority group is present, use the **oxo**- prefix with a location number when the aldehyde is part of the longest chain. If the aldehyde is a branch off of the longest chain it gets a location number and the prefix "formyl" Examples are provided.



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Drop the -e ending of the longest chain having the functional group and add -**one** (sounds like cone, tone, bone). If the ketone is the highest priority group, it will usually require a location number. If a higher priority group is present, use the **oxo**- prefix (same as the aldehydes) with a location number. Examples are provided. (Older ketone nomenclature used the "keto" prefix. We will not use this prefix.)



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17. Alcohol – you need to know this group. $(1^{\circ}, 2^{\circ}, 3^{\circ}$ are possible, refers to the number of carbons attached to the alcohol carbon atom)



Drop the -e ending of the longest chain having the functional group and add -ol. If a higher priority group is present, use the **hydroxy**- prefix with a location number. If one carbon is attached to the alcohol carbon, it is a primary alcohol (1°) , if two carbons are attached to the alcohol carbon, it is a secondary alcohol (2°) and if three carbons are attached to the alcohol carbon, it is a tertiary alcohol (3°) . Examples are provided.







18. Thiol – you need to know this group. $(1^{\circ}, 2^{\circ}, 3^{\circ}$ are possible, refers to the number of carbons attached to the thiol carbon atom)



Do not drop the -e ending of the longest chain having the functional group and add -**thiol** because it starts with a consonant If a higher priority group is present, use the **mercapto**- or **sulfanyl** prefix with a location number. If one carbon is attached to the thiol carbon, it is a primary thiol (1°) , if two carbons are attached to the thiol carbon, it is a secondary thiol (2°) and if three carbons are attached to the thiol carbon, it is a tertiary thiol (3°) . Examples are provided.





19. Amine – you need to know this group. $(1^{\circ}, 2^{\circ}, 3^{\circ}$ are possible, refers to the number of carbons attached to the

3-sulfanyl-4-(1-methylprop-2-ynyl)-5-formyl-7-cyanoheptanoic acid



Drop the -e ending of the longest chain having the functional group and add **amine**. If nitrogen is substituted with another alkyl group, indicate so with **N**- preceding the substituent name. If the nitrogen is substituted with two additional alkyl groups, use an **N**- before each of the substituents. An amine nitrogen with only one carbon attached is a primary amine (1°). If two carbons are attached to the nitrogen, it is a secondary amine (2°) and if three carbons are attached, it is a tertiary amine (3°). Amines can also be named as though the largest carbon portion is

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alkylamine and any other alkyl chains are named as **N-alkyl**. If a higher priority group is present, use the **amino**-prefix with a location number. Examples are provided.



20. Ether- you need to know this group.



Noncyclic ethers have two carbon chains to name (like the anhydrides and the esters). Usually, the smaller alkyl portion is named as a substituent on the higher priority portion. The smaller (lower priority) group is named as

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alkoxy (if 4 or fewer carbons are present) or **alkyloxy-** (if more than 5 carbons are present, we won't use this one). Ether substituents are <u>always</u> named as prefixes. When two simple alkyl groups are present ethers are sometimes named as **alkyl alkyl ether**. Symmetrical ethers are often named with a single alkyl name followed by ether. The word "ether" alone usually refers to diethyl ether (ethoxyethane).



22. Sulfone - not covered by us.



24. Hydrocarbon branches and miscellaneous substituents named as prefixes.

The hydrocarbon branches were discussed in prior sections.

Special Substituents (Know these five.)

There are several groups that occupy one bonding position on the carbon skeleton and are named only with a prefix and a number to indicate their position. Some of the more common ones are listed below. They should be listed in alphabetical order with their designating number. Priority among these groups, if no high priority functional group is present, is based on the lowest possible number at the first point of difference. Some of these groups must be drawn with formal charge and have resonance structures, if full Lewis structures are drawn.

1. Halogen Compounds– you need to know this group.

General Structure	Prefix Name		<u>Examples</u>
R—F	fluoro-	H ₃ C—F	fluoromethane
R—Cl	chloro-	Cl	chloroethane
R—Br	bromo-	Br	1-bromopropane
R—I	iodo-	∕I	1-iodobutane

Halogens are officially named with the **halo**- prefix name specific to the halogen present (**fluoro-, chloro-, bromo-, iodo-**) and a location number for each halogen present. If one carbon is attached to the halogen carbon, it is a primary halide (1°) , if two carbons are attached to the halogen carbon it is a secondary halide (2°) and if three carbons are attached to the halogen carbon it is a tertiary halide (3°) . Common nomenclature uses alkyl halide (like a salt) for simple names (e.g. methyl chloride). Examples are provided.



5. Nitroso Compounds– you need to know this group.



Aromatic versions of various functional groups. You are not required to know these names. They are included for reference only.



Chem 201/Beauchamp

Topic 4, Bare Bones Nomenclature



General Strategy For Naming Simple Organic Compounds (Bare bones summary sheets)

- 1. Find the highest priority group. These are listed in order of priority in the table of functional groups (next page).
- 2. Find the longest chain containing the highest priority group. You should know carbon chains of length C_1 - C_{19} (listed in the table).
- 3. Number the longest chain containing the highest priority group to give the highest priority group the lowest number possible in numbering the longest chain. For the first seven functional groups, the functional group carbon will be number 1 (if it is the highest priority group) and the "1" can be omitted, since it is understood that it has to be this way.
- 4. Usually the highest priority group is named as a suffix at the end of alkane, alk-#-ene or alk-#-yne. The final e is dropped if the suffix begins with a vowel and it is retained if the suffix begins with a consonant (only two for us, "nitrile" and "thiol"). A number will be present in front of the suffix name unless its position is unambiguously clear (e.g. carboxyl groups, aldehydes, nitriles, etc. always = 1, if highest in priority). If there is a C/C pi functional group to identify (alkene or alkyne), the number in front of its part of the name describes its position (see rule 6 below). If both a pi bond and a high priority substituent are present, then two (or more) numbers may be necessary, one for each functionality.
- 5. Lower priority groups are named with their prefix names and their location numbers based on the numbering of the parent chain (always true for substituents numbered 12 on the next page). The lower priority substituents should be listed in alphabetical order. Some parts of prefix names count in this regard and some don't. We will not emphasize this aspect in this course.
- 6. Double bonds and triple bonds are named as alk-#-ene or alk-#-yne, respectively. If both are present, name as alk-#-en-#-yne. Multiple pi bonds (or other substituents) use the prefixes di, tri, tetra, penta etc. with a number for each occurrence. In such cases, an "a" is added in front of the numerical prefix for better phonetics. (alka-#,#-diene or alka-#,#,#-triyne, alka-#,#-diene-#,#-diyne, etc.)

The essential functional groups to know (for our course) and their prefixes and suffixes are given in the attached table. In this table the term "alkan-#-suffix" is a generic term for any alkane with a functional group suffix, and it must be replaced with the correct parent stem name based on the number of carbons in the longest chain (C_1 - C_{19} for us). If there is a double bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and if there is a triple bond, the name will change to "alk-#-en-#-suffix and the advance to "advance to "advance to "advance to "advance to "advance to "advance to



Topic 4, Bare Bones Nomenclature

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Functional Group	0	prefix	<u>suffix</u>	The p	part of each na	me
1. Carboxylic acid	R ^{∕Ċ} ∖OH	not considered	alkan <u>oic acid</u>	speci group	fic to the func is in bold an	tional d
2. Anhydride	$\mathbf{R}^{\mathbf{C}} \mathbf{O}^{\mathbf{C}} \mathbf{R}$	not considered	alkan <u>oic anhydride</u> (if symmetrical)	see th are no	nose features. To part of the r	They names.
3. Ester	R ^C O ^{R'}	<u>#-alkoxycarbonyl</u>	alkyl alkan <u>oate</u> (R') (RCO ₂)			
4. Acid halide	R ^C Cl	#- <u>chlorocarbonyl</u>	alkan <u>oyl chloride</u>	#	"R" = carbon alkane chain	chains alkyl branch
5. Amide	R ^C .NH ₂	#- <u>carbamoyl</u> (or #-amido)	alkan <u>amide</u>	carbons	name	name
6. Nitrile	R-CEN	#- <u>cyano</u>	alkane <u>nitrile</u>	$\begin{array}{c} 2\\ 2\\ 3\\ 4\end{array}$	ethane propane butane	ethyl propyl butyl
7. Aldehyde	R ^C .H	#- <u>oxo</u>	alkan <u>al</u>	5 6 7	pentane hexane heptane	pentyl hexyl heptyl
8. Ketone	°C'R'	#- <u>oxo</u> (older = #- <u>keto</u>)	#-alkan <u>one</u>	8 9 10	octane nonane decane	octyl nonyl decyl
9. Alcohol	R-OH	#-hydroxy	#-alkan <u>ol</u>	10 11 12 13	undecane dodecane tridecane	undecyl dodecyl tridecyl
10. Thiol	R-SH	#- <u>mercapto</u> (or #-sulfanyl)	#-alkane <u>thiol</u>	13 14 15 16	tetradecane pentadecane hexadecane	tetradecyl pentadecyl hexadecyl
11. Amine	R-NH ₂	#- <u>amino</u>	#-alkyl <u>amine</u> #-alkan <u>amine</u>	17 18 19	heptadecane octadecane nonadecane	heptadecyl octadecyl nonadecyl
12. Ether	R-O-R'	#-alk <u>oxy</u> (if more than 50 (can also use "#	C's, then #-alkyloxy) -oxa" prefix and			
12. Halogen	R-X	count as carbo #- <u>fluoro</u> , #- <u>chloro</u> , #- <u>bro</u>	n in longest chain) 2000, #- <u>iodo</u>			
12. Azide*	R-N ₃	#- <u>azido</u>		always	prefixes	
12. Diazo*	R-N ₂	#- <u>diazo</u>		(no suff	fix names)	
12. Nitro*	R-NO ₂	#- <u>nitro</u>				
12. Nitroso	R-NO	#- <u>nitroso</u>	J			
12. Carbon branches	R-	#-alkyl, #-(alk-#-enyl), #-	-(alk-#-ynyl)			

* = formal charge is necessary in these Lewis structures and there are two reasonable resonance structures

stereoisomerism	prefixes	parent stem	C/C pi bonds	high priority suffix
R/S and E/Z branches low prior functiona		d see box above roups	ene -yne	see list above

Problem 9 – Provide an acceptable name for each of the following structures.



Problem 10 – Provide an acceptable name for each of the following structures.







Lecture problems to work in class.



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