1:   Organic Molecules and Chemical Bonding

•*Organic Molecules*
•*Chemical Bonds*
•*Organic Chemistry*
•*Bon voyage*

Preview

Organic chemistry describes the structures, properties, preparation, and reactions of a vast array of molecules that we call **organic compounds**. There are many different types of organic compounds, but all have **carbon** as their principal constituent atom. These carbon atoms form a **carbon skeleton** or **carbon backbone** that has other bonded atoms such as H, N, O, S, and the halogens (F, Cl, Br, and I).

We frequently hear the term "organic" in everyday language where it describes or refers to substances that are "natural". This is probably a result of the notion of early scientists that all organic compounds came from living systems and possessed a "vital force". However, chemists learned over 170 years ago that this is not the case. Organic compounds are major components of living systems, but chemists can make many of them in the laboratory from substances that have no direct connection with living systems. Chemically speaking, a pure sample of an organic compound such as Vitamin C prepared in a laboratory is chemically identical to a pure sample of Vitamin C isolated from a natural source such as an orange or other citrus fruit.

Your journey through organic chemistry will be challenging because of the large amount of information that you will need to learn and understand. However, we will explore this subject in a systematic manner so that it is not a vast collection of isolated facts. What you learn in one chapter will serve as building blocks for the material in the chapter that follows it. In this sense, you may find that organic chemistry is different from general chemistry. That course consists of a variety of discrete topics usually divided into separate segments in textbooks. In contrast, your organic chemistry instructors will present a course in which each new topic uses information from previous topics to raise your understanding of organic chemistry to successively higher levels.

This chapter provides a foundation for your studies of organic chemistry. It begins with an introduction to the important **classes** of organic molecules followed by a description of

chemical bonding in those molecules. It concludes with a brief survey of the various topics in organic chemistry and a description of the way that we present them in this text.

1.1 Organic Molecules

All organic molecules contain *carbon (C)*, virtually all of them contain *hydrogen (H)*, and most contain *oxygen (O)* and/or *nitrogen (N)* atoms. Many organic molecules also have halogen atoms such as *fluorine (F)*, *chlorine (Cl)*, *bromine (Br)*, or *iodine (I)*. Other atoms in organic compounds include *sulfur (S)*, *phosphorous (P)*, and even *boron (B)*, *aluminum (Al)*, and *magnesium (Mg)*.

The number of different types of atoms in organic compounds suggests they are structurally complex. Fortunately, we find these atoms in a relatively few specific arrangements because of their preferred bonding characteristics. For example, C atoms primarily bond to each other to form the **molecular skeleton** or **backbone** of organic molecules, while H atoms bond to the various C atoms, or to other atoms such as N and O, almost like a "skin" surrounding the molecule. You can see some of these features in the organic molecule *lauric acid* that is one of a group of molecules called *fatty acids*. [graphic 1.1] Since atoms such as N, O, and the halogens (generally referred to as X) connect to the carbon skeleton in characteristic ways that determine the properties of a molecule, we call these groups of atoms **functional groups**. Functional groups define the **class** to which the organic molecule belongs.

Bonding Characteristics of Atoms (1.1A)

You can see that most of the atoms that we have mentioned above are in the first three *rows* of the **periodic table**. [graphic 1.2] However, it is their location in a particular *column* of the periodic table that tells us how many chemical bonds they usually form to other atoms in a molecule. For example, C and Si are in the fourth column (Group 4A) and they each typically have four bonds in their molecules, while F, Cl, Br, and I are in Column 7A and they typically form just one bond.

> **Periodic Tables**. The partial periodic table shown here does not include columns with the "transition elements" (Groups 1B through 8B). We show these in the full periodic table located inside the cover of your text. Some of these transition elements are present in organic molecules, but to a much smaller extent than the other atoms we have mentioned. We will consider bonding preferences of transition elements as needed throughout the text.

1.1.   Lauric Acid-A Fatty Acid with the formula $C_{12}H_{24}O_2$.

The Carbon backhone

The attached H atoms

A functional group
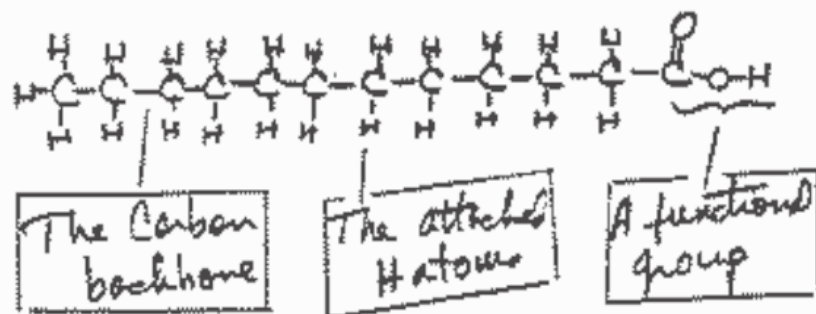
Partial Periodic Table

Group	1A	2A	3A	4A	5A	6A	7A	8A
	H							He
	Li	Be	B	C	N	O	F	Ne
	Na	Mg	Al	Si	P	S	Cl	Ar
							Br	Kr
							I	Xe
Bonds	1	2	3	4	3	2	1	0

Figure [graphic 1.2]. A partial periodic table of the elements showing the typical number of bonds to each element when it is present in an organic compound.

Bonds and Unshared Electron Pairs for C, N, O, and F. C, N, O, and halogens such as F, are particularly important atoms in organic molecules. The neutral compounds that they form with H (CH_4, NH_3, H_2O, and HF) illustrate their bonding preferences. You can see in Figure [graphic 1.3] that each atom in these molecules has the preferred number of bonds that we listed at the bottom of our partial periodic table (Figure [graphic 1.2]). [graphic 1.3]
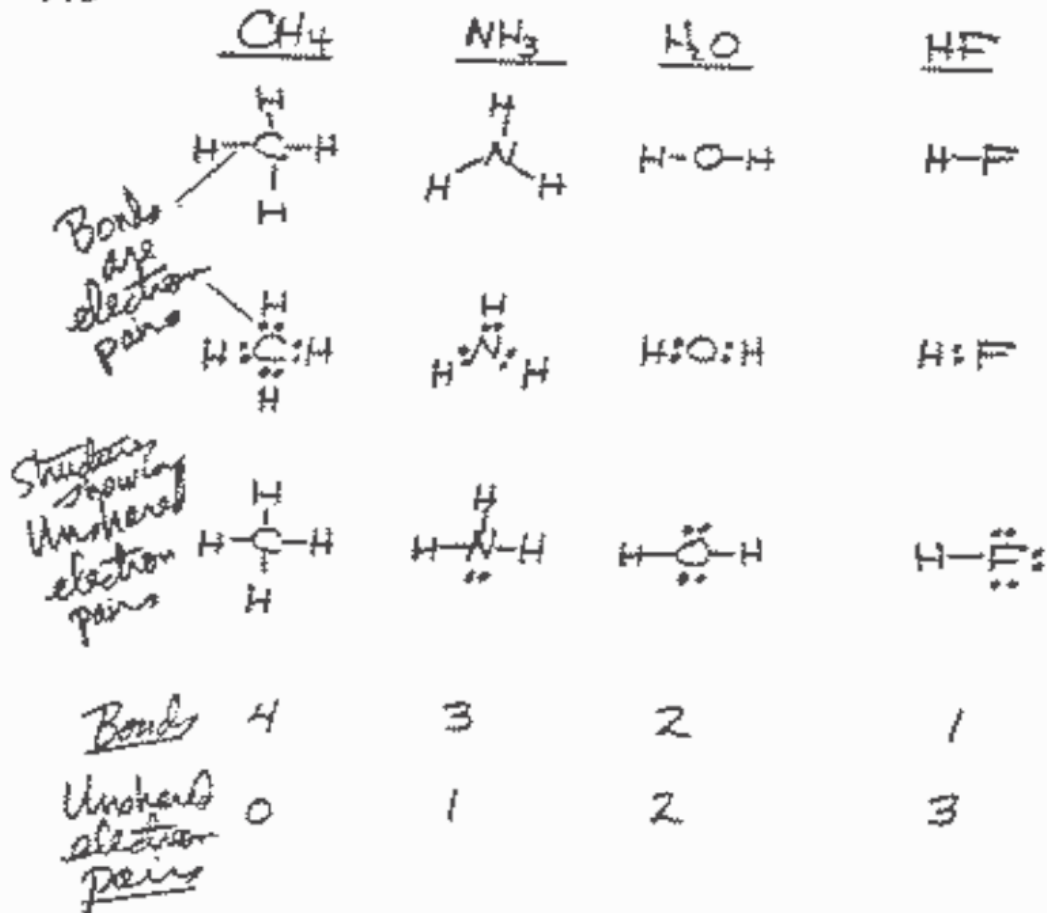
Besides their chemical bonds (**bonding electron pairs**), we show that N, O, and F have **unshared electron pairs** that are not in chemical bonds. The combined total of *number of bonds* and *number of unshared electron pairs* that we show equals 4 for C, N, O, or F. Since each chemical bond contains 2 electrons, our drawings of these molecules show 8 electrons on C, N, O, or F that come from their bonds <u>and</u> these unshared electron pairs.

Because each of these atoms has 8 electrons in bonds and unshared pairs, they satisfy the "**octet rule**". The "*octet rule*" states that atoms in rows 2 and 3 of the partial periodic table prefer to form compounds where they have 8 electrons in their **outer valence electron shell**. C, N, O, and F obey this rule not only in these compounds, but in all stable organic compounds.
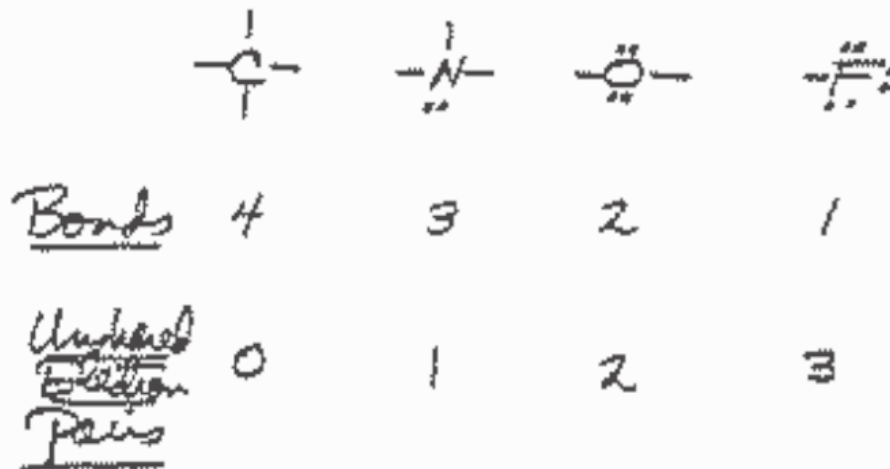
These characteristics of C, N, O, and F are so important that we summarize their preferred number of bonds and unshared electron pairs again in Figure [graphic 1.4] and offer the reminder that they are identical to those in CH_4, NH_3, H_2O, and HF. [graphic 1.4] (We give a more detailed description of bonds and electron pairs in these atoms on the next page at the end of this section.)

Bonds and Unshared Electron Pairs for Other Atoms. *H* and other atoms in column 1A, as well as those in columns 2A, and 3A of Figure [graphic 1.2] do not have enough outer shell electrons to achieve an octet when they form bonds so they have no unshared electron pairs in their compounds. *Si* (column 4a) typically has four bonds and no unshared electron pairs like C. The halogen atoms *Cl*, *Br*, and *I* have the same number of unshared electron pairs and preferred bonds as F because they are all in the same column. When *P* and *S* have 3 and 2 bonds, respectively, they have the same number of unshared electron pairs as N and O. However P and S sometimes form compounds where they have more than 8 outer valence shell electrons.

1.3

	CH₄	NH₃	H₂O	HF

Bonds are electron pairs

Structures showing unshared electron pairs

Bonds	4	3	2	1
Unshared electron pairs	0	1	2	3

1.4

Bonds	4	3	2	1
Unshared electron pairs	0	1	2	3

Structures of Organic Molecules. In the following sections, we use the preferred numbers of bonds for C, H, N, O, and the halogen atoms (X) to draw structures for common types of organic molecules and describe their organization into specific **classes**. We follow this introduction with a detailed description of their *chemical bonds*.

The Basis for the Number of Bonds and Unshared Electrons on C, N, O, and F. The number of bonds and unshared electrons on C, N, O, and F in their compounds depends on the total number of electrons of each free atom as described here:

	C	N	O	F
(a) Total electrons on free atom	6	7	8	9
(b) Inner shell electrons	2	2	2	2
(c) Outer shell electrons	4	5	6	7
(d) Electrons to complete octet	4	3	2	1
(e) Preferred number of bonds	4	3	2	1
(f) Number of Unshared electrons	0	2	4	6

(a) The *total number of electrons* is identical to the **atomic number** of the atom.

(b) C, N, O, or F each has 2 *inner shell electrons* not shown in the drawings.

(c) The number of *outer shell electrons* equals [*total electrons (a) - inner shell electrons (b)*].

(d) The *number of electrons to complete an octet* is [8 - *number of outer shell electrons*].

(e) The *preferred number of bonds* to C, N, O, or F is identical to the *number of electrons to complete an octet* (d) since each new electron comes from another atom that forms a bond containing the new electron and one of the outer shell electrons of C, N, O, or F.

(f) The number of *unshared electrons* on C, N, O, or F is the number of *outer shell electrons* not involved in forming chemical bonds to other atoms and this equals (c)-(d).

Compounds with Four Single Bonds to C (1.1B)

We can think of CH_4 as the simplest organic compound since it contains just one C with its four bonds to H atoms. Now let's look at other examples where C bonds not only to H, but to other C's, as well as to N, O, or X. These compounds include **alkanes** (C and H), **haloalkanes** (C, H, and X), **alcohols** and **ethers** (C, H, and O), and **amines** (C, H, and N). [graphic 1.5]

Alkanes (C-C and C-H Bonds). **Alkanes** have **C-H** and **C-C** bonds and are the structural foundation for all other organic molecules. While the simplest *alkane* CH_4 has no C-C bonds (it contains only one C), C-C bonds are present in all other alkanes. For example, you can draw a structure for the alkane H_3C-CH_3 (most often written CH_3-CH_3) by bonding two C atoms to each other and adding six H's to satisfy the bonding requirements of the C's.

[graphic 1.6] We can draw CH_3-CH_2-CH_3 with two C-C bonds in a similar way from 3 C atoms and 8 H's.
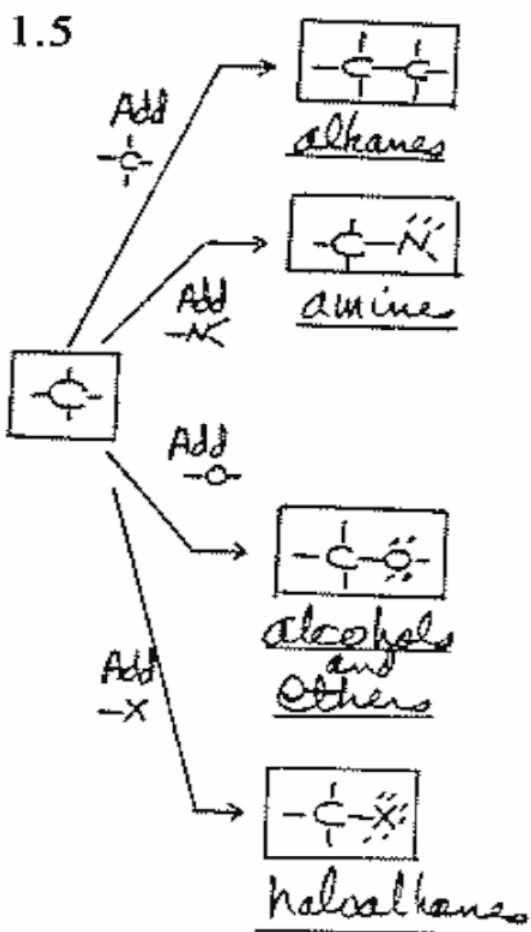
By bonding more C's and H's in this way we can draw a series of *alkanes* such as those shown in Figure [graphic 1.7]. [graphic 1.7] All of these alkanes result from adding H's to **linear chains** of C atoms, but we can bond C's to each other in other ways that we illustrate using four C atoms. [graphic 1.8] Besides the *linear* C4 skeleton, the four C's can be **branched** or in a **ring**. Subsequent addition of H's gives a **branched** alkane or a **cyclic** alkane (**cycloalkane**), that are different than the *linear alkane*. *Alkanes* and *cycloalkanes* are called **hydrocarbons** because they contain only C and H atoms.

> **Names of Organic Molecules**. We show individual names of alkanes for reference purposes. These names come from a system of **nomenclature** that we will begin studying in Chapter 2. You will learn how to name many organic molecules using relatively few *nomenclature* rules. Alkanes serve not only as the basis for the structures of all other organic compounds, but also their nomenclature.
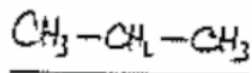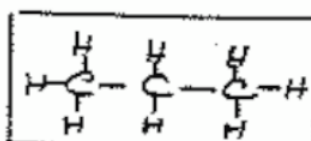
> **More About Alkanes**. Alkanes occur naturally in the earth in petroleum and natural gas and have a variety of commercial uses. Examples are *methane* (CH_4) (the major component of **natural gas**) and *propane* ($CH_3CH_2CH_3$) that are cooking and heating fuels. Gasoline, used to power most automobiles, is a complex mixture of alkanes including *hexanes* (C_6 alkanes), *heptanes* (C_7 alkanes), *octanes* (C_8 alkanes), and *nonanes* (C_9 alkanes). Alkanes also serve as starting materials for the preparation of other types of organic compounds that we are about to describe.

Compounds with C-X, C-O, or C-N Bonds. Alkanes contain only C and H atoms, but most other organic compounds contain additional atoms. We can draw structures for some of these, by replacing an H on an *alkane* (or *cycloalkane*) with an N, O, or halogen atom (X). We illustrate this below with the simplest alkane CH_4 so the resulting compounds are the simplest examples of each class. Since O and N atoms prefer more than one bond, we have added H's to complete their bonding requirements:
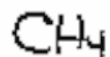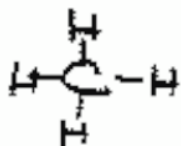
Simplest Examples	Class	General Formula
CH_3F	*Haloalkanes*	R-X
CH_3Cl		
CH_3Br		
CH_3I		
CH_3-O-H	*Alcohols*	R-OH
CH_3-NH_2	*Amines*	R-NH_2

1.5
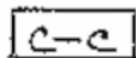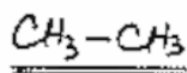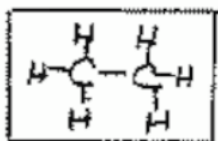
1.6

(1) Combine 2 C's

(1) Combine 3 C's

(2) Add Six H's

(2) Add Eight H's

CH_3-CH_3

$CH_3-CH_2-CH_3$

ethane

propane

1.7

CH_4 Methane

CH_3-CH_3 ethane

$CH_3-CH_2-CH_3$ propane

$CH_3-CH_2-CH_2-CH_3$ butane
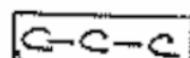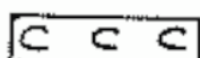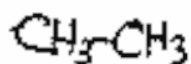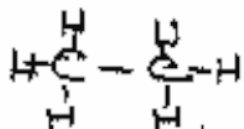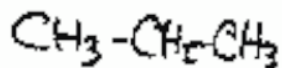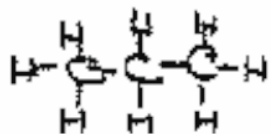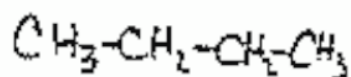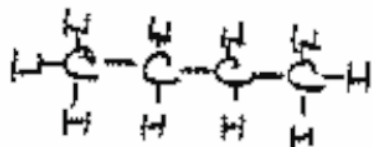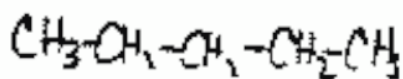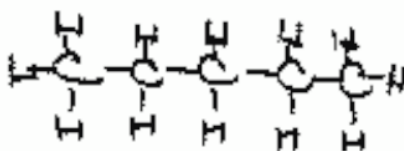
$CH_3-CH_2-CH_2-CH_2-CH_3$ pentane

1.8.   Linear, Branched and Cyclic Alkanes

Linear   Branched   Cyclic

$CH_3-CH_2-CH_2-CH_3$

$CH_3-CH-CH_3$
    |
   CH_3

CH_2-CH_2
| |
CH_2-CH_2
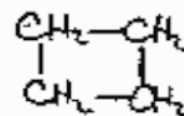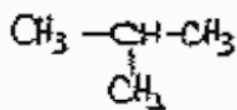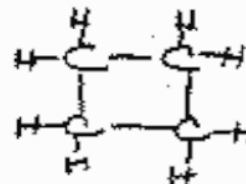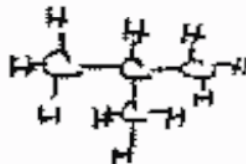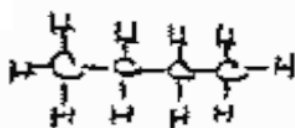
butane   2-Methylpropane   Cyclobutane

The general formulas **R-X**, **R-OH**, and **R-NH$_2$** symbolize the great variety of possible *haloalkanes*, *alcohols*, and *amines*. They indicate that an *X* atom, an *OH* group, or an *NH$_2$* group replaces an *H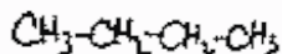* atom in an alkane or cycloalkane (**R-H**) to give a haloalkane, alcohol, or amine such as the examples we show in Figure [graphic 1.9]. [graphic 1.9] **R** represents all of the bonded C and H atoms other then the X, OH, or NH$_2$ groups. The OH group is called a **hydroxyl** (or **hydroxy**) group, or simply an *alcohol* group, while NH$_2$ is an **amino** group.

Additional R Groups on N or O. We can replace H's on the O$\underline{H}$ of R-OH and the N$\underline{H}_2$ of R-NH$_2$ with R groups and this leads to the types of organic compounds shown here:

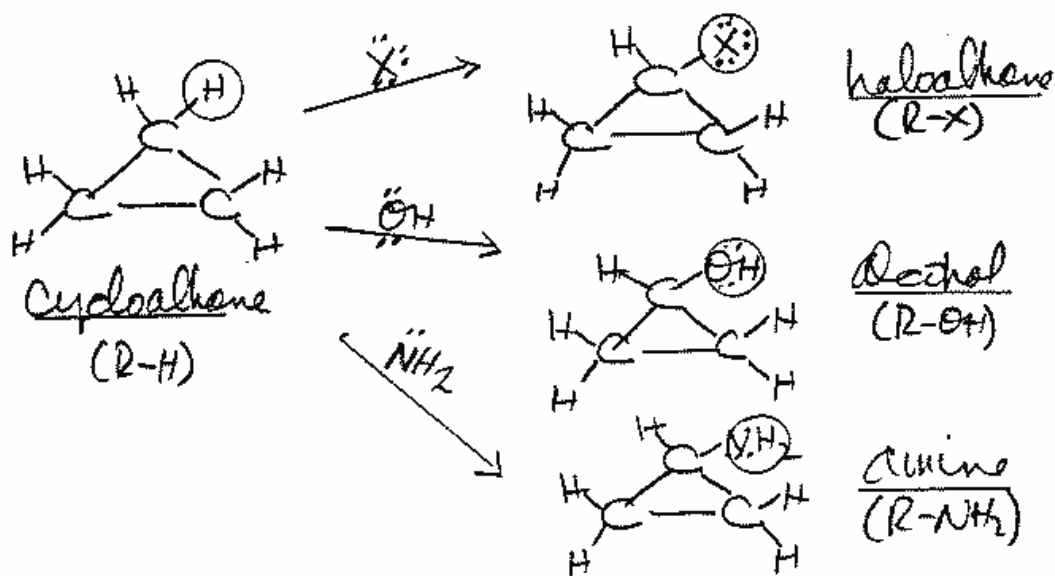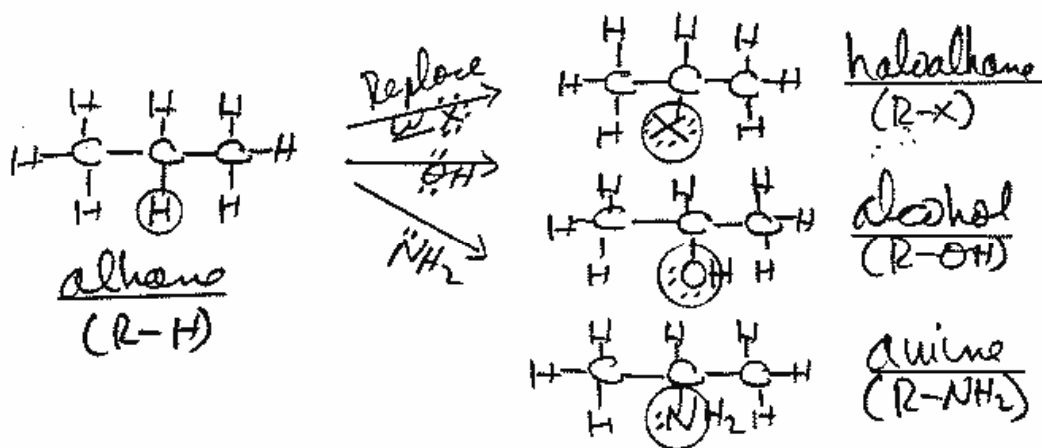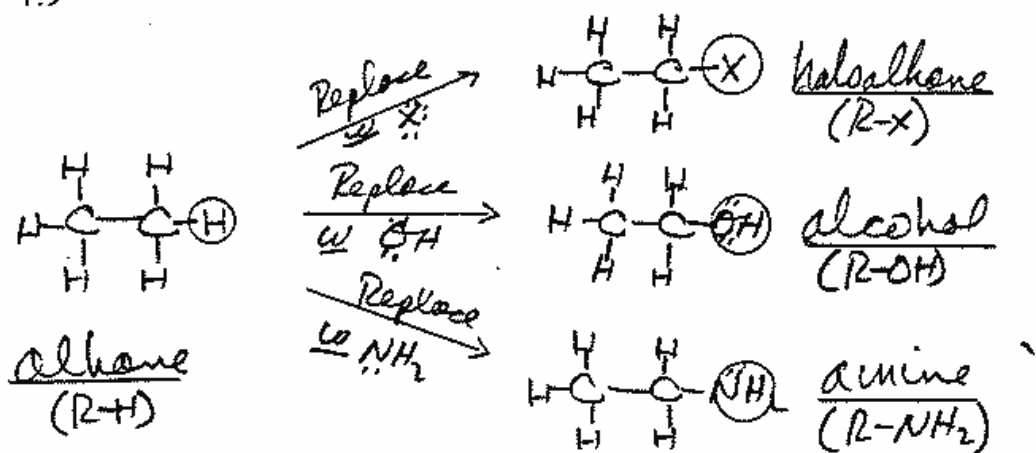| General Formula	Class	Simplest Example
R-O-R	*Ethers*	CH$_3$-O-CH$_3$
R-NHR	*Amines*	CH$_3$-NHCH$_3$
R-NR$_2$		CH$_3$-N(CH$_3$)$_2$

When we replace $\underline{H}$ of an *alcohol* (R-O-$\underline{H}$) with another R, we obtain a <u>new</u> class of organic compounds that we call *ethers* (R-O-R). In contrast, when we replace one or both $\underline{H}$'s on R-N$\underline{H}_2$ with other R's, we continue to call the resulting compounds *amines*! We shall see in Chapter 3 that this apparent inconsistency results from observations of early chemists that the chemical and physical properties of alcohols (ROH) are quite different than those of ethers (ROR), while they are very similar for all amines (RNH$_2$, RNHR, and RNR$_2$).

Functional Groups. We summarize how to draw *alkanes*, *haloalkanes*, *alcohols*, *ethers*, and *amines* using C, N, O, X, and H atoms in Figure [graphic 1.10]. [graphic 1.10] We refer to the groups **X**, **OH**, **OR**, **NH$_2$**, **NHR**, and **NR$_2$** as **functional groups** because they determine the physical properties and chemical reactions of their particular class of compounds.

Compounds with Double and Triple Bonds to C (1.1C)
So far, all organic compounds that we have seen have C atoms with **4 single** bonds to **4** other atoms. [graphic 1.11] Although C always prefers four bonds, we can provide these four bonds with 3 atoms or even 2 atoms using **double** or **triple** bonds. [graphic 1.12] We find such *double* and *triple* bonds in **alkenes** (C=C), **alkynes** (C≡C), **imines** (C=N), **nitriles** (C≡N), and **aldehydes** or **ketones** (C=O). [graphic 1.13]

1.9

1.10.   Some Functional Groups with Single Bonds

1.11

1.12

C Bonds to Three Atoms

Double Bond

C Bonds to Two Atoms

Triple Bond

1.13

alkenes

alkynes

imines

Nitrile

aldehydes and ketones
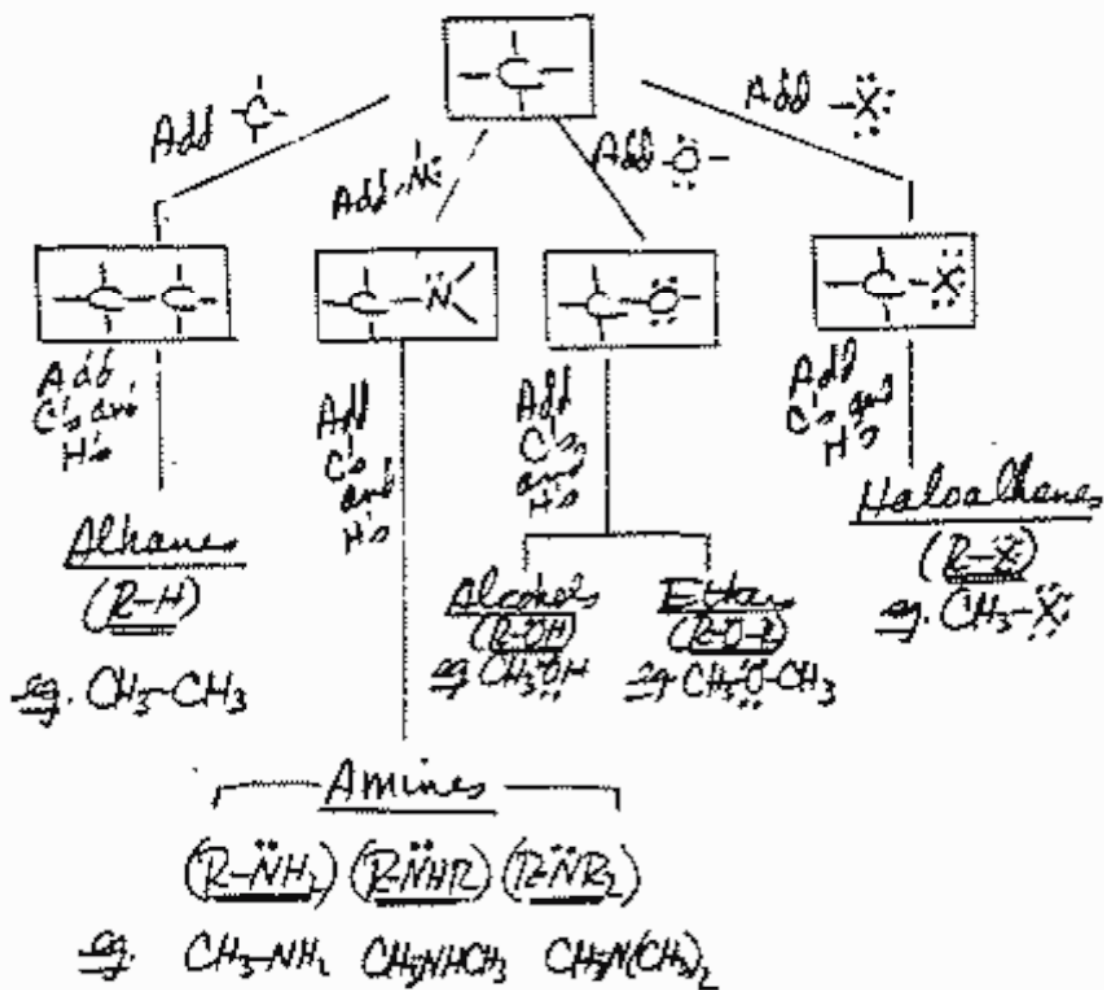
Alkenes (C=C) and Alkynes (C≡C). **Alkenes** contain a *C=C double* bond. We can draw the simplest *alkene* $H_2C=CH_2$ by adding four H's to a C=C so that each C has four bonds. [graphic 1.14] Alkenes are *hydrocarbons* that contain one C=C while all of their other C-C bonds are single bonds. [graphic 1.15] We think of the C=C bond as a functional group because it cause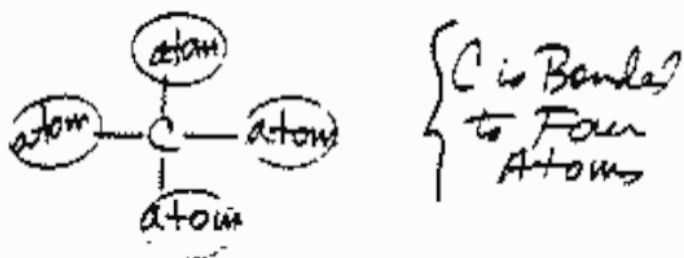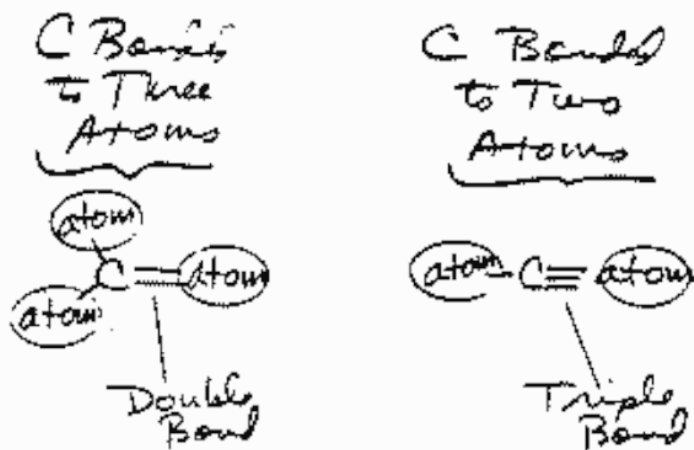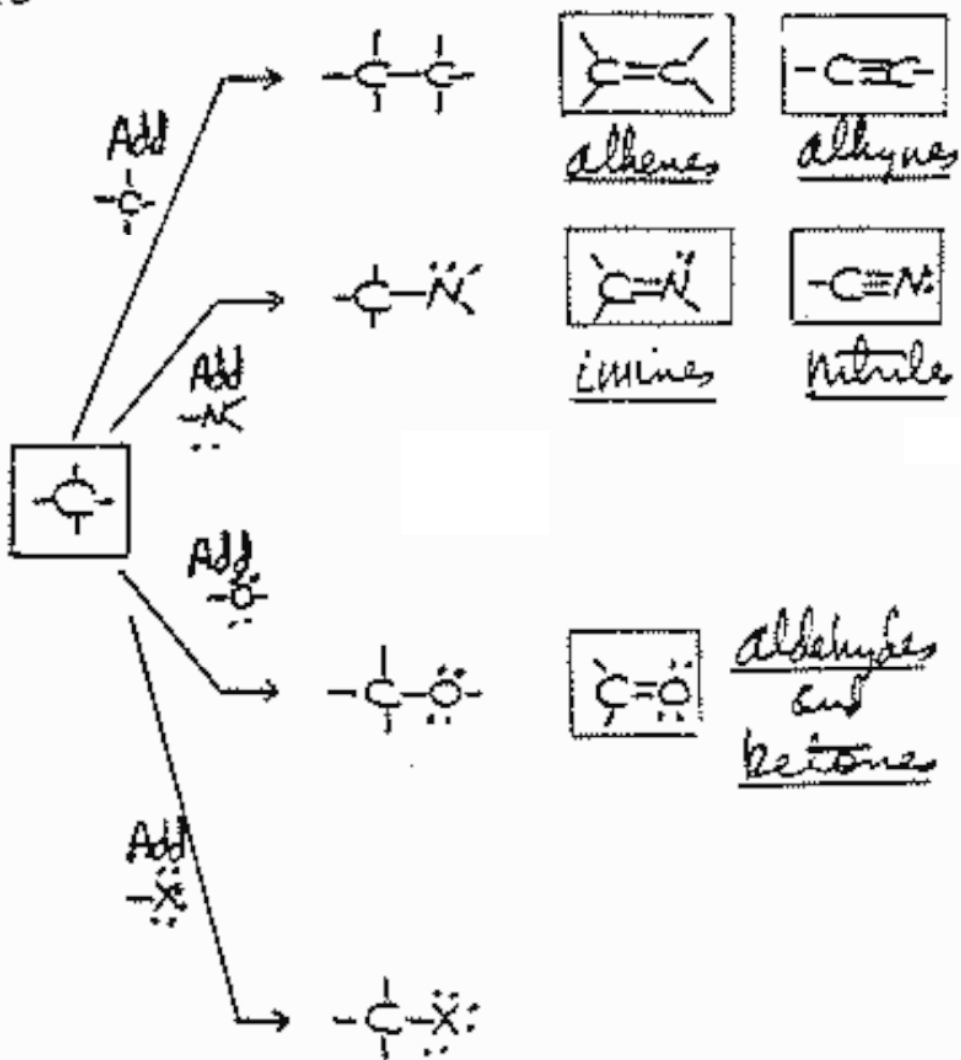s *alkenes* to be much more chemically reactive than *alkanes*. Alkenes have the general structure **$R_2C=CR_2$**. **Alkynes** are hydrocarbons with a C≡C bond and the general structure **R-C≡C-R**. [graphic 1.16] The *C≡C triple* bond is also a functional group that is more chemically reactive than a C-C single bond.

> **Molecules with more than One C=C or C≡C**. Organic compounds can have more than one C=C or C≡C bond. Many such compounds exist and have very important chemical and physical properties as we will see throughout this text. A biologically important organic molecule called **β-carotene** has <u>eleven</u> C=C bonds. [graphic 1.17] Compounds with two C=C bonds are **dienes**, compounds with three C=C bonds are **trienes**, compounds with four C=C bonds are **tetraenes**, while compounds with many C=C bonds are **polyenes**. Compounds with two or more C≡C bonds are named like *polyenes* except that the ending *ene* is replace with *yne*.

Compounds with C=N, C≡N, and C=O Bonds. Organic compounds can also have double or triple bonds between C and N, and double bonds between C and O. These are some of the classes with these double and triple bonds:

General Formula	Class	Simple Examples
$R_2C=N-H$	*Imines*	$(CH_3)_2C=N-H$
$R_2C=N-R$		$(CH_3)_2C=N-CH_3$
R-C≡N	*Nitriles*	$CH_3-C≡N$
R-C(=O)-H*	*Aldehydes*	$CH_3-C(=O)-H$
R-C(=O)-R*	*Ketones*	$CH_3-C(=O)-CH_3$

*The atomic grouping C(=O)-R means that R and (=O) are directly bonded to C.

As we saw for amines, *imines* can have either H or R on their N atom. In contrast, the presence or absence of an H on the C of the C=O group distinguishes *ketones* and *aldehydes*. *Aldehydes* always have at least one H directly bonded to C=O (H-C=O), while *ketones* have no H's directly bonded to C=O. [graphic 1.18] We call C=O a **carbonyl group** whether it is in an aldehyde (**R-C(=O)-H**), or a ketone (**R-C(=O)-R**). The C≡N group is referred to as a *nitrile* group, while C=N is usually not separately named.

14

1.14
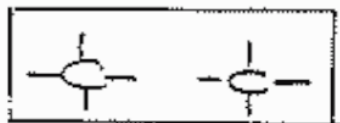
Combine Two C's

Make a C=C

Add Four H's

$$CH_2=CH_2$$

1.15. Some Alkenes

$$CH_3-CH=CH_2$$

$$CH_3-CH=CH-CH_3$$

$$(CH_3CH_2)_2C=CH_2$$

1.16. Some Alkynes

$$H_3C-C\equiv C-H \qquad\qquad H_3C-C\equiv C-CH_3$$

$$CH_3CH_2-C\equiv C-H$$
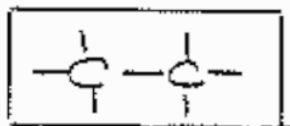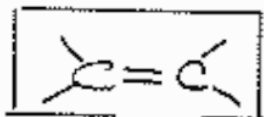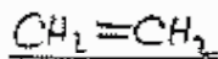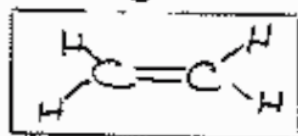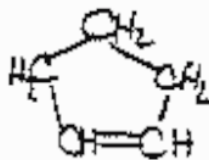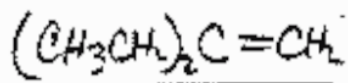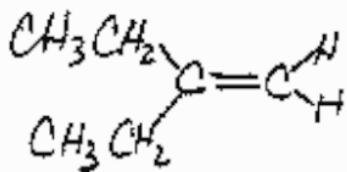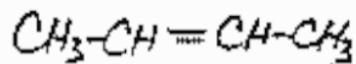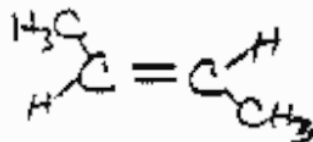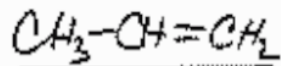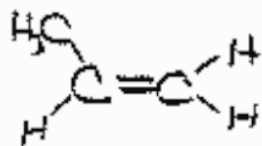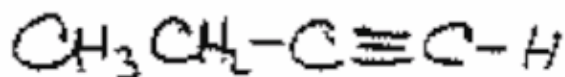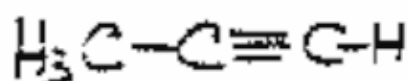
1.17. β-Carotene
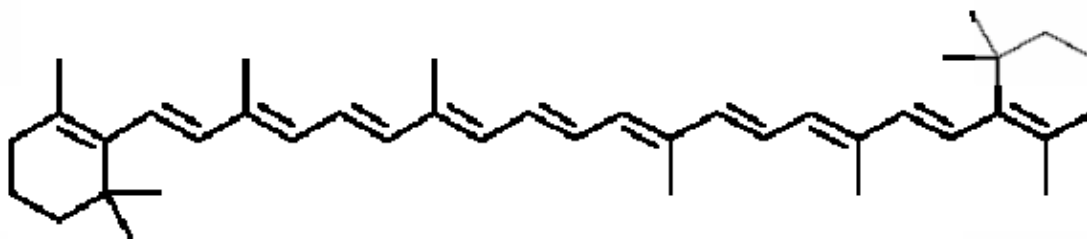
1.18. Some Simple Aldehydes

$$H-\overset{\oplus}{\underset{:\overset{..}{O}:}{C}}-H \qquad CH_3-\overset{\oplus}{\underset{:\overset{..}{O}:}{C}}-H \qquad \left\{ R-\overset{\oplus}{\underset{:\overset{..}{O}:}{C}}-H \right.$$

Some Simple Ketones

$$CH_3-\underset{:\overset{..}{O}:}{C}-CH_3 \qquad CH_3-\underset{:\overset{..}{O}:}{C}-CH_2CH_3 \qquad \left\{ R-\underset{:\overset{..}{O}:}{C}-R' \right.$$
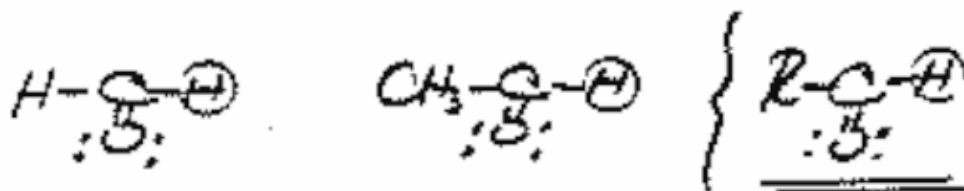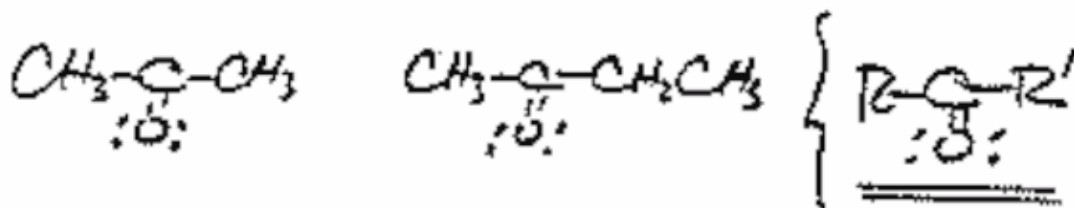
  Functional Group Summary. We summarize all these classes of organic compounds with double and triple bonds to C in Figure [graphic 1.19]. [graphic 1.19] Their functional groups are **C=C** and **C≡C**, **C=N** and **C≡N**, and **C=O**.

Compounds With C=O Bonded to N, O, or X (1.1D)

We finish our survey of important classes of organic compounds, with the four classes that have N, O, or X bonded to C of the C=O group:

General Formula	Class	Simple Examples
R-C(=O)-NH$_2$	*Amides*	CH$_3$-C(=O)-NH$_2$
R-C(=O)-NHR		CH$_3$-C(=O)-NHCH$_3$
R-C(=O)-NR$_2$		CH$_3$-C(=O)-N(CH$_3$)$_2$
R-C(=O)-O-H	*Carboxylic Acids*	CH$_3$-C(=O)-O-H
R-C(=O)-O-R	*Esters*	CH$_3$-C(=O)-O-CH$_3$
R-C(=O)-X	*Acid Halides*	CH$_3$-C(=O)-X

Like *amines* and *imines*, *amides* can have H's and/or R's on N. The O of the **carboxyl group** (C(=O)-O) can also bond to either an H or an R group, but the resulting compounds are separately classified as *carboxylic acids* or *esters* because of their very different properties. [graphic 1.20] We illustrate how we can draw these compounds from the C=O group and N, O, or X in Figure [graphic 1.21]. [graphic 1.21]

An Overview of Organic Functional Groups (1.1E)

Figure [graphic 1.22] summarizes all of the *functional groups* we have introduced in this chapter along with the names of their *classes*. [graphic 1.22] We have seen that we can systematically draw compounds in these classes by assembling C, N, O, X, and H atoms following the bonding requirements of these atoms that depend on their location in the periodic table. We will consider each of these classes in detail in later chapters.

   Other Functional Groups. You may wonder if there are additional organic functional groups that also follow the C, N, O, X, and H bonding requirements. In fact, there are a variety of other possibilities, but many of them don't exist or are much less common. In each of the functional groups that we have seen above, N, O, or X atoms bond only to C's and H's. While a few functional groups are present in organic compounds that do have N, O, or X bonded to each other, we encounter them much less frequently than those that we have seen here and will introduce them as needed throughout the text.

1.19. Some Functional Groups
with Double and Triple Bonds

1.20

Carboxyl group

Add
an O

Add
H to O

Add
C to O

Add
C and
on H

Add
Change
on H

Carboxylic
Acid

Ester

1.21

Amides

Carboxylic Acids and Esters

Acid Halides

1.22. Major Classes of Organic Compounds

$R-H$	$R_2C=CR_2$	$R-C\equiv C-R$
Alkanes	Alkenes	Alkynes

$R-\ddot{N}R_2$	$R_2C=\ddot{N}R$	$R-C\equiv\ddot{N}$
Amines	Imines	Nitriles

$R-\ddot{O}H$	$R-\underset{\ddot{O}}{\overset{}{C}}-H$	$R-\underset{\ddot{O}}{\overset{}{C}}-\ddot{N}R_2$
Alcohols	Aldehydes	Amides

$R-\ddot{O}-R$	$R-\underset{\ddot{O}}{\overset{}{C}}-R$	$R-\underset{\ddot{O}}{\overset{}{C}}-\ddot{O}H$
Ether	Ketone	Carboxylic Acid

$R-\ddot{X}$		$R-\underset{\ddot{O}}{\overset{}{C}}-\ddot{O}R$
Haloalkane		Esters

$$R-\underset{\ddot{O}}{\overset{}{C}}-\ddot{X}$$
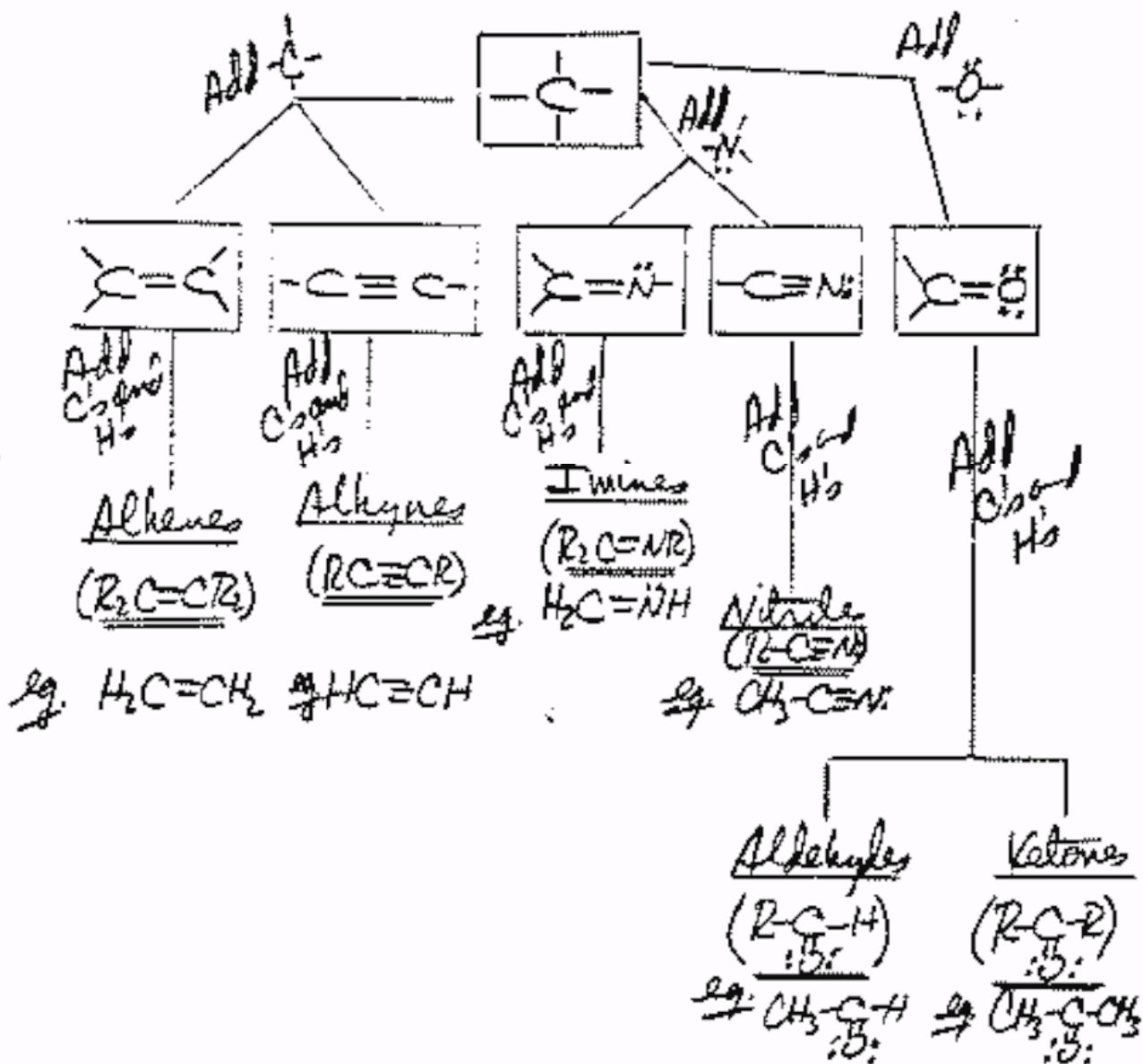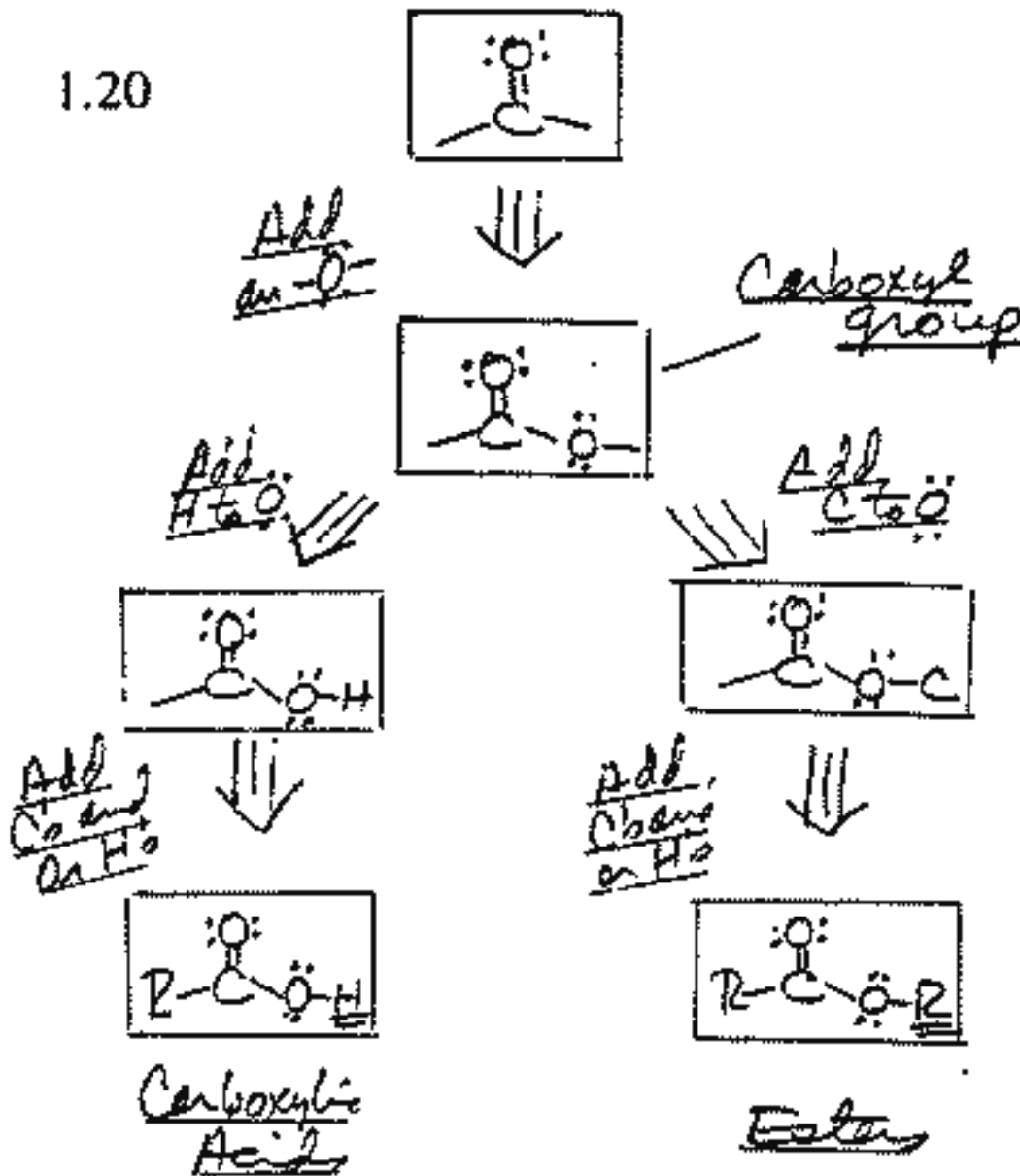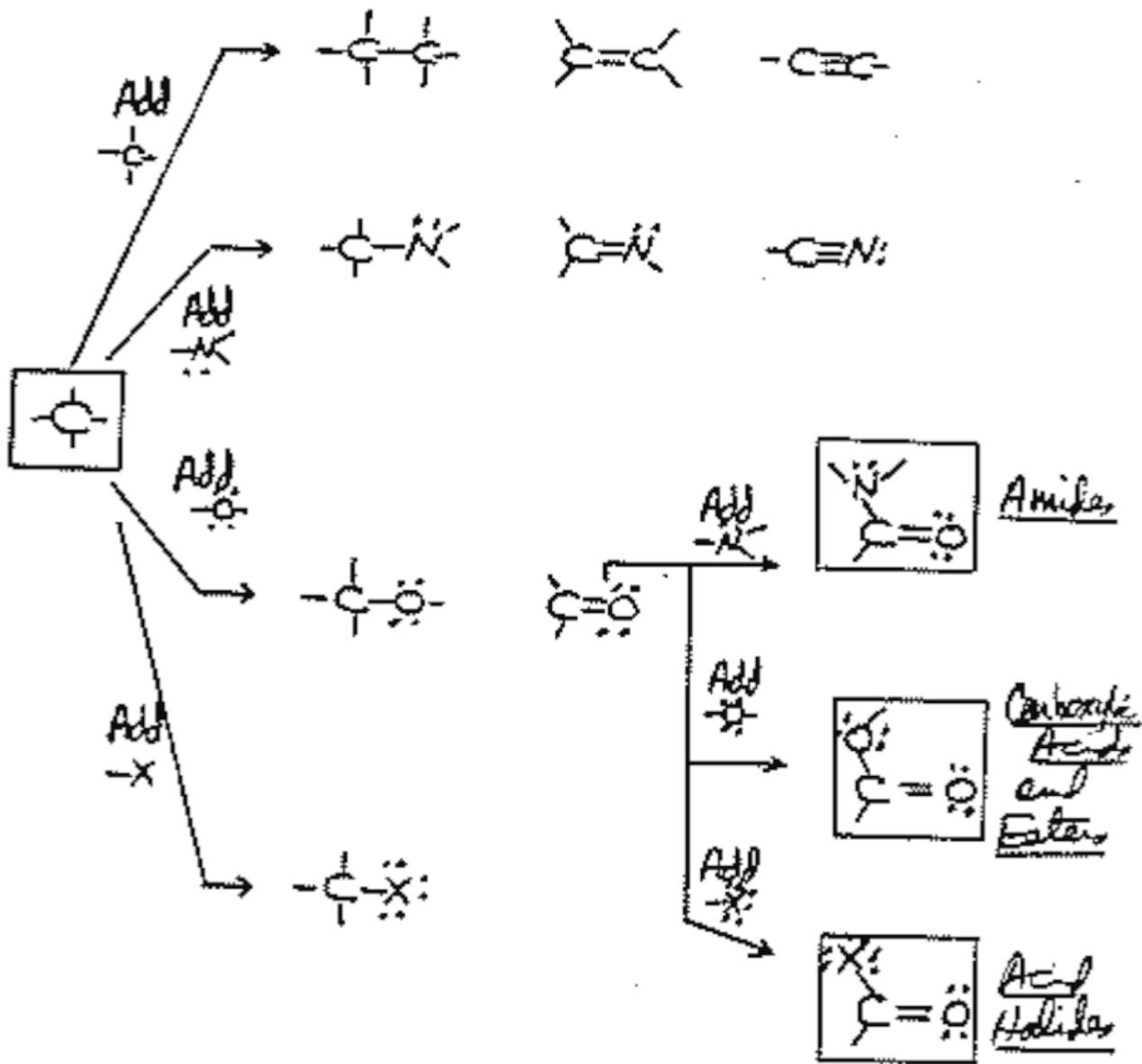
Acid Halides
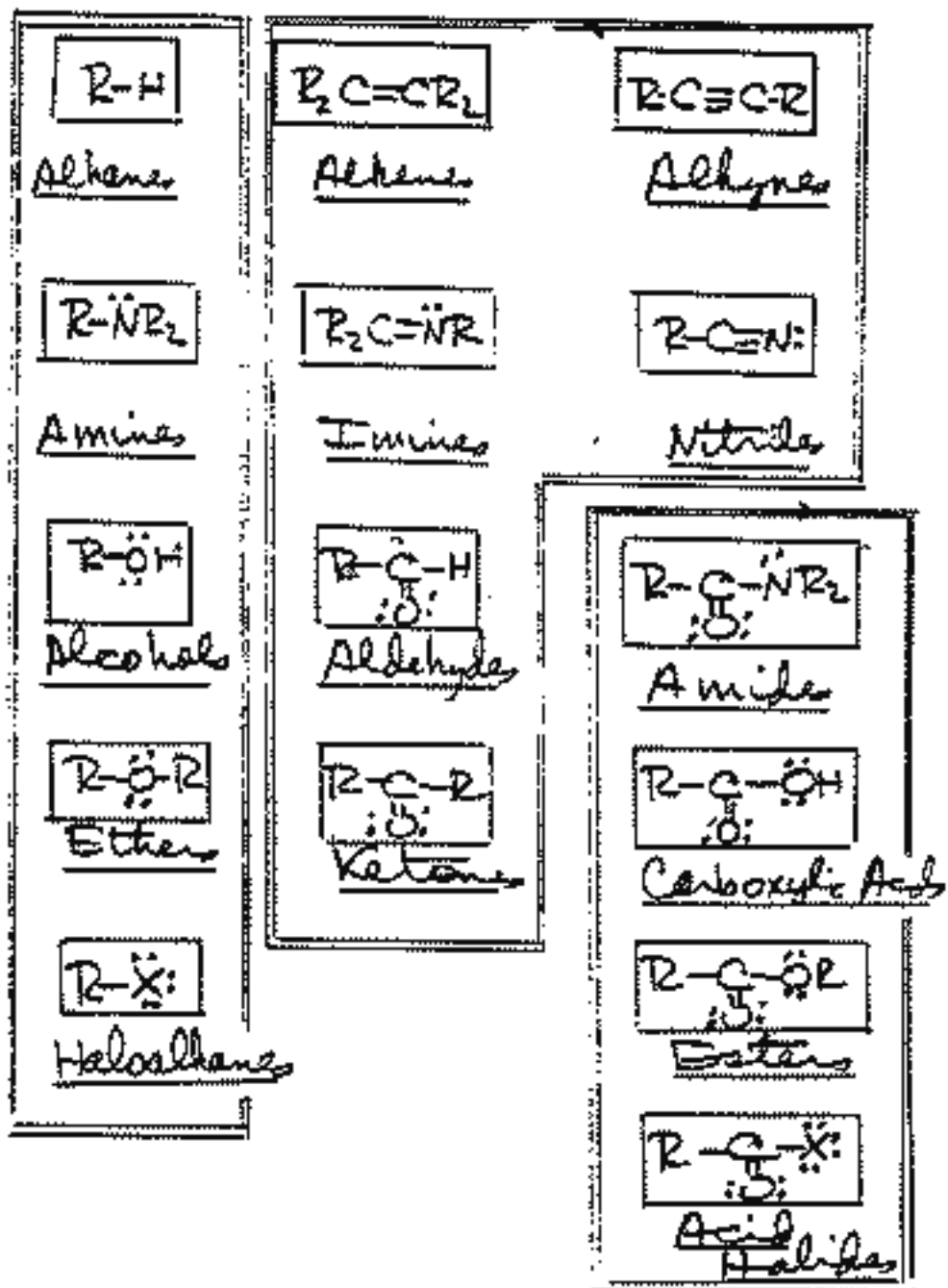
1.2 Chemical Bonds

Now that we have surveyed the important classes of organic molecules, it is time to talk about their chemical bonds. We have shown these chemical bonds as lines between the atoms and stated that they represent pairs of electrons. This representation of a bond makes it easy to draw structures of molecules, but in order to understand properties and chemical reactivity of molecules we need to look at these bonds more closely.

Organic chemists describe chemical bonds in organic compounds using theoretical models such as the **valence bond (VB)** or the **molecular orbital** (**MO**) models that you may have studied in general chemistry. Each has advantages and disadvantages and both are mathematically sophisticated. In order to explain structural, physical, and chemical properties of organic molecules at a level appropriate to our needs in this course, we will use a pictorial description of chemical bonds based on these models that chemists call the **localized molecular orbital** model.

Localized Molecular Orbitals (1.2A)

We will describe each chemical bond as a *localized molecular orbital* that overlaps the two bonded atoms and contains a pair of bonding electrons. [graphic 1.23] We form a *localized molecular orbital* by combining one **atomic orbital** from each of the two bonded atoms. To illustrate this, let's look at the single chemical bond in molecular hydrogen (H-H) that we can imagine arises from combination of two H atoms. We will see below that the single electron of an isolated H atom is in a spherical **1s atomic orbital**. [graphic 1.24] Combination of the *1s atomic orbitals* from two H atoms gives a *localized molecular orbital* that surrounds the H atoms and contains the two electrons of the H-H bond. From this point forward we will refer to *localized molecular orbitals* simply as *molecular orbitals* or *MO's*.

> **Localized versus Delocalized Molecular Orbitals**. The complete *molecular orbital theory* for chemical bonding places the bonding electrons of a molecule in **delocalized** molecular orbitals that arise from simultaneous combination of all *valence shell atomic orbitals* of all atoms in the molecule. The electrons in *delocalized* molecular orbitals bind the atoms in a molecule into a cohesive structure, but these *delocalized* molecular orbitals do not provide the classical descriptions of chemical bonds between atoms familiar to you and routinely used by organic chemists. In order to explain properties of organic molecules and their chemical reactions, we will treat most chemical bonds as electron pairs in *localized* molecular orbitals. In later chapters we will use certain types of *delocalized molecular orbitals* to explain structural, physical, and chemical properties not adequately described by localized molecular orbitals.

1.23. Localized Molecular Orbital

A Chemical Bond is an Electron Pair in a Molecular Orbital
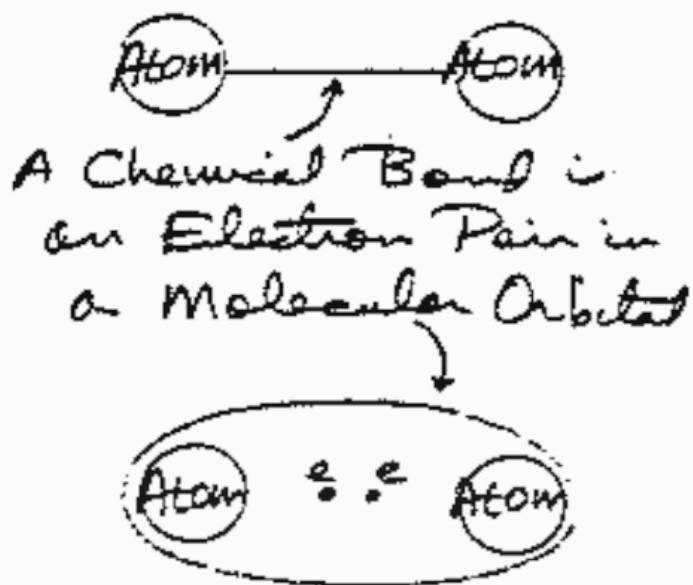
1.24.   H-H Bond Formation by Atomic Orbital Overlap

1s atomic orbital

H nucleus

electron

bonding Molecular orbital

H——H
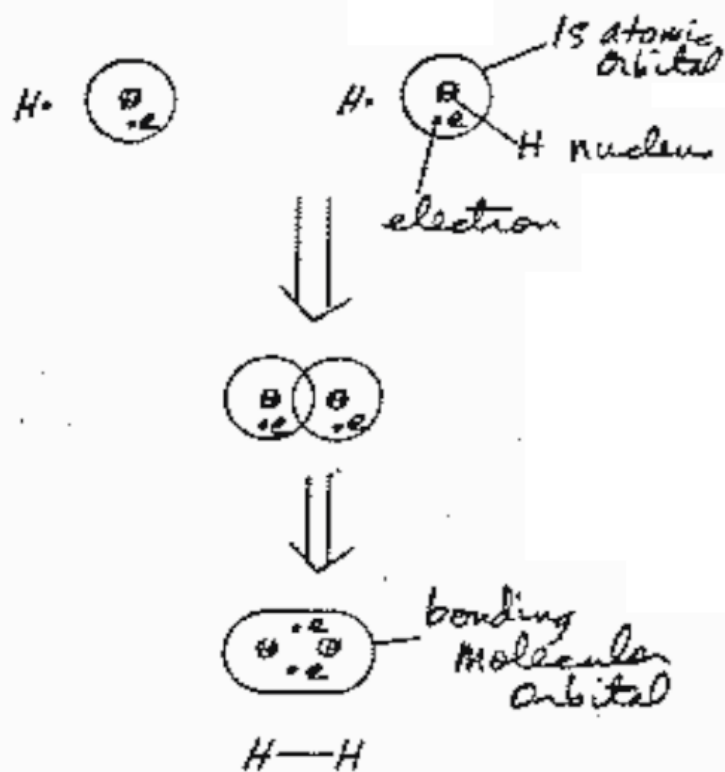
Bonding and Antibonding Molecular Orbitals. <u>Two</u> molecular orbitals always arise from the combination of <u>two</u> atomic orbitals. These are the **bonding molecular orbital** (shown above for H-H) and a molecular orbital with higher energy called an **antibonding molecular orbital**. [graphic 1.25] The two electrons in a chemical bond are in the lower energy *bonding molecular orbital*. We will not discuss *antibonding molecular orbitals* here since they contain no electrons, but we will see later in the text that they are important in determining chemical reactivity.

Electronic Structure of Atoms (1.2B)

Since we visualize a chemical bond as a molecular orbital with an electron pair formed by combination of two atomic orbitals that each contains one electron, it is important to review the **electronic structures** for the atoms that we find in organic molecules.

Electron Configurations. *Electron configurations* of atoms describe the *atomic orbital* locations of electrons in these atoms, and we show them here for the first ten atoms in the periodic table. [graphic 1.26] We represent the electrons as *arrows* pointing up or down to indicate their two possible **spin states**. These electrons are in the lowest energy atomic orbitals consistent with the following rules that you studied in general chemistry:

(1) An atomic orbital may contain no more than two electrons because electrons in the same orbital must have different spin states. (Pauli Exclusion Principle)

(2) All atomic orbitals of equal energy must each contain one electron before a second electron of opposite spin is added to any of them. (Hund's Rules)

The shorthand designations in Table 1.1 show these **normal** or **ground state** (*lowest energy*) electron configurations for the atoms. For example, the designation $1s^22s^1$ for Li means that there are 2 electrons in its 1s atomic orbital and 1 electron in its 2s atomic orbital.

Table 1.1.   **Electron Configurations for Elements 1-10**

Atom	No. of e	Electron Configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^22s^1$
Be	4	$1s^22s^2$
B	5	$1s^22s^22p^1$
C	6	$1s^22s^22p^12p^1$
N	7	$1s^22s^22p^12p^12p^1$
O	8	$1s^22s^22p^22p^12p^1$
F	9	$1s^22s^22p^22p^22p^1$
Ne	10	$1s^22s^22p^22p^22p^2$

1.25. Bonding and Antibonding Molecular Orbitals for H₂
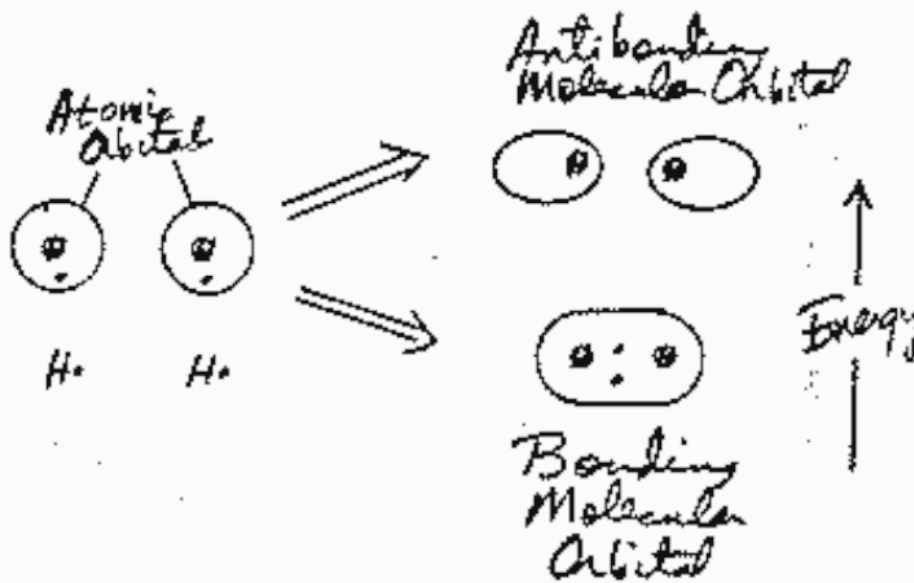
1.27. Shapes of Some Atomic Orbitals
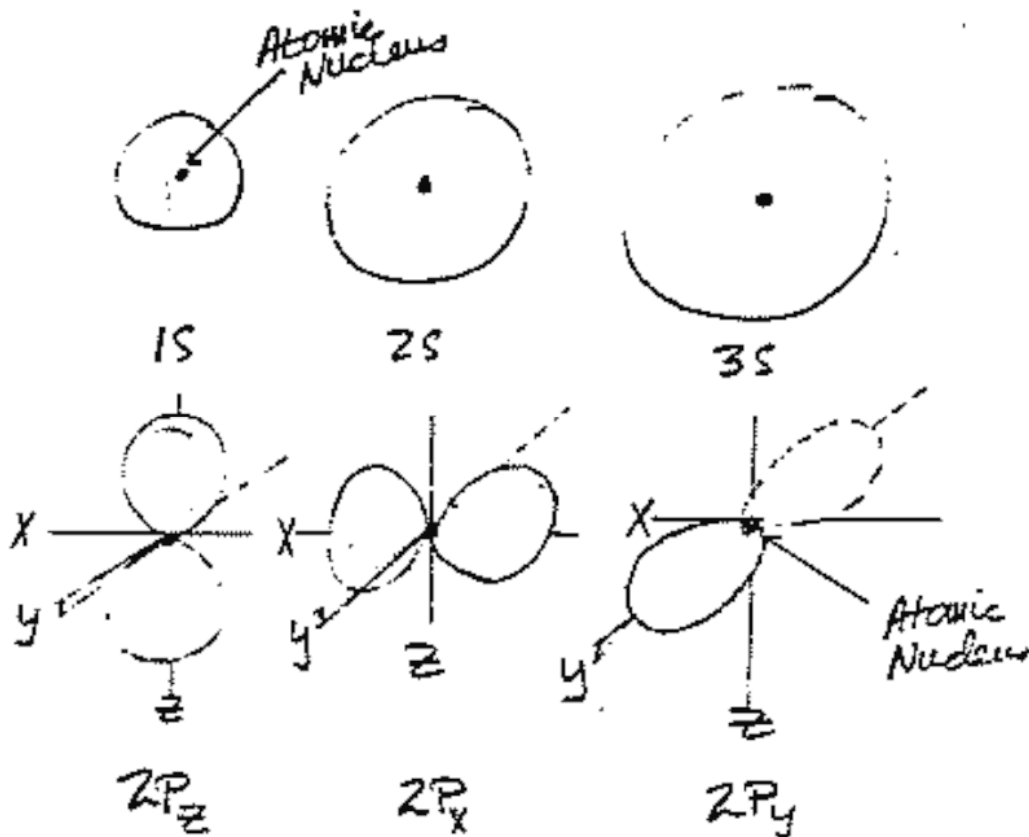
Figure [graphic 1.26]**. Electron Energy Diagrams for The First Ten Elements**

<u>**H (1e)**</u>
3s ___

↑   2p ___ 2p ___ 2p ___

E   2s ___

        1s ↑__

<u>**He (2e)**</u>
3s ___

2p ___ 2p ___ 2p ___

2s ___

1s ↑↓

<u>**Li (3e)**</u>
3s ___

2p ___ 2p ___ 2p___

2s ↑__

1s ↑↓

<u>**Be (4e)**</u>
3s ___

↑   2p ___ 2p ___ 2p ___

E   2s ↑↓

        1s ↑↓

<u>**B (5e)**</u>
3s ___

2p ↑__ 2p ___ 2p ___

2s ↑↓

1s ↑↓

<u>**C (6e)**</u>
3s ___

2p ↑__ 2p ↑__ 2p___

2s ↑↓

1s ↑↓

<u>**N (7e)**</u>
3s ___

↑   2p ↑__ 2p ↑__ 2p ↑__

E   2s ↑↓

        1s ↑↓

<u>**O(8e)**</u>
3s ___

2p ↑↓ 2p ↑__ 2p ↑__

2s ↑↓

1s ↑↓

<u>**F (9e)**</u>
3s ___

2p ↑↓ 2p ↑↓ 2p ↑__

2s ↑↓

1s ↑↓

<u>**Ne (10e)**</u>
3s ___

↑   2p ↑↓ 2p ↑↓ 2p ↑↓

E   2s ↑↓

        1s ↑↓
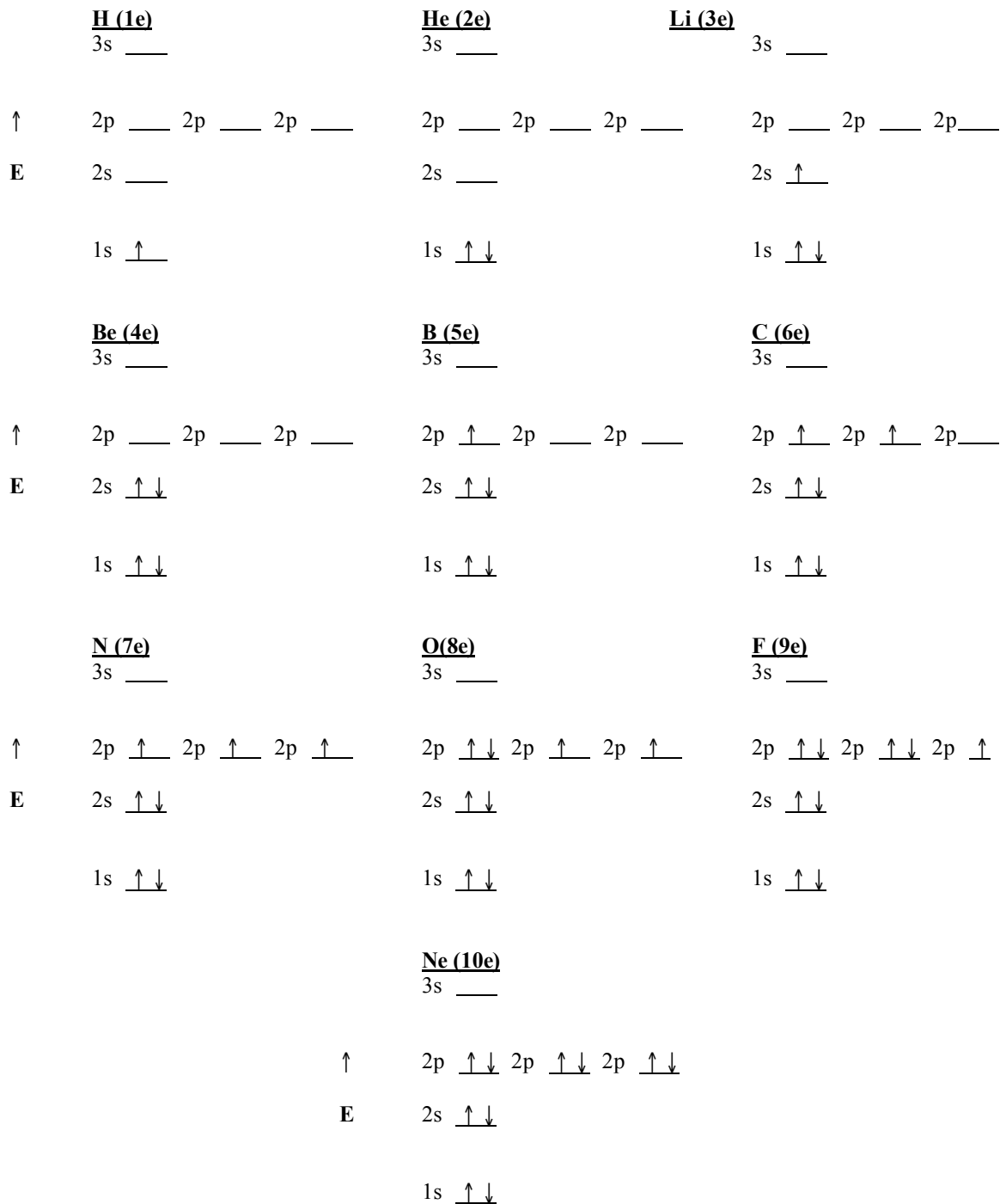
Atomic Orbitals. We can imagine that the 1s, 2s, 3s, and 2p atomic orbitals have the three-dimensional shapes that we show here. [graphic 1.27] We draw the *s* atomic orbitals as spheres of increasing size, and the *2p* atomic orbitals as "dumbbells". In reality, atomic orbitals have no boundaries, and these shapes represent spatial volumes around the atom that contain 90 to 95 % of the **electron density** in each atomic orbital. We can imagine that the three equal energy 2p atomic orbitals lie along mutually perpendicular x, y, and z axes of a rectangular coordinate system with the atomic nucleus at the origin so they are commonly designated $2p_x$, $2p_y$, and $2p_z$. Using these x, y, and z subscripts, the shorthand notation for the electron configuration of O is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$.

> **Electrons as Particles or Waves**. Chemists think of electrons both as **particles** and as **waves**. The term *electron density* describes electron distribution in a volume of space when they are thought of as *waves*. When they are thought of as *particles*, the atomic orbital shapes shown above represent the volumes of space where the electrons are present 90 to 95% of the time. There are other atomic orbitals (e.g., 3d and 4f atomic orbitals) besides those shown here, but they contain no electrons for most atoms found in organic molecules.

Lobes and Nodes. Each 2p atomic orbital has two **lobes** that join at a point called a **node**. [graphic 1.28] The electron density is the same in each *lobe*, but electron density is zero at the *node*. While 1s atomic orbitals have no nodes, 2s atomic orbitals have <u>one</u> node and 3s atomic orbitals have <u>two</u> nodes. Because the nodes in 2s and 3s atomic orbitals are spherical surfaces located <u>within</u> the 90 to 95% spherical boundaries of the atomic orbitals shown above, they often do not appear in pictures of these s atomic orbitals. The single spherical node in a 2s atomic orbital is represented by the dotted circle in the cross-section of a 2s atomic orbital. [graphic 1.29] The shading in this figure shows that most of the electron density in the 2s atomic orbital is between the inner nodal sphere and the 90 to 95% spherical outer boundary.

Chemical Bonds in Alkanes (1.2C)

Like the H-H bond in H_2, we can picture C-H and C-C bonds in alkanes as molecular orbitals (with electron pairs) that arise from combination of atomic orbitals of C and H atoms. Let's first examine this atomic orbital combination for C-H bonds in CH_4 and then look at it for other alkanes.

C-H Bonds in CH₄. Experiments show that methane (CH_4) has a three-dimensional shape in which the four C-H bonds point away from the C atom toward the four corners of a

1.28. Features of a 2p atomic orbital.

Orbital Lobes

Orbital Node

1.29.   A 2s Atomic Orbital

node

nucleus

90 to 95% Boundary

(Cross-Section)
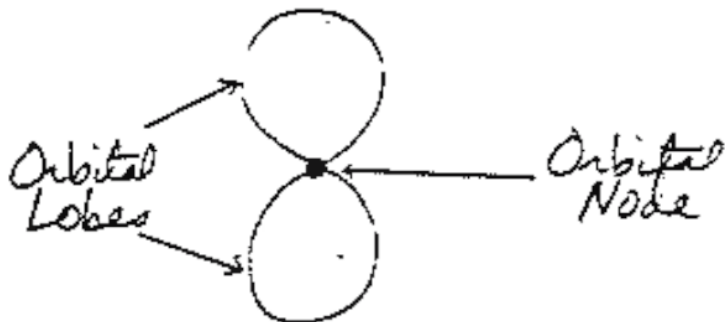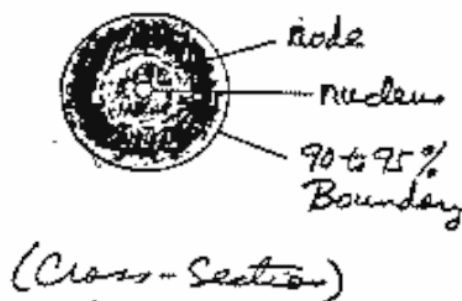
1.30.   Tetrahedral C in CH4

109.5° H-C-H angle

Tetrahedron

1.31. Methane Formation from Atoms

or

tetrahedron. [graphic 1.30] As a result, the H-C-H bond angles are all 109.5° and we describe the C atom as **tetrahedral**.

You can imagine formation of the C-H bonds in CH_4 from combination of a C with four H atoms. [graphic 1.31] The H atoms use their 1s atomic orbitals that each contain one electron. [graphic 1.32] However, to provide the tetrahedral shape of CH_4, the atomic orbitals of C need to poi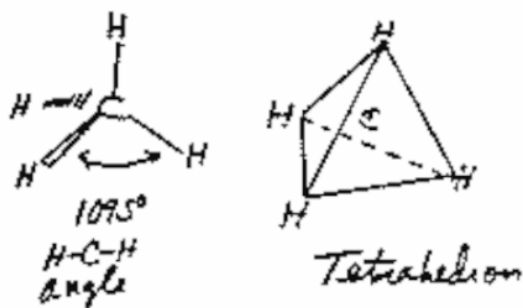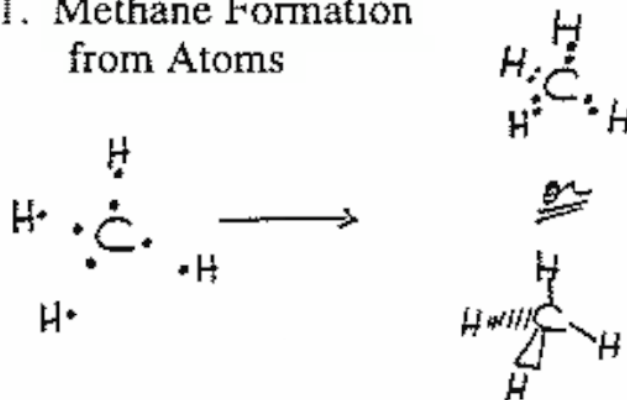nt away from each other with 109.5° angles and must each contain an electron. We do not find four atomic orbitals of this type in the **ground state** electron configuration of C (Table 1.1 and Figure [graphic 1.26]), but we will see in the next section that a process called **atomic orbital hybridization** gives us the four atomic orbitals of the correct geometry that we need.

sp³ Hybrid Atomic Orbitals of C. Combination of the **wave functions** (equations that mathematically define atomic orbitals) for the 2s and three 2p atomic orbitals of C provides mathematical descriptions of four **hybrid** atomic orbitals of equal energy directed away from C at 109.5° angles. [graphic 1.33] We describe these *hybrid atomic orbitals* as **sp³ atomic orbitals** because each contains one part *s* and three parts *p atomic orbital character*. By convention, the "2" of 2s and 2p is not included in the name of the *sp³ hybrid atomic orbital.* Each sp³ atomic orbital has two unequal lobes joined at a node. [graphic 1.34] The location of the C nucleus is inside the smaller lobe close to the node.

A comparison of the elec tron configurations for a *ground state* C atom and an *sp³ hybridized* C atom shows that the new hybrid sp³ atomic orbitals are at an energy level intermediate between those of the original 2s and 2p atomic orbitals. [graphic 1.35] If you use the rules outlined earlier to place the six electrons of C in the atomic orbitals of sp³ hybridized C, one electron ends up in each of the four sp³ hybrid atomic orbitals. As a result, all four of these sp³ electrons are suitable for C-H bond formation with H atoms.

C-H and C-C Bonds in Ethane. Ethane (CH_3-CH_3) has a three-dimensional shape where the H-C-H and H-C-C bond angles are approximately 109.5° like the bond angles in methane. [graphic 1.36] Since its C's are approximately tetrahedral, we can view the C-C bonds as the result of combination of an sp³ atomic orbital on each C. [graphic 1.37] We then picture each C-H bond as the result of the combination of one of remaining sp³ atomic orbitals on each C with a 1s atomic orbital of H. [graphic 1.38] Since all C atoms in alkanes are approximately tetrahedral, we can use sp³ hybridized C for formation of all of their C-H and C-C bonds.

1.32.　　　(a) AO's on H and C Used for C-H Bonds

H atom

one e̱
in a
spherical
atomic
orbital

Tetrahedral C Atom

four atomic
orbital each
containing
one e̱

109.5°
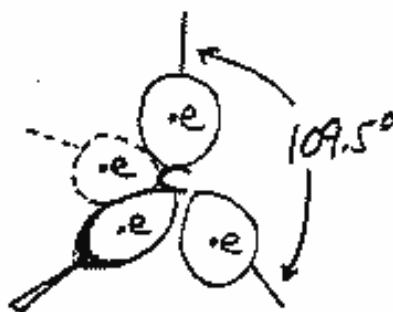
(b) C-H MO's from Overlap of C and H AO's

C Atomic Orbital

H Atomic Orbital

Bonding C-H Molecular Orbital

109.5°
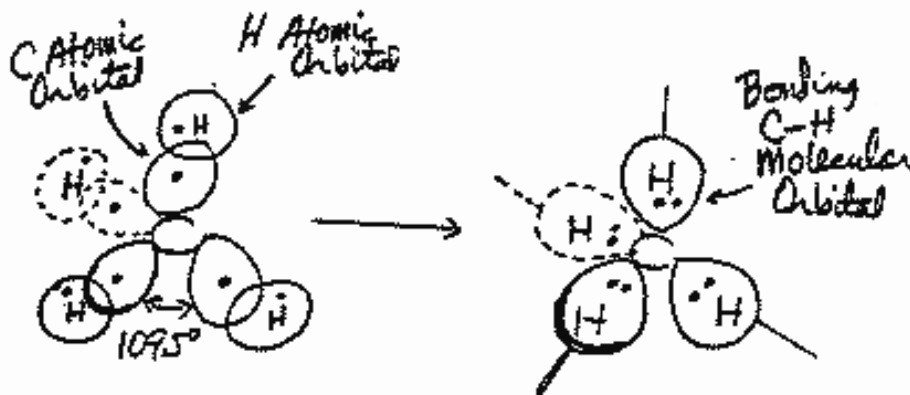
Four H Atoms
Overlap their
Atomic Orbital
with the four
atomic orbital
of C

Four Bonding
Molecular Orbitals
are Formed which
are the Four
C-H Bonds

1.33. Formation of sp³ Hybrid AO's

Overlapping 2S and 2P Orbital

Hybridization

Four Hybrid SP3 Orbital
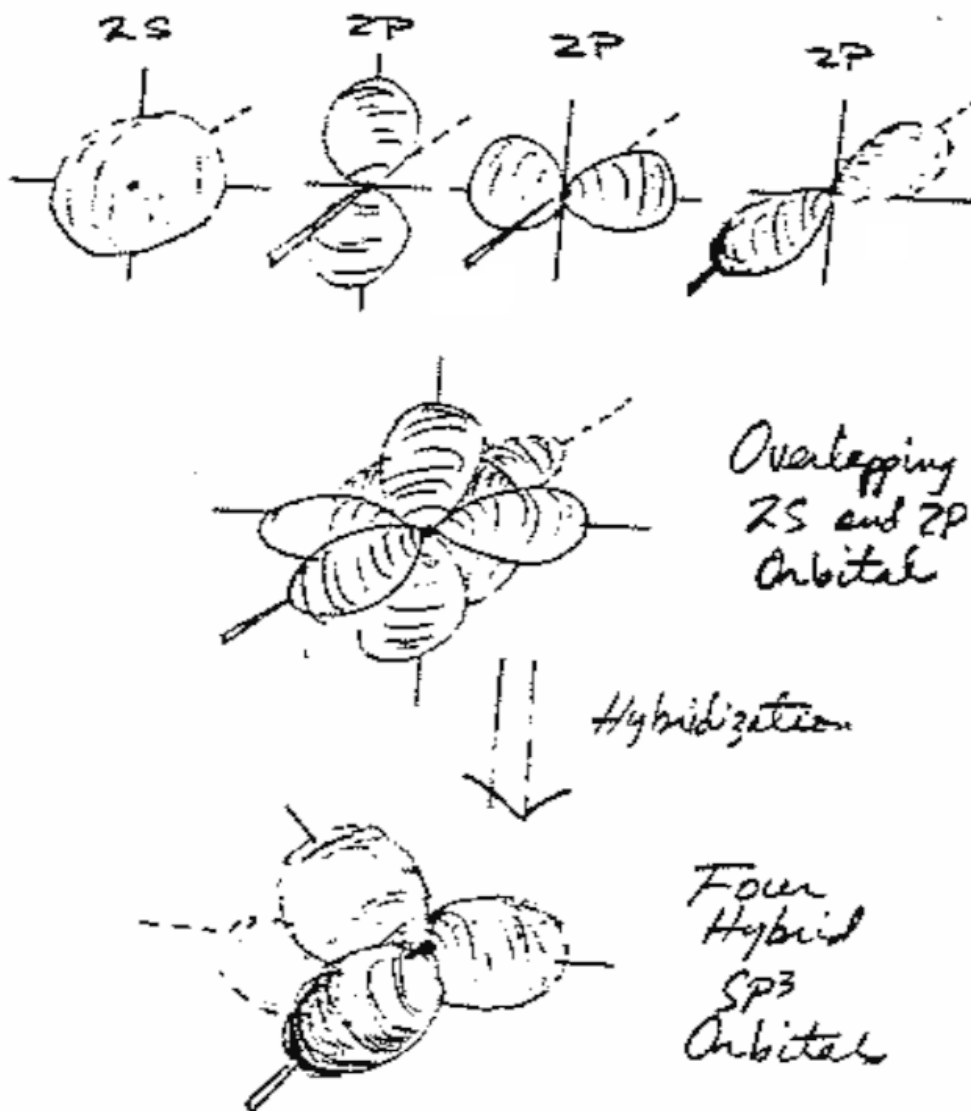
1.34.　Lobes and Node of an sp³ AO

C Nucleus　　Node

Lobe
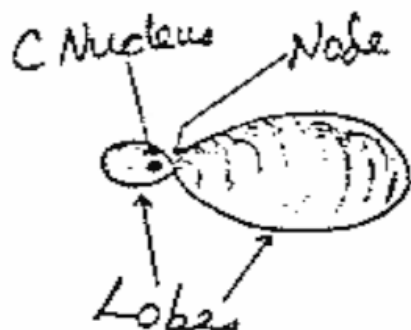
Figure [graphic 1.35]**. Electron Energy Diagrams for Ground State and sp^3 Hybridized C.**

Normal C   sp^3 Hybridized C

3s ___   3s ___

2p ↑ 2p ↑ 2p ___

↑   .... { sp^3 ↑   sp^3 ↑   sp^3 ↑   sp^3 ↑

E   2s ↑↓

1s ↑↓   1s ↑↓

$1s^2 2s^2 2p^1 2p^1 2p^0$ $1s^2 (sp^3)^1 (sp^3)^1 (sp^3)^1 (sp^3)^1$
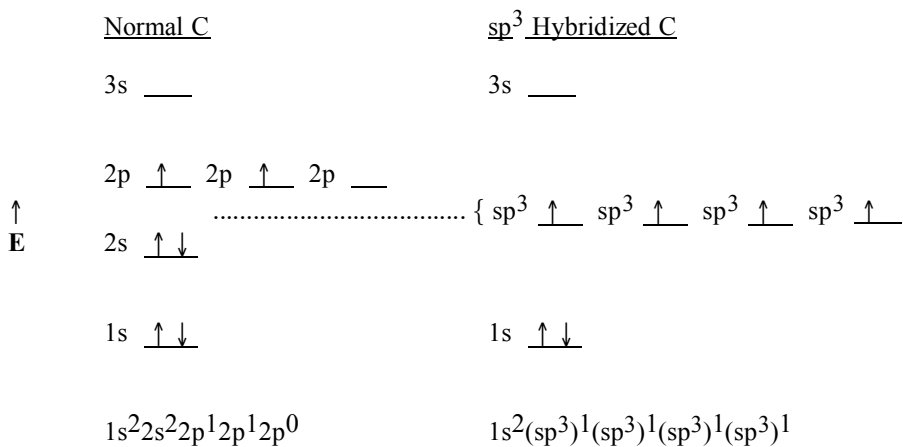
1.36.   Ethane (CH$_3$-CH$_3$)
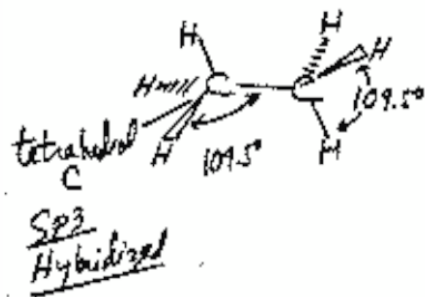
1.37.   C-C Formation from sp^3 AO's of C
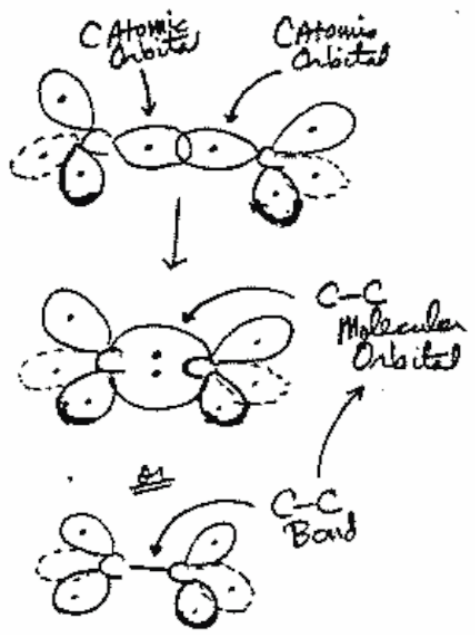
1.38.   C-H Formation from sp^3 C and 1s H AO's
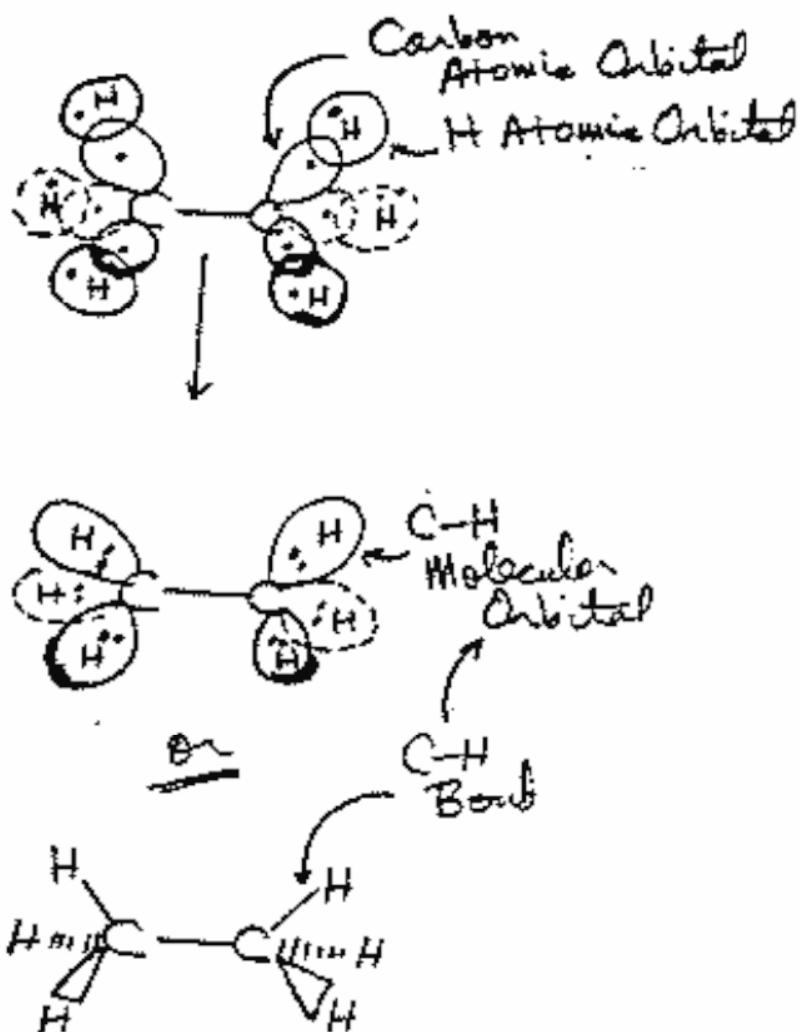
1.39.   MO's in Ethane
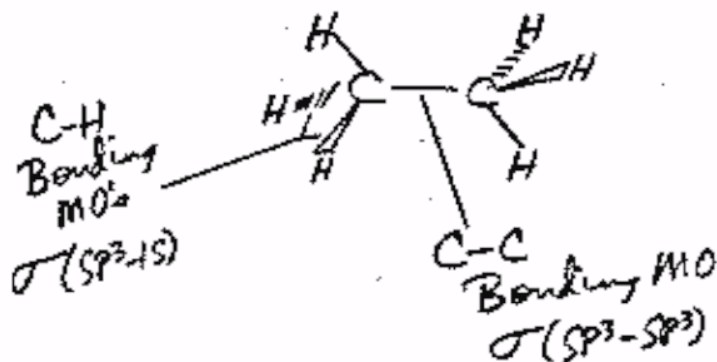
Alkane Bond Angles are Not Exactly 109.5°. We will see in Chapter 2 that bond angles in alkanes are not exactly 109.5°. Bond angles at a tetrahedral C usually differ from this preferred value because they adjust to accommodate different size atoms or groups on a C. Since these deviations from tetrahedral bond angles are relatively small we can generally approximate all tetrahedral C's as sp^3 hybridized.

C-H and C-C Molecular Orbitals. We designate each C-H bonding molecular orbital in alkanes as $\sigma(sp^3\text{-}1s)$ while the C-C bonding molecular orbital is $\sigma(sp^3\text{-}sp^3)$. [graphic 1.39] The atomic orbital names in the parentheses are those that combine to form the molecular orbital, and the prefix σ indicates that this combination occurs along the axes of the atomic orbitals ("end-on" combination) as we illustrated above for C-C bond formation in ethane. (We will see later for other types of compounds that atomic orbitals can also combine with their axes parallel to each other.)
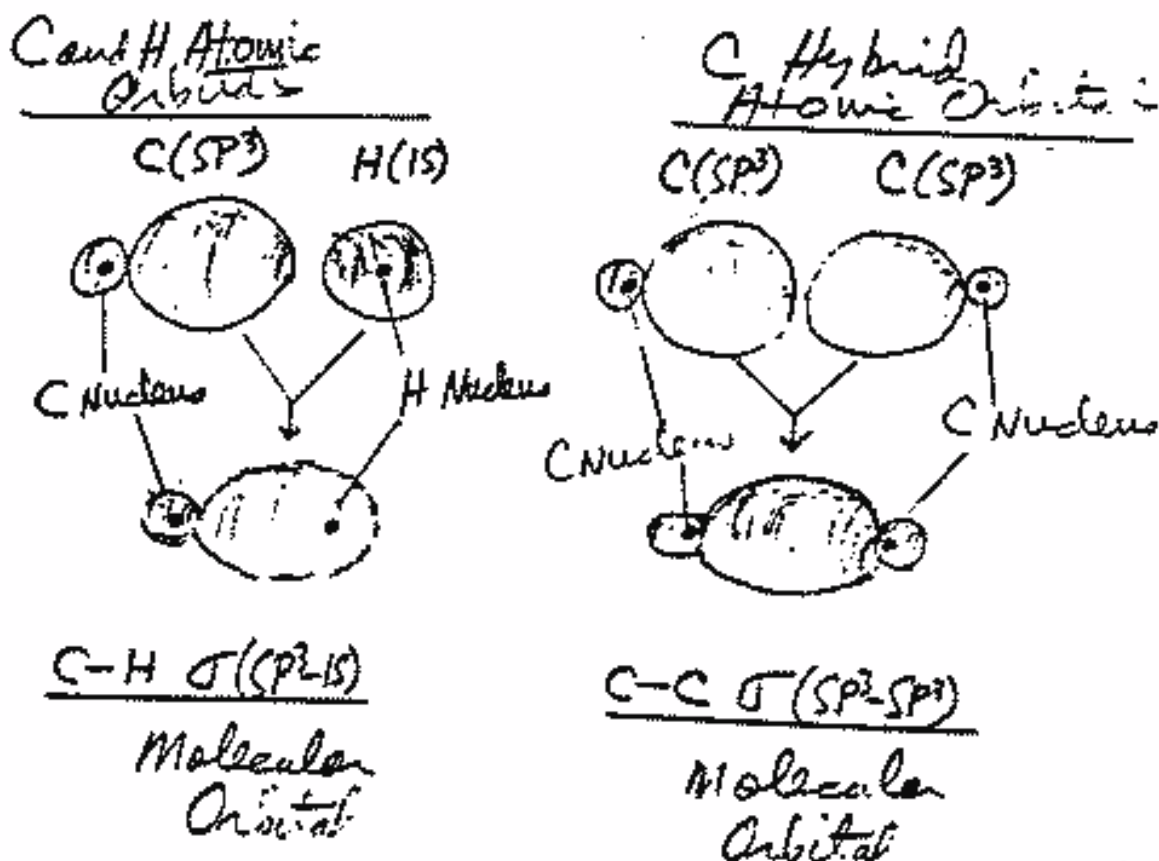
Molecular orbitals (MO's) share the characteristics of the two combining atomic orbitals (AO's). As a result, $\sigma(sp^3\text{-}1s)$ and $\sigma(sp^3\text{-}sp^3)$ MO's have different shapes because they arise from combination of different AO's. [graphic 1.40] A *C-H MO* has a large lobe containing the H nucleus, and a small lobe containing the C nucleus. H is in the large lobe because it is at the center of the 1s AO that overlaps with the large lobe of the sp^3 AO of C. The C nucleus lies just inside the smaller lobe of the C-H MO because of its original location in the small lobe of the sp^3 AO of C. In contrast, the *C-C MO* has three lobes and the C nuclei lie just inside the two smaller lobes.

Chemical Bonds in Alkenes and Alkynes (1.2D)

The three-dimensional shapes of alkenes and alkynes are much different than those of alkanes. In *alkenes*, the atoms directly attached to the C=C group lie in a plane that includes C=C as shown here for *ethene*. [graphic 1.41] In *alkynes*, the atoms directly attached to the C≡C group lie along a straight line that includes C≡C as we see for *ethyne*. As a result, H-C-H and H-C-C bond angles on C=C and C≡C groups are significantly different from the tetrahedral bond angles found in alkanes. In addition, there are just 2 atoms directly attached to each C of C≡C, and 3 atoms to each C of C=C, rather than 4 atoms as in alkanes. These observations are not consistent with the use of sp^3 hybridized C atoms in C=C and C≡C groups. They require two different hybridization states for C that we describe in the following sections.

Hybridization of C in C=C Bonds. If we combine just two 2p atomic orbitals of C with its 2s AO, the result is an **sp^2 hybridized** carbon atom with three sp^2 hybrid atomic orbitals.

1.40.   A Comparison of C-H and C-C MO's

C and H Atomic Orbitals

C(SP³)   H(1S)

C Nucleus   H Nucleus

C-H σ(SP³-1S)

Molecular Orbital

C Hybrid Atomic Orbitals

C(SP³)   C(SP³)

C Nucleus   C Nucleus

C-C σ(SP³-SP³)

Molecular Orbital

1.41

Alkanes :   Ethane   H 109.5°   109.5°

Alkenes :   Ethene   120°   120°

Alkynes :   Ethyne   H—C≡C—H   ~180°
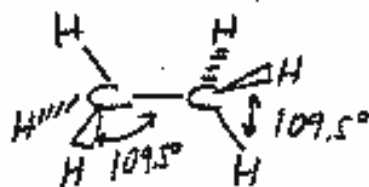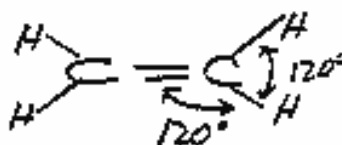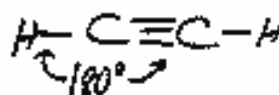
[graphic 1.42] These three sp^2 atomic orbitals all lie in the same plane separated from each other by 120° angles. This is a perfect arrangement of atomic orbitals to form C-H and C-C bonds in *ethene* since it is planar and its bond angles are all about 120°! [graphic 1.43]

However this picture accounts for only one bond between the two C atoms. What is the origin of the second bond in each C=C? The electron configuration of the sp^2 C atom provides the answer. [graphic 1.44] While each sp^2 atomic orbital with its electron participates in formation of one C-H or C-C bond, there is an additional electron in the unhybridized 2p atomic orbital of the sp^2 C. The second bond between the C's in $H_2C=CH_2$ forms from a sideways combination of these 2p atomic orbitals on each of C. [graphic 1.45]

> **More about the sp^2 Electron Configuration**. The placement of the sixth electron of sp^2 C in the 2p atomic orbital (Figure [graphic 1.44]) is inconsistent with our rules that govern the placement of electrons in atomic orbitals of the lowest possible energy. We rationalize this inconsistency by noting that sp^2 C does not exist by itself outside of a molecule. As is also the case for sp^3 C, the sp^2 C has a hypothetical electron configuration that we use to explain the formation of MO's by combination of AO's. The same is true for **sp hybridized C** that we introduce below to explain C≡C bonding.

C-H and C=C Molecular Orbitals. Molecular orbitals for C-H bonds in $H_2C=CH_2$ are **σ(sp²-1s)**, while the C-C MO from overlap of two sp^2 hybrid AO's is **σ(sp²-sp²)**. [graphic 1.46] The other C-C molecular orbital resulting from sideways combination of two 2p AO's is **π(2p-2p)**. The symbol π means that the atomic orbitals overlap sideways (with their axes parallel) rather than along their axes as for a σ MO. The π MO, with two lobes located above and below the plane of the C and H atoms, is quite different from a σ MO. As a result, we describe a C=C double bond as consisting of one **σ bond** and one **π bond**.

Hybridization of C in C≡C Bonds. Hybrid atomic orbitals suitable for making bonds between a C and <u>two</u> other atoms, as in ethyne (HC≡CH), arise from combination of <u>one</u> 2p and the 2s atomic orbital of an unhybridized C. [graphic 1.47] This atomic orbital combination gives two **sp hybrid** atomic orbitals on C that form a 180° angle with respect to each other. [graphic 1.48] These *sp atomic orbitals* participate in formation of the C-H bonds and <u>one</u> of the three bonds between the C's in H-C≡C-H. [graphic 1.49] The other two bonds between the C's form by sideways combination of the two remaining 2p atomic orbitals on one sp C with those on the other sp C. The result is two π(2p-2p) molecular orbitals at right angles to each other. The C≡C triple bond has one σ bond and two π bonds. [graphic 1.50]

1.42. sp^2 Hybridized C

Three SP^2 Orbitals on C
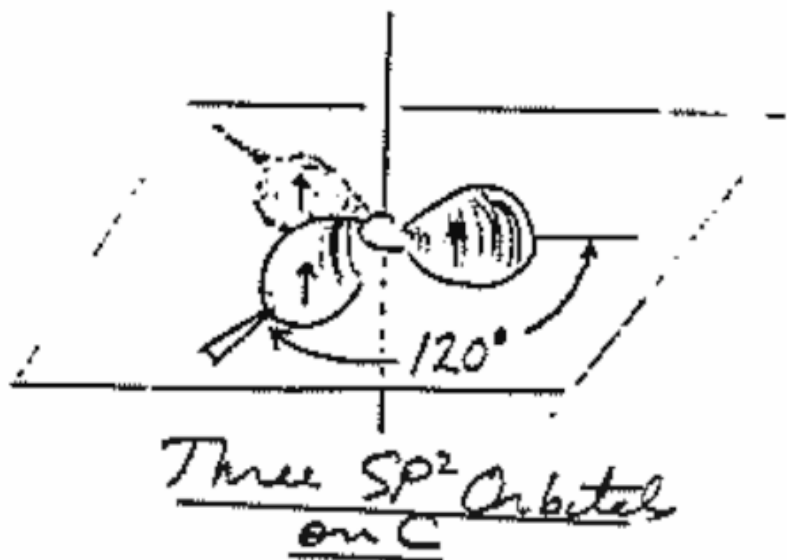
1.43. C-C and C-H Formation from sp^2 AO's
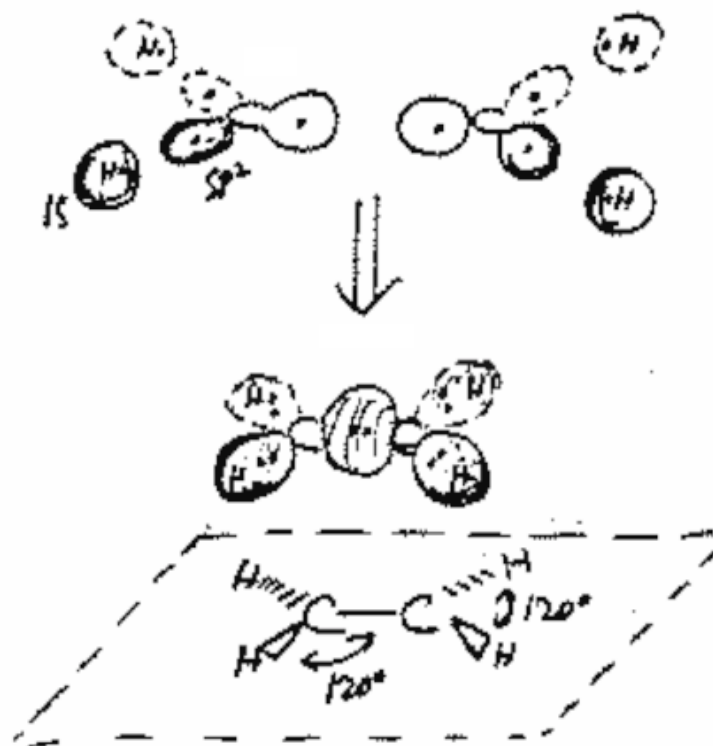
Figure [graphic 1.44]. Electron Energy Level Diagrams
for Ground State and sp² Hybridized C

Normal C   sp² Hybridized C

3s ___   3s ___

2p ↑   2p ↑   2p ___   2p ↑
↑   .... { sp² ↑   sp² ↑   sp² ↑
E   2s ↑↓

1s ↑↓   1s ↑↓

$1s^22s^22p^12p^12p^0$ $1s^2(sp^2)^1(sp^2)^1(sp^2)^12p^1$
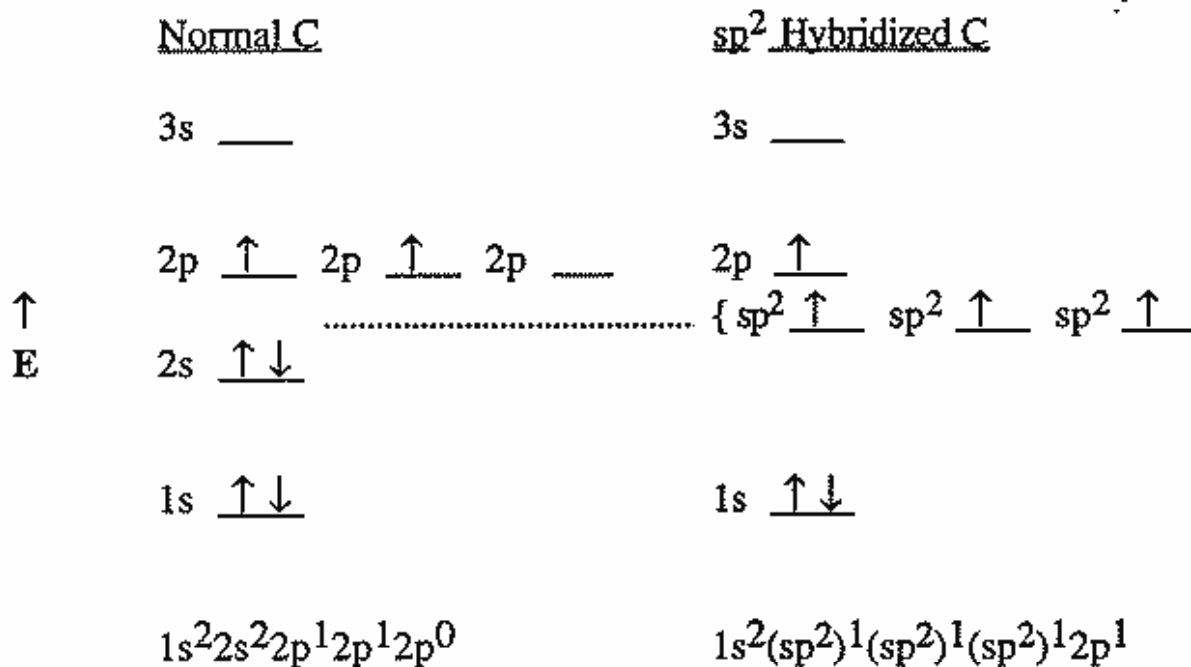
1.45.   Overlap of 2p AO's of sp² C

1.46.　　σ and π MO's

σ mo's　　　　　　　π mo
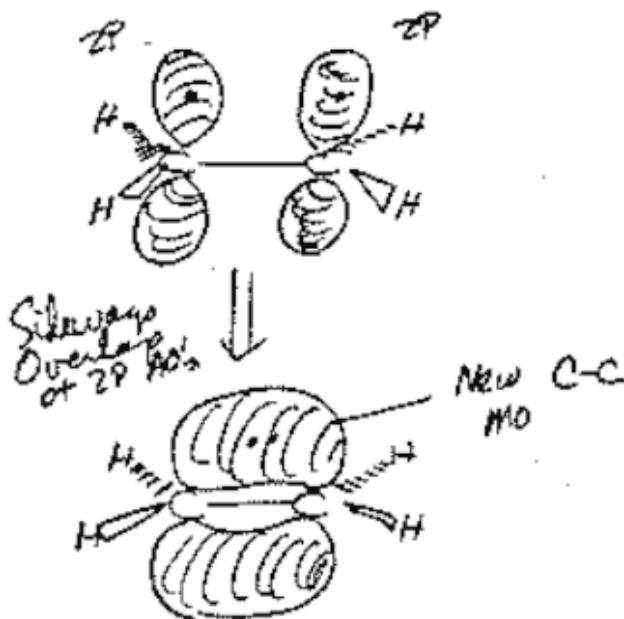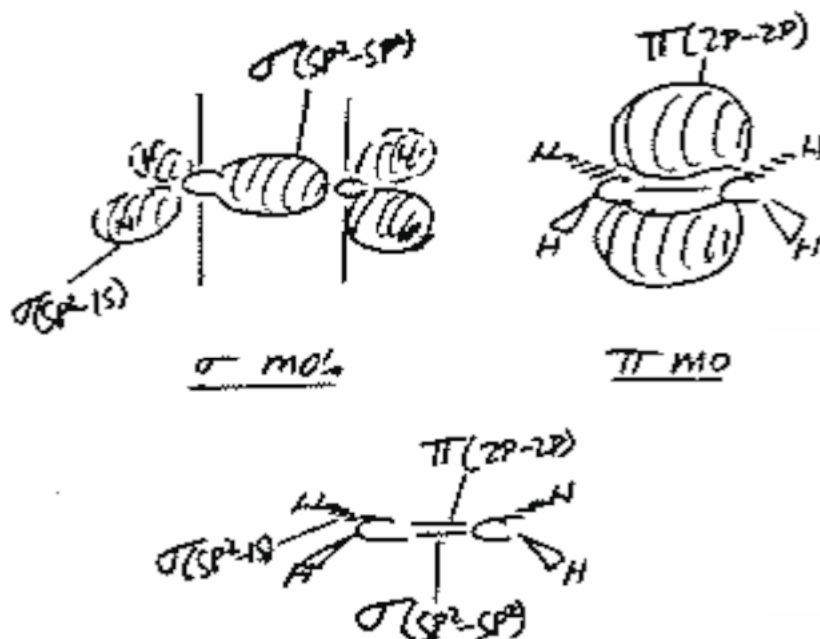
Figure [graphic 1.47]. Electron Energy Level Diagrams for Ground State and sp Hybridized C

Normal C			sp Hybridized C	

	Normal C			sp Hybridized C	
3s ___			3s ___		
2p ↑	2p ↑	2p ___	2p ↑	2p ↑	
			{ sp ↑	sp ↑	
2s ↑↓					
1s ↑↓			1s ↑↓		

↑
E

$1s^2 2s^2 2p^1 2p^1 2p^0$　　　　　　$1s^2 (sp)^1 (sp)^1 2p^1 2p^1$
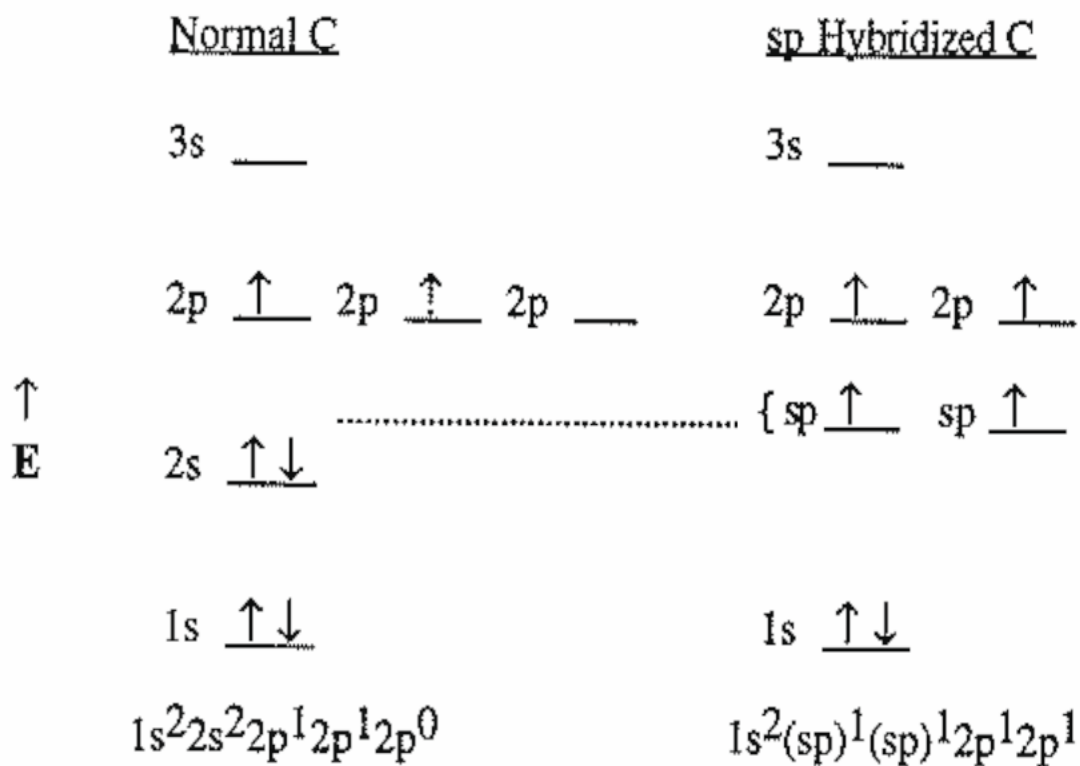
1.48.   sp Hybridized C

SP-AO SP-AO

$180°$
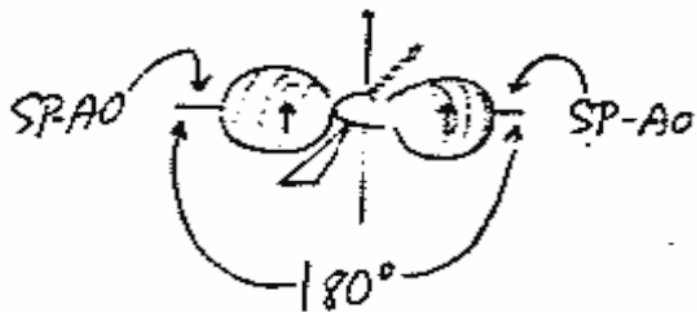
Two SP orbital
C~C

1.49.   Ethyne from sp C and 1s H

$\sigma(SP\text{-}1s)$
C-H MO

$\sigma(SP\text{-}1s)$
C-H
MO

$\sigma(SP\text{-}SP)$
C-C
MO

$2P$ $2P$

$\pi(2P\text{-}2P)$ C-C MO

$\pi(2P\text{-}2P)$
C-C MO
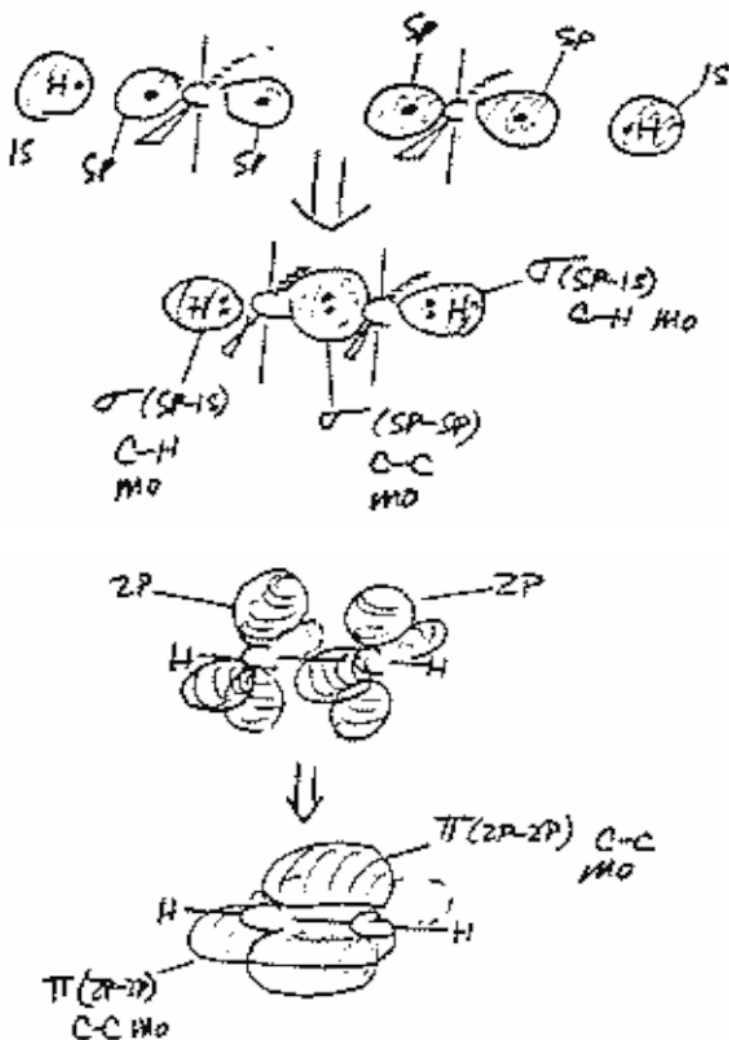
1.50.　　MO's in Ethyne

1.51.　　VSEPR and CH$_4$
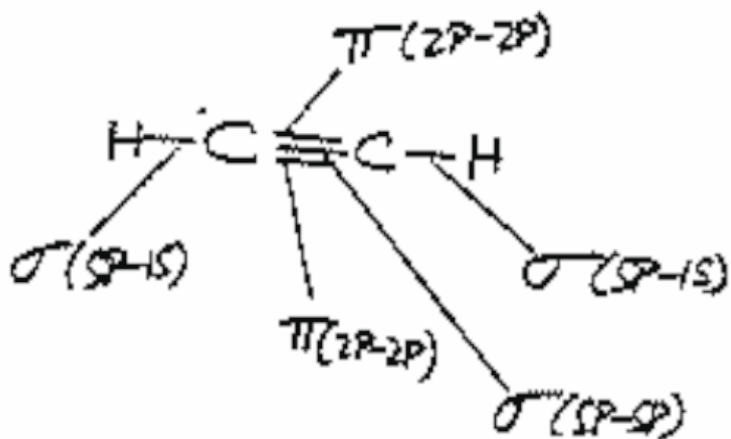
Planar
CH$_4$

Tetrahedral
CH$_4$

1.52.　　Planar Ethene

$\underline{a} \simeq \underline{b}$
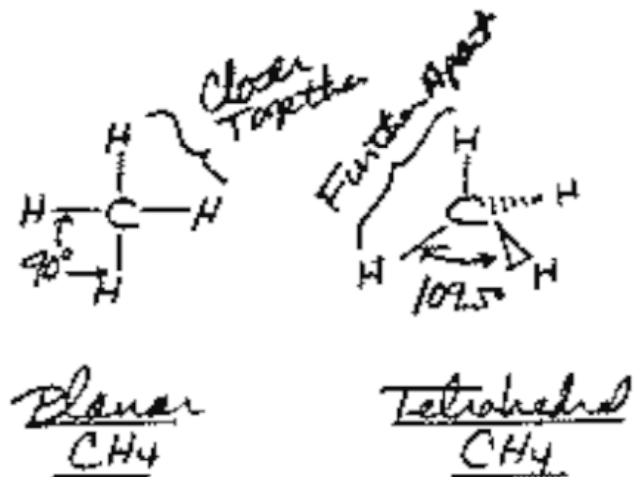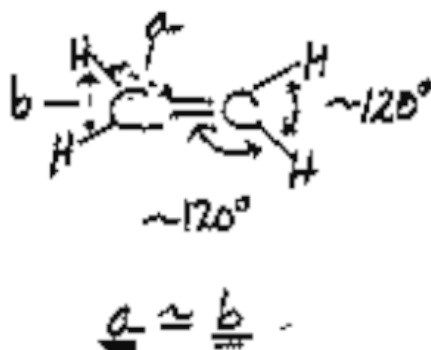
The Shapes of Molecules (VSEPR) (1.2E)

The tetrahedral shapes of C's in *alkanes*, the planar geometry of C=C in *alkenes*, and the linear geometry of C≡C in *alkynes*, dictate the hybrid C atomic orbitals we use to form the MO's in these compounds. We know these molecular shapes from experimental studies, but we can also use **Valence Shell Electron Pair Repulsion** theory (**VSEPR**) to predict them. *VSEPR* states that molecules prefer to adopt three-dimensional shapes that place their *valence shell electron pairs* as far apart as possible. Since all valence shell electrons in alkanes, alkenes, and alkynes (such as CH_4, CH_3CH_3, $CH_2=CH_2$, and $CH≡CH$) are in chemical bonds, the shapes of these molecules are those that maximize separation of their bonds. While you might have wondered earlier why *methane* (CH_4) is not planar with 90° H-C-H bond angles, such an arrangement places the four C-H bonds closer together than H-C-H bond angles of 109.5° in tetrahedral CH_4. [graphic 1.51]

In the case of ethene ($CH_2=CH_2$), a planar geometry with 120° bond angles places the C-H bonds on each C equidistant from each other and from the two bonds in C=C. [graphic 1.52] While the geometry of ethene is planar, the actual H-C-H bond angles are about 117° and the H-C=C angles are about 121°. VSEPR theory rationalizes the difference in these angles from 120° by recognizing that C=C has two bonding electron pairs (two bonds). As a result, there is more repulsion between the H-C and C=C bonds in $H_2C=CH_2$ than between its two C-H bonds. We will see that *VSEPR* is useful in predicting 3-dimensional shapes of most organic molecules.

Bonds between C and N, O, or X (1.2F)

We also use sp^3, sp^2, and sp hybridization states for N, O, or X atoms in organic compounds.

   Carbon-Nitrogen Bonds. Early in the chapter, we described C-N, C=N, and C≡N bonds. [graphic 1.53] We use the same hybridization states for the C's in these bonds that we used for the C's in C-C, C=C, and C≡C bonds. For example, the C in H_3C-NH_2 is sp^3, C in $H_2C=NH$ is sp^2, and C in a C≡N group is sp hybridized. The hybridization state of a C depends only on whether it has four single bonds (sp^3), one double bond and two single bonds (sp^2), or a triple bond and one single bond (sp). It does not depend on the specific atom to which C is bonded.

In a similar way, we can assign these same hybridization states to N based on whether it has only single bonds (sp^3), one single and one double bond (sp^2), or a triple bond (sp). Each of these sp^3, sp^2, and sp hybrid electron configurations of N are completely consistent with the

preference of N for 3 bonds because each has three atomic orbitals with one electron. [graphic 1.54]

> **Why Hybridize N**? You may wonder why we need to hybridize N to explain its 3 chemical bonds. *Unhybridized* N has three 2p AO's, each containing a single electron, that could form the three bonds to C in each of these compounds. This situation is quite different than that for *unhybridized* C since it has only <u>two</u> AO's with one electron available to form chemical bonds while <u>four</u> are needed. In the case of N, we will see below that hybridization explains its bond angles in molecules such as CH_3-NH_2 and CH_2=NH that are not consistent with 90° angles predicted for bonds made from 2p AO's of unhybridized N.

CH_3-NH_2 (sp^3 N). We use the three sp^3 atomic orbitals of sp^3 N that contain single electrons to form the three σ bonds to N in CH_3-NH_2. [graphic 1.55] The two electrons in the remaining sp^3 atomic orbital of N (Figure [graphic 1.54]) constitute its unshared electron pair. The use of sp^3 AO's on N as well as on C suggests that bond angles at these atoms should be tetrahedral. Calculations for this compound show that H-C-H angles are xx°, and H-C-N angles are yy°. [*xx and yy to be added*] [graphic 1.56] While these differ from the ideal angle of 109.5°, they are close enough to be consistent with sp^3 hybridized C. Their differences reflect differences in the size of H and the NH_2 group on C.

The C-N-H angles of 111°, and H-N-H angle of 107° are also consistent with sp^3 hybridized N. This result may surprise you since N has only <u>three</u> attached groups, but VSEPR predicts it. The *unshared electron pair* is one of the four valence shell electron pairs of N. We need to maximize its separation from the three bonding electron pairs as well as maximize the separations of the bonding electron pairs from each other. The result is the observed pyramidal geometry for N and its attached atoms. You can see in Figure [graphic 1.57] that the unshared electron pair in an sp^3 AO is farther from C-N and N-H bonding electron pairs than it would be in a 2p atomic orbital on planar (sp^2) N.   [graphic 1.57]

CH_2=NH (sp^2 N). sp^2 hybridized N has one sp^2 atomic orbital with the unshared electron pair and two sp^2 atomic orbitals with single electrons that form the σ N-H bond and the σ bond in C=N. [graphic 1.58] The 2p atomic orbital on N with one electron overlaps the 2p atomic orbital containing one electron on sp^2 hybridized C to form the π bond in C=N. The H_2C=NH bond angles are similar to predicted values of 120° expected for sp^2 C and sp^2 N and are consistent with VSEPR theory. [graphic 1.59]
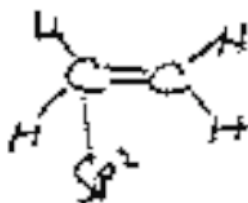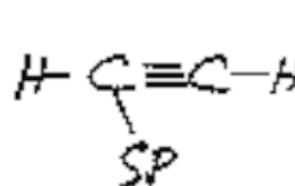
1.53.   Compounds with C-N, C=N, and C≡N Bonds
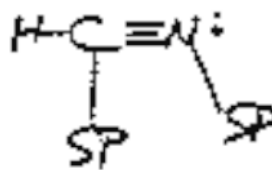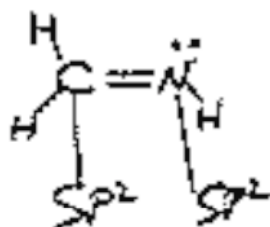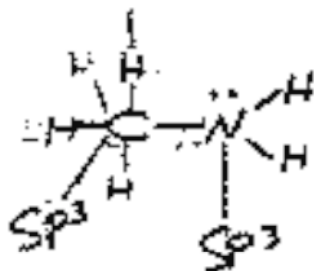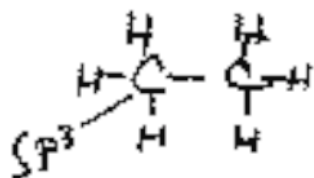
1.55.   Formation of CH₃-NH₂
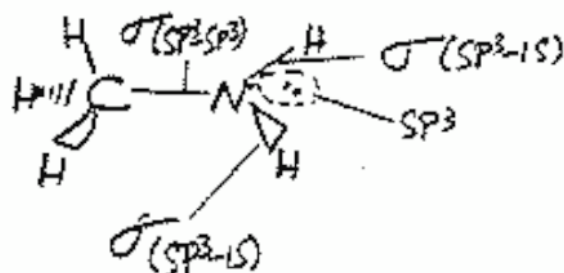
Figure [graphic 1.54]**. Electron Energy Level Diagrams for Normal,**
sp^3, sp^2, and sp Hybridized N

<u>Normal N</u>   <u>sp^3 Hybridized N</u>

3s ___   3s ___

2p ↑   2p ↑   2p ↑
↑   ....{ sp^3 ↑↓ sp^3 ↑   sp^3 ↑   sp^3 ↑
E   2s ↑↓

1s ↑↓   1s ↑↓

1s^{2}2s^{2}2p^{1}2p^{1}2p^1 1s^2(sp^3)^2(sp^3)^1(sp^3)^1(sp^3)^1

<u>Normal N</u>   <u>sp^2 Hybridized N</u>

3s ___   3s ___

2p ↑   2p ↑   2p ↑   2p ↑
↑   ....{ sp^2 ↑↓ sp^2 ↑   sp^2 ↑
E   2s ↑↓

1s ↑↓   1s ↑↓

1s^{2}2s^{2}2p^{1}2p^{1}2p^1 1s^2(sp^2)^2(sp^2)^1(sp^2)^{1}2p^1

<u>Normal N</u>   sp <u>Hybridized N</u>

3s ___   3s ___

2p ↑   2p ↑   2p ↑   2p ↑   2p ↑
↑   .... { sp ↑↓   sp ↑
E   2s ↑↓

1s ↑↓   1s ↑↓

1s^{2}2s^{2}2p^{1}2p^{1}2p^1 1s^2(sp)^2(sp)^{1}2p^{1}2p^1
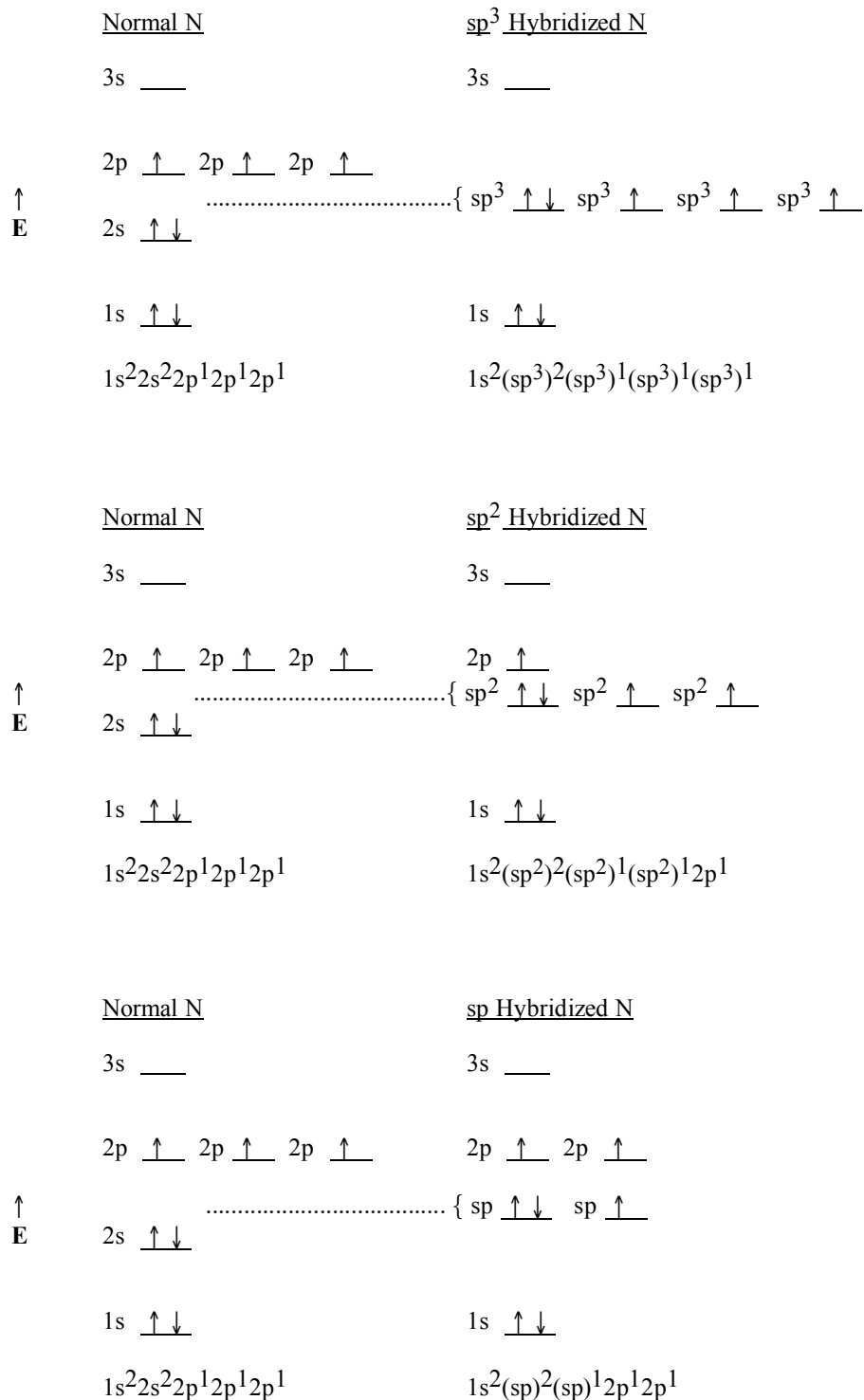
1.56
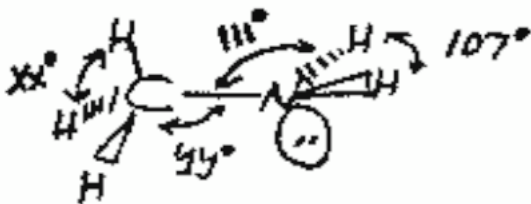
1.57
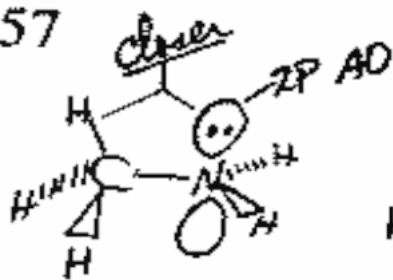
CH_3NH_2 with Planar N
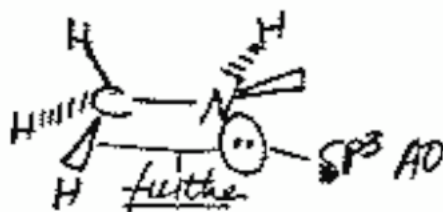
CH_3NH_2 with Pyramidal N

1.58. Formation of $CH_2=NH$

1.59. (Add Calculated Bond Angles)
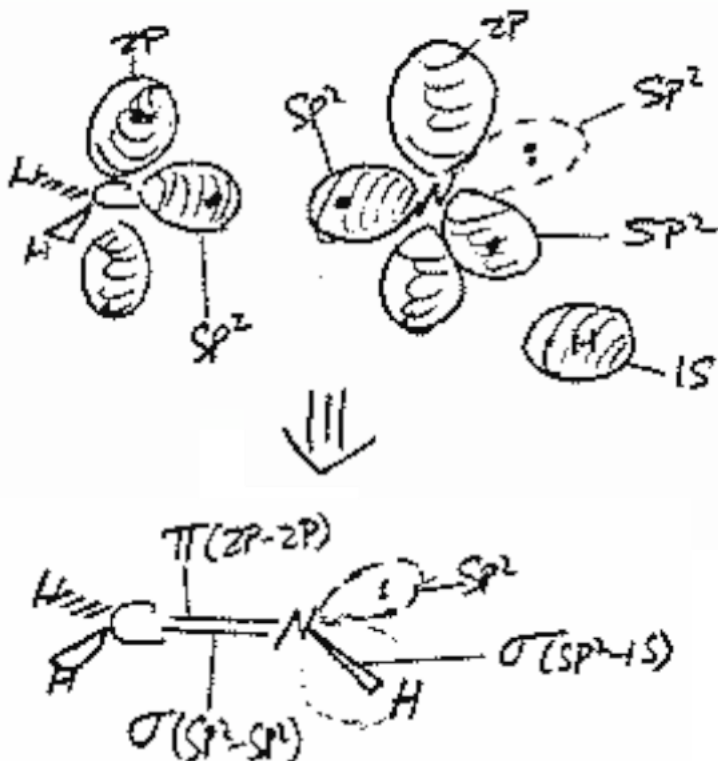
1.60. Formation of H-C≡N

1.61
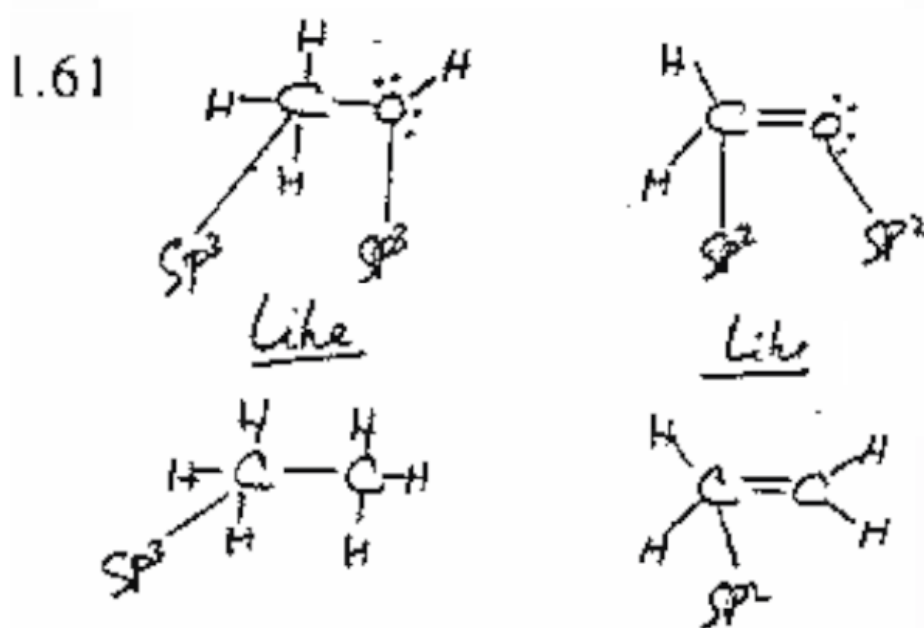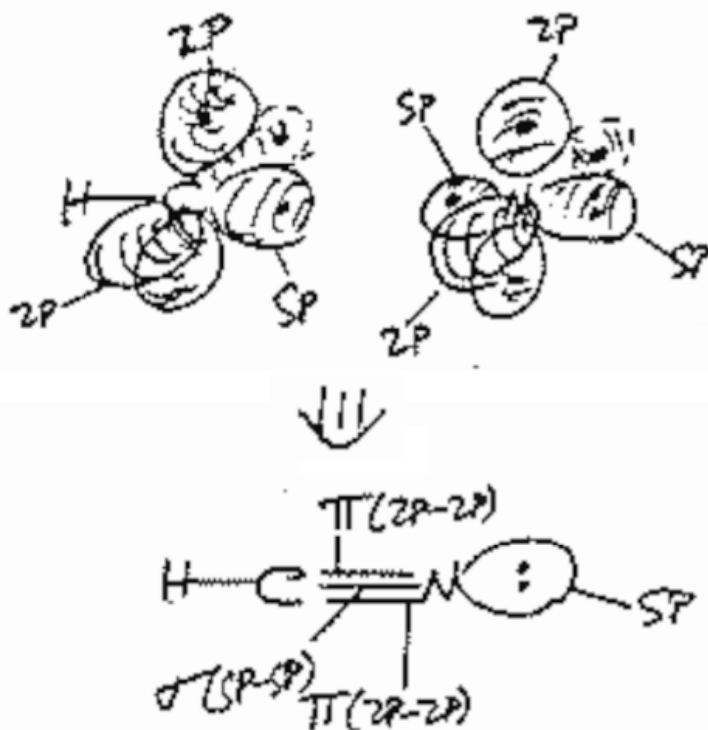
H-C≡N (sp N). The sp atomic orbital with a single electron in sp hybridized N forms the σ bond in C≡N, and the unshared electron pair on N is in the other sp atomic orbital. The two π bonds in C≡N result from combination of the 2p atomic orbitals on N with those on sp C. [graphic 1.60] Chemists think of H-C≡N as an inorganic compound, so the simplest organic molecule with a C≡N group is CH_3-C≡N.

Carbon-Oxygen Bonds. We treat bonding between C and O like bonding between C and N. We have seen that O prefers two bonds and forms single or double bonds to C. [graphic 1.61] In each case, the hybridization of a C bonded to O depends on whether it has four single bonds (sp^3) as in CH_3-OH, or two single bonds and a double bond (sp^2) as in H_2C=O. We similarly assign the hybridization state of O based on whether it has two single bonds (sp^3) as in CH_3-O-H, or one double bond (sp^2) as in H_2C=O. We compare the electron configurations of sp^2 and sp^3 hybridized O with that of unhybridized O in Figure [graphic 1.62]. [graphic 1.62] You can see that the two unshared electron pairs of sp^3 hybridized O are in sp^3 AO's while those of sp^2 hybridized O are in sp^2 AO's. Both of these electron configurations are consistent with the preference of O for two bonds since each has just two atomic orbitals with single electrons.
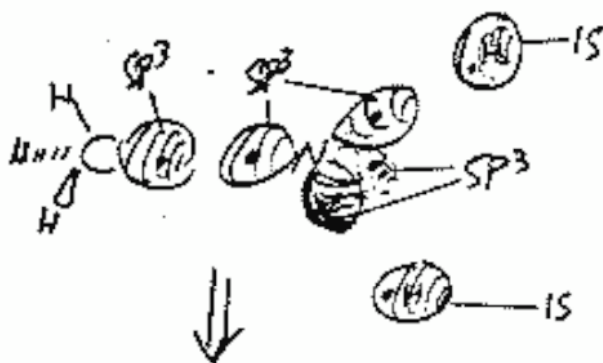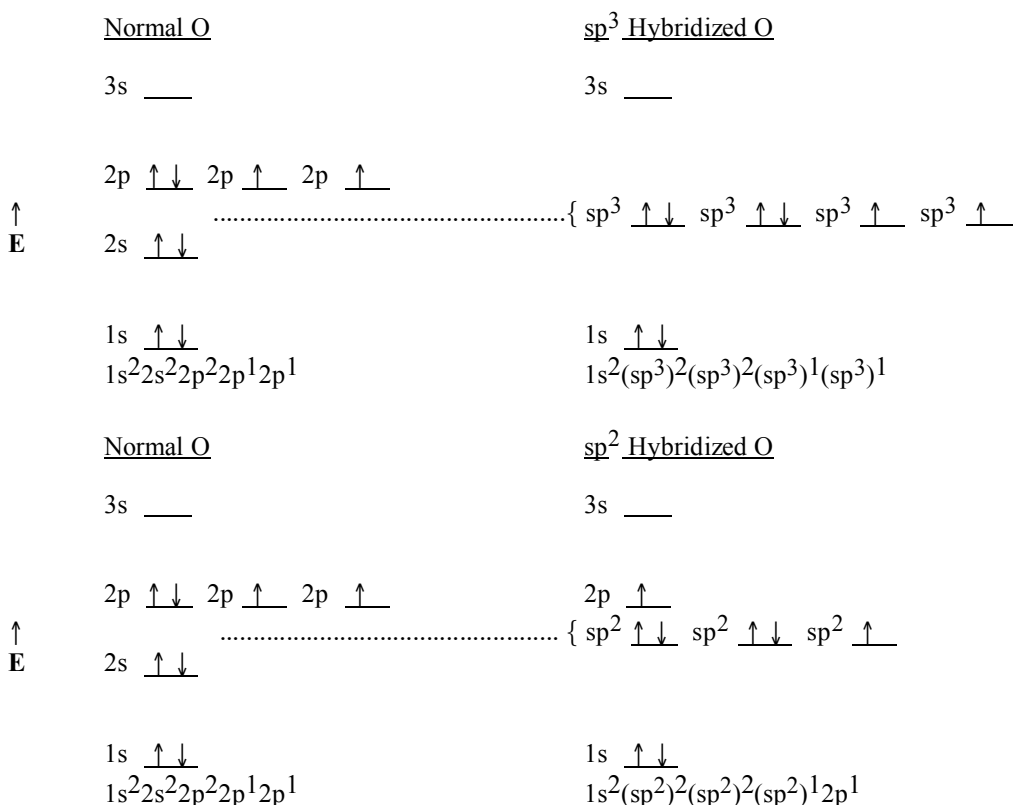
Figure [graphic 1.62]. **Electron Energy Level Diagrams for Ground State, sp^3, and sp^2 Hybridized O**

We show the MO descriptions in Figure [graphic 1.63] of all of the σ and π bonds between C and O in these compounds that arise from overlap of their hybrid AO's. [graphic 1.63] The C-O-H bond angle of about 110° in CH_3-O-H is consistent with sp^3 hybridization, but we cannot fully verify a tetrahedral geometry at O with only two attached atoms. [graphic 1.64] Similarly, with only one atom (C) bonded to O in H_2C=O, there is no experimental verification that O is sp^2 hybridized.

*Carbon-Halogen Bonds*. Halogen atoms form only one bond to C such as that in CH_3-F. As a result, there is no possibility of using a bond angle at the halogen to choose its hybridization state. Since we can form that single C-F bond using the one 2p AO with one electron of unhybridized F, there seems to be no need to hybridize F. [graphic 1.65] In spite of this, we prefer to think of F as sp^3 hybridized in CH_3-F. [graphic 1.66] One rationalization is based on VSEPR. The sp^3 hybridization places both unshared and bonding electron pairs of F in sp^3 AO's, so all valence shell electron pairs on F have a separation that is greater than expected for those of unhybridized F. Since we cannot test this idea, and also for theoretical reasons associated with complete bonding theories, some organic chemists prefer to think of F as unhybridized.

The other halogens Cl, Br, and I have more electrons than F, but the unhybridized and sp^3 hybridized electron configurations of their *valence shell atomic orbitals* are analogous to those of F. As a result, there is an sp^3 AO for each halogen that can overlap with an sp^3 AO of C to form a C-X bond (Table 1.2) [next page], or we can imagine that they form C-X bonds using their unhybridized p orbital with one electron.

1.3 Organic Chemistry

Now that we have examined the major *classes of organic compounds*, their *functional groups*, and their *chemical bonds*, let's preview the rest of the course. We can divide organic chemistry into the two broad categories of **molecular structure** and **chemical reactions**. We can further break these broad categories into a number of individual topics that we will examine below. Because the principles of organic chemistry serve as the basis for understanding the biochemistry of living systems, we will also discuss topics in **bioorganic chemistry**.

1.63.   MO's for C-O and C=O Bonds
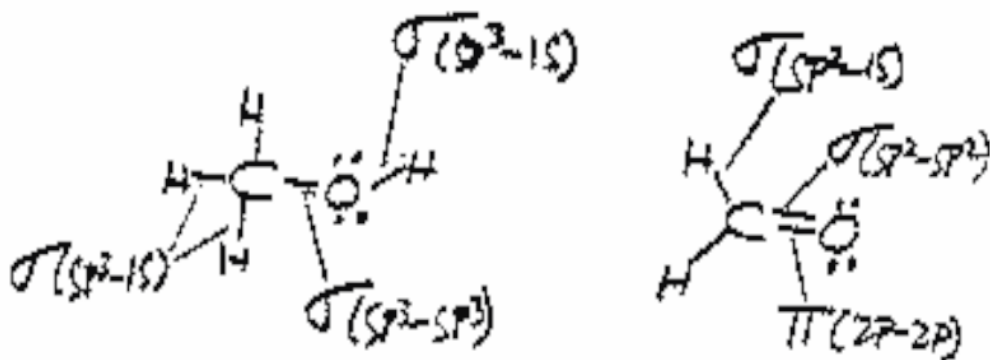
1.64
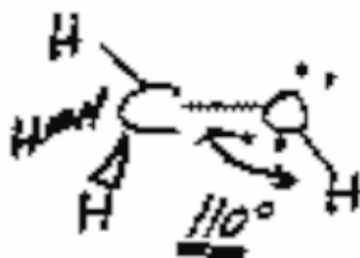
1.66

Table 1.2. Normal and sp^3 Electron Configurations* of F, Cl, Br, and I

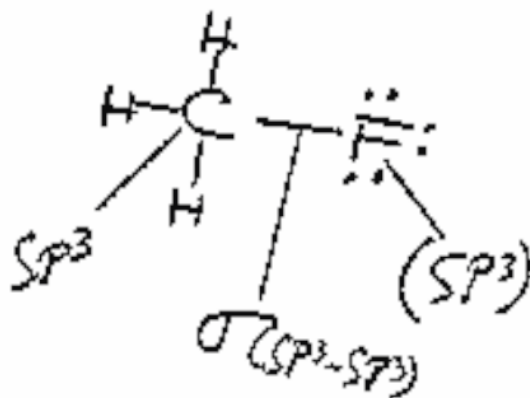| Atom	Normal Configuration	sp^3 Configuration
F (9e)	$1s^2\underline{2s}^2\underline{2p}^2\underline{2p}^2\underline{2p}^1$ or $[He]\underline{2s}^2\underline{2p}^2\underline{2p}^2\underline{2p}^1$	$1s^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^1$ or $[He](\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^1$
Cl (17e)	$1s^22s^22p^22p^22p^2\underline{3s}^2\underline{3p}^2\underline{3p}^2\underline{3p}^1$ or $[Ne]\underline{3s}^2\underline{3p}^2\underline{3p}^2\underline{3p}^1$	$[Ne](\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^1$
Br (35e)	$[Ar]\underline{4s}^2\underline{4p}^2\underline{4p}^2\underline{4p}^1$	$[Ar](\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^1$
I (53e)	$[Kr]\underline{5s}^2\underline{5p}^2\underline{5p}^2\underline{5p}^1$	$[Kr](\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp}^3)^2(\underline{sp})^3$

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*Abbreviated electron configurations show only those filled or partially filled atomic orbitals that come after those of the preceding Noble Gas. Both full and abbreviated electron configurations are shown for F and Cl (note that [He] means $1s^2$ and [Ne] means $1s^22s^22p^22p^22p^2$). The shorthand electron configurations of each halogen (X) is represented as *[noble gas]ns^{2}np^{2}np^{2}np^1* where *[noble gas]* stands for the electron configuration of the preceding noble gas, and *n* is 2 for F, 3 for Cl, 4 for Br, and 5 for I.

Molecular Structure (1.3A)

We have drawn chemical formulas, and three-dimensional structures, for a variety of different organic compounds in this chapter. We have also discussed chemical bonds that hold atoms together in these molecules. However, there is much more to learn about molecular structure. In our exploration of the individual classes of organic compounds, we will study their systematic names (**nomenclature**), and their physical and chemical properties such as their **acidity** and **basicity**. We will also consider their three-dimensional shapes and other features relating to the arrangements of their atoms in space that we refer to as **stereochemistry**.

We have seen that electrons in chemical bonds bind individual atoms to each other in molecules. The distribution of the electrons in the bonds and molecules depends on the types of bonded atoms, whether the bonds are π or σ bonds, and the arrangements of π and σ bonds with respect to each other. We will see that the electron distribution in bonds causes molecules and their functional groups to have varying degrees of **polar character** that significantly affects their physical properties and chemical reactions. We will also explore **instrumental methods** that chemists use to determine the structures of organic molecules.

These techniques, generally referred to as **organic spectrometry**, appear early in this text because the determination of molecular structure is vitally important in organic chemistry.

Chemical Reactions (1.3B)

Chemical reactions are the core of organic chemistry. They convert one class of organic molecules into another class and permit the **synthesis** of new molecules from those which already exist. Organic chemical reactions take place by a series of steps in which existing chemical bonds break and new chemical bonds form. During these transformations, the molecules undergoing chemical reaction experience changes in their chemical bonds and their three-dimensional shapes. We refer to the details of these changes as the **reaction mechanisms** and we will discuss them in depth for various types of chemical reactions.

The types of mechanisms that characterize organic reactions depend to a significant extent on the classes of molecules that are being interconverted. They also depend on the polarity and electron distribution in the molecules undergoing the reaction (the **reactants**), and those that form in the reaction (the **products**). For this reason, aspects of *molecular structure* are of crucial importance in understanding the *chemical reactivity* of organic compounds.

Bioorganic Chemistry (1.3C)

If your academic major is in one of the life sciences, you are studying organic chemistry because all organisms are complex molecular assemblies made up of a vast number of organic molecules. You will see later in this text that these **bioorganic molecules** have functional groups identical to those described in this chapter. You will also learn that most of the **biochemical reactions** that occur in organisms are organic reactions with mechanisms analogous to those that you will study in this course.

The bioorganic molecules that we will learn about include **carbohydrates**, **proteins**, **amino acids**, **nucleic acids**, and **lipids**. You probably already know that *carbohydrates* are important as sources of energy in metabolism and as structural support in plants. *Proteins* are large molecules, made up of many *amino acids*, that make up muscle tissue and serve as enzymes. *Nucleic acids* are not only the molecular repository of our genetic code, but also act as the templates and assembly lines for the synthesis of proteins. Finally, *lipids* include a large collection of structurally diverse bioorganic molecules including **fats**, **waxes**, **terpenes**, and **steroids**.

1.4 Bon Voyage!

The next chapter in this text begins our exploration of specific topics that we have previewed in this chapter. The amount of detail in that chapter is significant so it is important that you attempt to read the chapter before your instructor presents material from it in lecture. You may understand only a little of the chapter before hearing the lectures that cover it, but that advance reading will have an enormous impact on your ability to get the full benefit from your instructor's lectures. A second reading after the lectures will hopefully show you that you have significantly increased your level of understanding.

The questions included in each chapter will help you determine your level of understanding of the material that you have just covered. Be sure to try them early in your reading. Don't think that two or three readings of a chapter before attempting these questions will make them easier. An early attempt at answering questions will help you focus on the important concepts in each chapter.

It is important to do your own work and make your own mistakes. While it may make you more comfortable to check out the answers to the questions in the study guide, or to work on them with other students before you try to solve them yourself, it is likely that neither those answers nor your study group will be available to you when you take your midterm and final exams. Listening to the explanation of a problem or a concept by another, or reading the answer to a question in the text, may make much sense at the time, but it's amazing how quickly that clarity vanishes when you are all by yourself with your examination paper. Be sure that you ultimately challenge yourself to show you can close the text and the study guide and answer questions on your own that you think you understand.

Many successful students rewrite their lecture notes as soon as possible after a lecture. You might want to try this too. The process will help you implant the material into your memory and it will also show you places in your notes that are unclear and need further explanation or clarification from the text or your instructor. You might try to do this with the material in the text as well!

Best wishes to you in your journey through organic chemistry. It will be difficult and challenging. Along the way you will encounter many new things that you may find interesting and perhaps even exciting. In the end, you will have learned much from your excursion. *Bon voyage*!