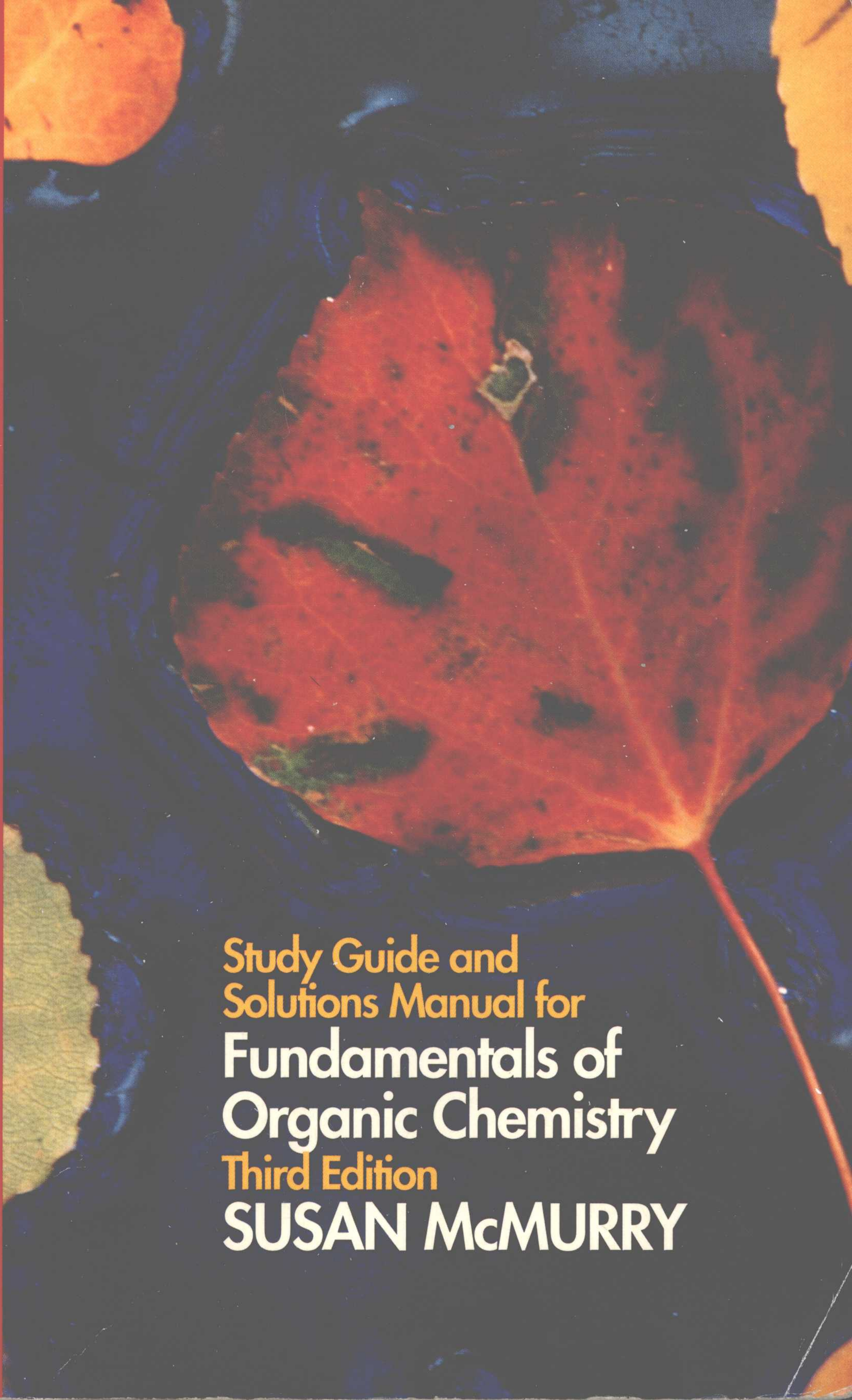

Study Guide and Solutions Manual for

Fundamentals of Organic Chemistry

Third Edition

SUSAN McMURRY

Study Guide and Solutions Manual for

THIRD EDITION

FUNDAMENTALS OF ORGANIC CHEMISTRY

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Cornell University

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Preface

If you're in a typical organic chemistry course, you go to lecture and take notes, read the text, work some problems, and take tests. For many of you, performing this ritual is all that's necessary to succeed in organic chemistry. Many others of you, however, follow all the correct steps but still feel bewildered by the course. In such a situation, supplementary material is often needed.

This book has been written with two functions in mind. First, it gives an overview of the course, both in chapters and in appendices. Second, it furnishes solutions to the problems presented in the text. The first of these functions might be described as "the big picture," and the second as "the details." Understanding both the big picture and the details is necessary if organic chemistry is to be more than the memorization of unrelated facts.

How to use this book

This *Study Guide and Solutions Manual* can't perform miracles if you don't read the textbook, *Fundamentals of Organic Chemistry*. In all cases, step one is to go to class, take notes, and read the text. At this point, the Study Guide should be helpful.

Study the Chapter Outline. The outline should help you to see how the topics in the chapter are related. Many people are able to learn the facts in each chapter, but are unable to recognize the principles underlying them. The outline will make clearer both the relationships between reactions and how these reactions are related to larger concepts.

Solve the problems in the text. Initially, don't use the *Solutions Manual* to help you with the problems. After completing the problems, consult the *Solutions Manual* to see if your answer is correct and if your method of solution is logical and systematic. If you're confused by a problem, carefully read the solution; then try to solve similar problems on your own.

Check the Study Guide at the end of each chapter in the *Solutions Manual*. All the skills you should have acquired after studying the chapter are listed here, along with the numbers of the problems that reinforce each skill. If a particular type of problem is difficult for you, work related problems until you feel confident.

Before a test or final exam, look at the appendices in the Study Guide and use them as a self-test to see if you know the relevant information. Many of these appendices summarize or tabulate information that has been presented over several chapters. Especially helpful before an exam are the following sections: Reagents Used in Organic Synthesis, Summary of Functional Group Preparations, and Summary of General Reaction Mechanisms. Other appendices present interesting chemical facts and tables.

For most people, understanding organic chemistry takes a long time — sometimes longer than the duration of an organic chemistry course. I hope that the combination of *Fundamentals of Organic Chemistry* plus this *Study Guide and Solutions Manual* makes the study of organic chemistry easier and more rewarding for you.

Acknowledgements: I would like to thank John McMurry for his advice and encouragement during this enjoyable project. I also thank David and Paul McMurry for their understanding and patience during the months I was busy with this book.

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Solutions to Problems:

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Chapter 1 – Structure and Bonding

1.1 The elements of the periodic table are organized into groups that are based on the number of outer-shell electrons each element has. For example, an element in group 1A has one outer-shell electron, and an element in group 5A has five outer-shell electrons. To find the number of outer-shell electrons for a given element, use the periodic table to find the element's group.

a) Potassium is a member of group 1A and thus has one outer-shell electron.
b) Calcium (group 2A) has two outer-shell electrons.
c) Aluminum (group 3A) has three outer-shell electrons.

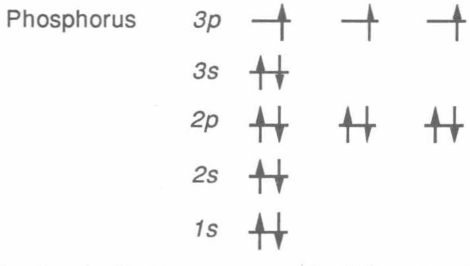
1.2 a) To find the ground-state electronic configuration of an element, first locate its atomic number. For boron, the atomic number is 5; boron thus has 5 protons and *5 electrons*. Next, assign the electrons to the proper energy levels (shown in Figure 1.3), starting with the lowest level:

Remember that only two electrons can occupy the same orbital and that they must be of opposite spin.

A different way to represent the ground-state electron configuration is to simply write down the occupied orbitals and to indicate the number of electrons in each orbital. For example, the electron configuration of boron is $1s^22s^22p$.

Often, we are interested only in the electrons in the outer shell. We can then represent all filled levels by the symbol for the noble gas having the same levels filled. In the case of boron, the filled $1s$ energy level is represented by [He], and the *valence shell configuration* is symbolized by $[He]2s^22p$.

b) Let's consider an element with many electrons. Phosphorus, with an atomic number of 15, has *15 electrons*. Assigning these to energy levels:



Notice that the $3p$ electrons are all in different orbitals. According to *Hund's rule*, we must place one electron into each orbital of the same energy until all orbitals are half-filled.

The more concise way to represent the ground-state electron configuration for phosphorus is: $1s^22s^22p^63s^23p^3$
Valence-shell electron configuration: $[Ne]3s^23p^3$

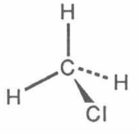
c) Oxygen (atomic number 8)

$1s^22s^22p^4$
$[He]2s^22p^4$

d) Argon (atomic number 18)

$1s^22s^22p^63s^23p^6$
$[Ne]3s^23p^6$

1.3



Chloromethane

1.4 Use the periodic table to find the group to which an element belongs. For any element, the group number is the same as the number of valence shell electrons.

	Element	*Group*	*Valence Shell Electrons*
a)	Be	2A	2
b)	S	6A	6
c)	Br	7A	7

1.5 Elements on the left of the periodic table are electropositive; elements on the right of the periodic table are electronegative.

a) Oxygen is more electronegative than potassium.
b) Bromine is more electronegative than calcium.

1.6 a) Carbon (group 4A) has four electrons in its valence shell and forms four bonds to achieve the noble-gas configuration of neon. Hence, a likely formula is CCl_4.

Element	*Group*	*Likely Formula*
b) Al	3A	AlH_3
c) C	4A	CH_2Cl_2
d) Si	4A	SiF_4

1.7 Writing Lewis structures of a molecule requires that you first determine the number of valence, or outer-shell, electrons for each atom in the molecule. For chloroform, we know that carbon has four valence electrons, hydrogen has one, and each chlorine has seven.

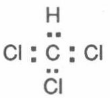
4 x 1 = 4

1 x 1 = 1

7 x 3 = 21

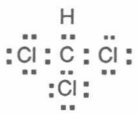
26 total valence electrons

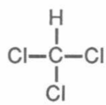
Next, use two electrons for each single bond.



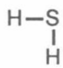
Finally, use the remaining electrons to achieve an noble-gas configuration for all atoms.

a) $CHCl_3$

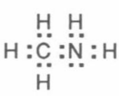


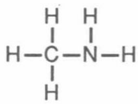


b) H_2S Total valence electrons = 8



c) CH_3NH_2 Total valence electrons = 14

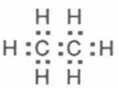




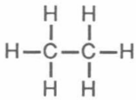
1.8 Bonds formed between an electropositive element and an electronegative element are ionic. Bonds formed between an element in the middle of the periodic table and another element are most often covalent, but exceptions can be found.

Ionic bonds: LiI, KBr, $MgCl_2$
Covalent bonds: CH_4, CH_2Cl_2, Cl_2

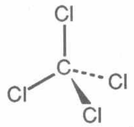
1.9



Ethane



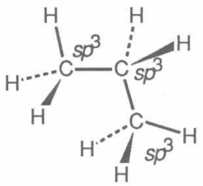
1.10



Tetrachloromethane

1.11 An electron in an sp^3 orbital is farther from the nucleus than an electron in a 1*s* orbital. Thus, a bond that uses an sp^3 orbital of carbon and a 1*s* orbital of hydrogen is longer than a bond that uses two 1*s* orbitals (H-H bond).

1.12

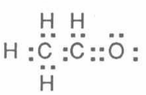


Propane

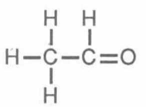
All carbon atoms are tetrahedral, and all bond angles are approximately 109.5°.

1.13 The two carbons bond to each other by overlap of two sp^3 hybrid orbitals. Six sp^3 hybrid orbitals (three from each carbon) are left over, and they can bond with a maximum of six hydrogens. Thus, a formula such as C_2H_7 is not possible.

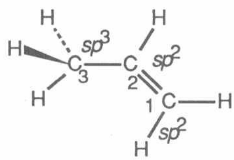
1.14



Acetaldehyde



1.15



Propene

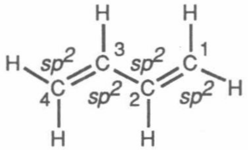
The C3-H bonds are sigma bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen. Bond angles at C3 are approximately 109°.

The C2-H and C1-H bonds are sigma bonds formed by overlap of an sp^2 orbital of carbon with an *s* orbital of hydrogen.

The C2-C3 bond is a sigma bond formed by overlap of an sp^3 orbital of carbon 3 with an sp^2 orbital of carbon 2.

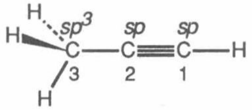
There are two C1-C2 bonds. One is a sigma bond formed by overlap of an sp^2 orbital of carbon 1 with an sp^2 orbital of carbon 2. The other is a pi bond formed by overlap of a 2*p* orbital of carbon 1 with a 2*p* orbital of carbon 2. All four atoms connected to the carbon-carbon double bond lie in the same plane, and all bond angles between these atoms are 120°.

1.16



All atoms lie in the same plane, and all bond angles are approximately 120°

1.17



Propyne

The C3-H bonds are sigma bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen. Bond angles at C3 are approximately 109°.

The C1-H bond is a sigma bond formed by overlap of an *sp* orbital of carbon 1 with an *s* orbital of hydrogen.

The C2-C3 bond is a sigma bond formed by overlap of an *sp* orbital of carbon 2 with an sp^3 orbital of carbon 3.

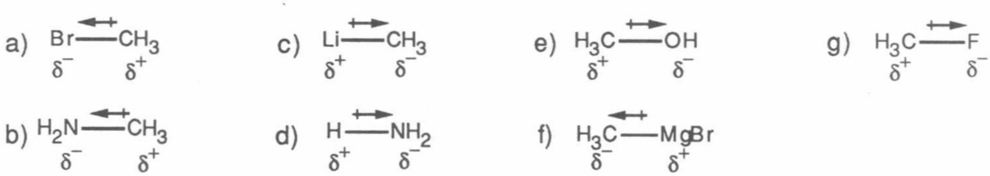
There are three C1-C2 bonds. One is a sigma bond formed by overlap of an *sp* orbital of carbon 1 with an *sp* orbital of carbon 2. The other two bonds are pi bonds formed by overlap of two 2*p* orbitals of carbon 1 with two 2*p* orbitals of carbon 2.

The three carbon atoms of propyne lie on a straight line, with a bond angle of 180°.

1.18 Use Figure 1.17 to answer this problem. The larger the EN number, the more electronegative the element.

	More electronegative	*Less electronegative*
a)	H (2.1)	Li (1.0)
b)	Br (2.8)	Be (1.6)
c)	Cl (3.0)	I (2.5)

1.19 As in Problem 1.18, use Figure 1.17. Remember that the arrow points toward the more electronegative atom in the bond.



1.20 Use Figure 1.17 to locate the EN of each element. The larger the difference in EN, the more ionic the bond.

CCl_4	$MgCl_2$	$TiCl_3$	Cl_2O
Cl : EN = 3.0	Cl : EN = 3.0	Cl : EN = 3.0	Cl : EN = 3.0
C : EN = 2.5	Mg : EN = 1.2	Ti : EN = 1.5	O : EN = 3.5
Δ EN = 0.5	Δ EN = 1.8	Δ EN = 1.5	Δ EN = 0.5

Least ionic —> Most ionic

CCl_4 and ClO_2, $TiCl_3$, $MgCl_2$

1.21 Since a lower pK_a value indicates a stronger acid, picric acid is stronger than formic acid.

1.22

Conjugate base		*Acid*	
stronger	$^-NH_2$	NH_3	weaker
weaker	^-OH	H_2O	stronger

The conjugate base of a strong acid is a weak base, and the conjugate base of a weak acid is a strong base. In line with this reasoning, water is a stronger acid than ammonia.

1.23

a) $$\underset{\substack{pK_a = 9.2 \\ \text{weaker acid}}}{H{-}CN} + CH_3COO^-\,Na^+ \overset{?}{\dashrightarrow} Na^+\,{}^-CN + \underset{\substack{pK_a = 4.7 \\ \text{stronger acid}}}{CH_3COO{-}H}$$

The lower the pK_a, the stronger the acid. Since CH_3COOH is the stronger acid and gives up a proton more readily than HCN, the reaction will not take place as written.

b) $$\underset{\substack{pK_a = 16.0 \\ \text{weaker acid}}}{CH_3CH_2O{-}H} + Na^+\,{}^-CN \overset{?}{\dashrightarrow} CH_3CH_2O^-\,Na^+ + \underset{\substack{pK_a = 9.2 \\ \text{stronger acid}}}{H{-}CN}$$

Using the same reasoning as in part (a), we can see that the above reaction will not take place.

1.24 A Lewis base has a non-bonding electron pair to share. A Lewis acid has a vacant orbital to accept an electron pair. Look for a lone electron pair when identifying a Lewis base.

Lewis acids: $MgBr_2$, $B(CH_3)_3$, $^+CH_3$

Lewis bases: $CH_3CH_2\ddot{\underset{..}{O}}H$, $CH_3\ddot{N}HCH_3$, $CH_3\ddot{P}(CH_3)CH_3$

1.25 See Problem 1.1 if you need help.

	Element	*Group*	*Number of outer shell electrons*
a)	Oxygen	6A	6
b)	Magnesium	2A	2
c)	Fluorine	7A	7

1.26

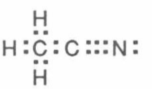
	Element	*Atomic Number*	*Number of outer shell electrons*
a)	Li	3	$1s^2 2s$
b)	Na	11	$1s^2 2s^2 2p^6 3s$
c)	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
d)	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$

1.27 a) $AlCl_3$ b) CF_2Cl_2 c) NI_3

1.28 Ionic bonds: BeF_2
Covalent bonds: SiH_4, CBr_4

1.29

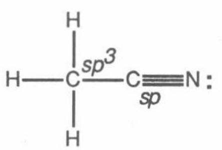
1.30



Acetonitrile

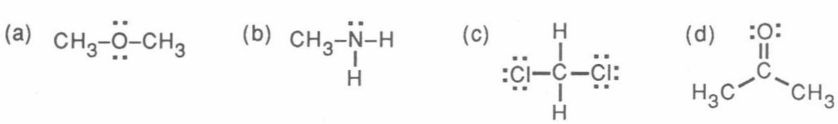
Nitrogen has five electrons in its valence shell. Three are used in the carbon-nitrogen triple bond, and two are a nonbonding electron pair.

1.31

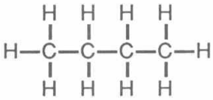


Acetonitrile

1.32



1.33



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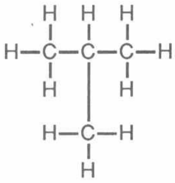
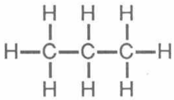
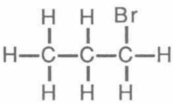


1.34 In order to work a problem of this sort, you must examine all possible structures that have the correct number of bonds. You must systematically consider all possible attachments, including those that have branches, rings and multiple bonds.

a) 

b) 

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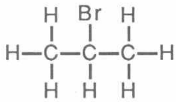
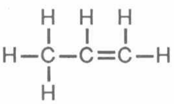


These are the only two possible structures with the formula C_3H_7Br.

c) 

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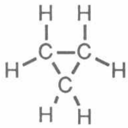
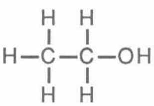


d) 

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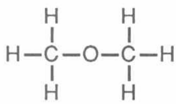
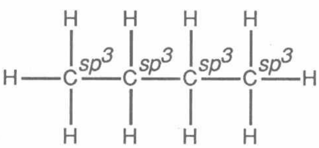
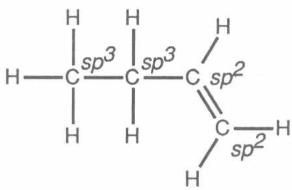


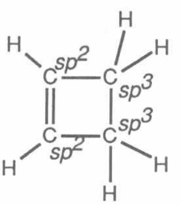
1.35

a) 

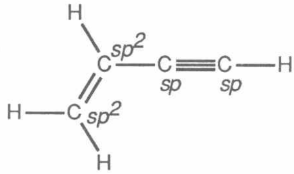
Butane

b) 

1–Butene

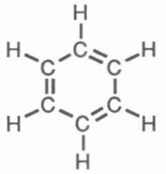
c) 

Cyclobutene

d) 

1–Buten–3–yne

1.36

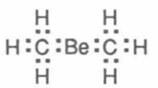


Benzene

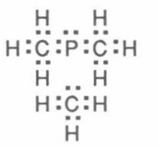
All carbon atoms of benzene are sp^2 hybridized, and all bond angles of benzene are 120°. Benzene is a planar molecule.

1.37

a) 16 valence electrons



b) 26 valence electrons



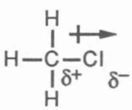
c) 32 valence electrons
(4 from Ti, 7 from each Cl)

1.38-1.39

a) Br—Br

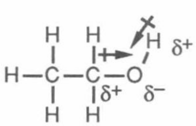
nonpolar

b)



c)

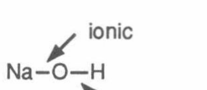
d)



Molecules b-d are polar. Carbon-hydrogen bonds are only slightly polar.

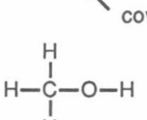
1.40

a)



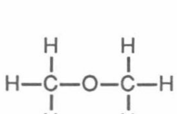
b)

c)



all covalent

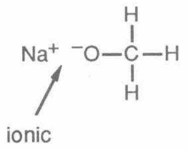
d)



all covalent

e) F—F covalent

1.41



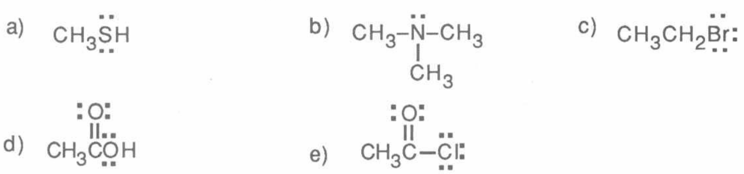
All other bonds are covalent.

1.42 The most electronegative element is underlined.

a) $CH_2\underline{F}Cl$ b) $\underline{F}CH_2CH_2CH_2Br$ c) $H\underline{O}CH_2CH_2NH_2$ d) $CH_3\underline{O}CH_2Li$

1.43-1.44

1.45



1.46

Chloroform Ethanol

1.47

The above reaction will take place as written because acetone is a stronger acid than ammonia.

1.48 Lewis acids: $AlBr_3$, HF

Lewis bases: $CH_3CH_2\ddot{N}H_2$, $CH_3\ddot{\underset{\cdot\cdot}{S}}CH_3$

1.49 The reaction between methanol and bicarbonate does not take place in the indicated direction because methanol (pK_a = 15.5) is a weaker acid than bicarbonate (pK_a = 6.4).

1.50

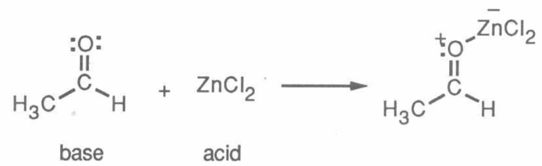
a) $CH_3\ddot{\underset{\cdot\cdot}{O}}H + H^+ \longrightarrow CH_3\overset{+}{\underset{\cdot\cdot}{O}}H_2$

base acid

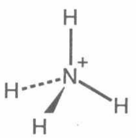
b) $CH_3\ddot{\underset{\cdot\cdot}{O}}H + {}^{-}\!:\!\underset{\cdot\cdot}{N}H_2 \longrightarrow CH_3\ddot{\underset{\cdot\cdot}{O}}:^{-} + :NH_3$

acid base

c)



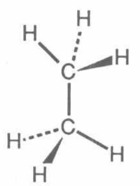
1.51



Ammonium ion

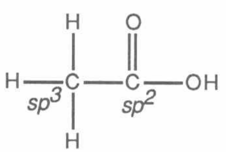
The nitrogen atom of the tetrahedral ammonium ion is sp^3 hybridized because, like the carbon atom of methane, nitrogen forms bonds to four different hydrogen atoms.

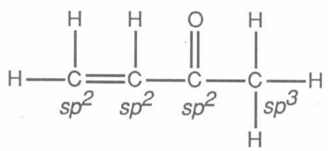
1.52

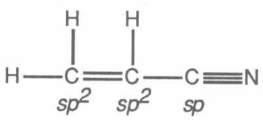


Ethane

1.53

a) 

b) 

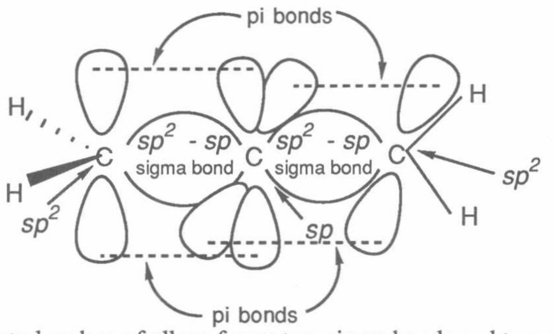
c) 

1.54 Carbon is most positive when it is bonded to the most electronegative atom.

Most negative carbon ⟶ Most positive carbon.

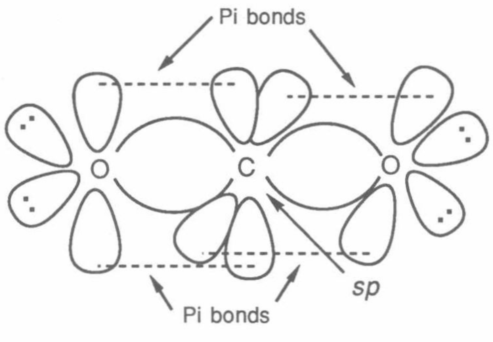
CH_3Li, CH_3-CH_3, CH_3-I, CH_3-NH_2, CH_3-OH, CH_3-F

1.55



The central carbon of allene forms two sigma bonds and two pi bonds. The central carbon is *sp*-hybridized, and the two terminal carbons are sp^2-hybridized. The carbon-carbon bond angle is 180°, indicating linear geometry for the carbons of allene.

1.56 The carbon atom of CO_2 is *sp*-hybridized. Allene and CO_2 are both linear molecules.



1.57 The carbon atom, which has three valence shell electrons, is sp^2 hybridized. A carbocation is planar and is *isoelectronic* with (has the same number of electrons as) a trivalent boron compound.