

STUDY GUIDE TO

MORRISON
AND BOYD

ORGANIC
CHEMISTRY
FOURTH EDITION



STUDY GUIDE
TO
**Organic
Chemistry**

Fourth Edition

*by R. T. Morrison
and R. N. Boyd*

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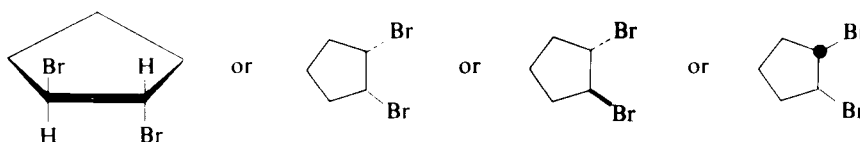
Stereochemical Formulas of Cyclic Compounds

For convenience, organic chemists use a variety of ways to show the stereochemistry of cyclic compounds.

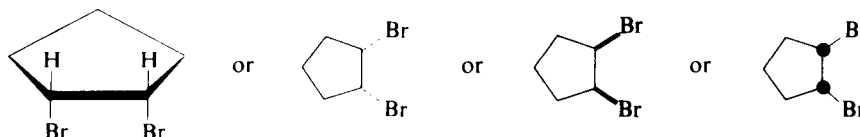
A solid line (often thickened) indicates a bond coming *out of* the plane of the paper; a dashed line indicates a bond going *behind* the plane.

Alternatively, a round dot represents a hydrogen atom coming out of the plane of the paper; the other bond to that carbon is then understood to be going behind the plane. Where a dot is absent, hydrogen lies behind the plane, and the bond shown is understood to be coming out of the plane.

Thus, we may encounter *trans*-1,2-dibromocyclopentane represented as



and the *cis*-isomer represented as



Synthesis: Working Backwards

Granting that we know the chemistry of the individual steps, how do we go about planning a route to more complicated compounds—alcohols, say? In almost every organic synthesis it is best to begin with the molecule we want—the *target* molecule—and *work backwards* from it. There are relatively few ways to make a complicated alcohol, for example; there are relatively few ways to make a Grignard reagent or an aldehyde or ketone; and so on back to our ultimate starting materials. On the other hand, our starting materials can undergo so many different reactions that, if we go at the problem the other way round, we find a bewildering number of paths, few of which take us where we want to go.

We try to limit a synthesis to as few steps as possible, but nevertheless do not sacrifice purity for time. To avoid a rearrangement in the preparation of an alkene, for example, we take two steps via the halide rather than the single step of dehydration.

Analyzing Spectra

Squeeze as much information as you can from the molecular formula: use chemical arithmetic, deciding where you can and how many rings and/or double bonds are present. Combine this with characteristic infrared bands, δ values, proton counts, and splitting of various NMR signals to give you structural units. If the spectrum (or combination of spectra) is unambiguous, you should have only one possible structure left; go back and check this against all the information you have.

For problems on spectra, answers are presented in two stages: names of the unknown compounds are given in their proper sequence along with the other answers; then, at the end of the Study Guide, spectra are reproduced with infrared bands identified and NMR signals assigned. We suggest that you check each of your answers in two stages, too. First, check the name; if your answer is wrong, or if you have not been able to work the problem at all, return to the spectrum in the textbook and, knowing the correct structure, have another go at it: see if you can now identify bands, assign signals, and analyze spin-spin splittings. Then, finally, turn to the back of the Study Guide and check your answer against the analyzed spectrum.

Table 33.1 WOODWARD-HOFFMANN RULES FOR ELECTROCYCLIC REACTIONS

Number of π electrons	Reaction	Motion
$4n$	thermal	conrotatory
$4n$	photochemical	disrotatory
$4n + 2$	thermal	disrotatory
$4n + 2$	photochemical	conrotatory

Table 33.2 WOODWARD-HOFFMANN RULES FOR $[i + j]$ CYCLOADDITIONS

$i + j$	Thermal	Photochemical
$4n$	supra-antara antara-supra	supra-supra antara-antara
$4n + 2$	supra-supra antara-antara	supra-antara antara-supra

Acknowledgments

Our thanks to Sadtler Research Laboratories for the infrared spectra labeled "Sadtler" and to the Infrared Data Committee of Japan for those labeled "IRDC," and to Dr. David Kritchevsky of the Wistar Institute for permission to quote the words of his song, "Farnesol."

To the Student

Right now, confronted with the array of unfamiliar material in your textbook, you must be wondering: *what am I expected to get out of all this?*

The best way to find out is to work problems: first, to see if you understand the facts and principles you have been reading about; second, and more important, to learn how to *use* this chemistry in the same practical ways that an organic chemist does.

Give yourself a fair chance to work each problem. Don't give up too easily. Re-read the pertinent part of the text. *Think* about it. Use paper and pencil and really work at it.

Only after you have done all that, check your answer against the one in this Study Guide. If you were on the right track, fine. If you went off the track, try to see *where*. Follow through the explanation carefully to see how you should approach this kind of problem next time.

You must *learn* how to use your brand-new organic chemistry, and to do this you must push yourself. You must try to work difficult problems, and you will not always succeed. But you can learn from your failures as well as your successes.

With some answers, we have given references to the chemical literature. It is not necessary for you to read all of these papers—or even any of them. But if some topic catches your fancy, follow it up. And, in any case, read one—or two or three—of these papers, so that you can see in down-to-earth detail the kind of experimental work that underlies any science.

Robert Thornton Morrison
Robert Neilson Boyd

Note

Reference to a page in this Study Guide will be given as "page 000 of this Study Guide." Any other reference is understood to be to a page in *Organic Chemistry, Fourth Edition*, by R. T. Morrison and R. N. Boyd.

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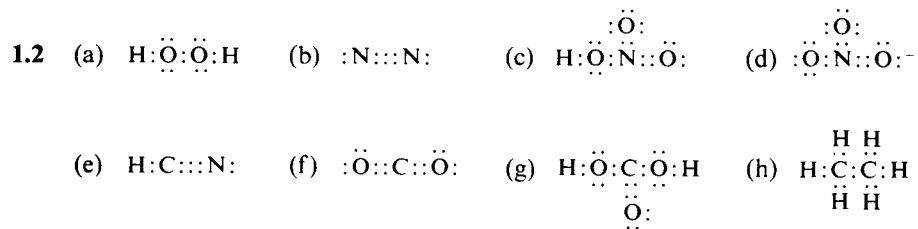
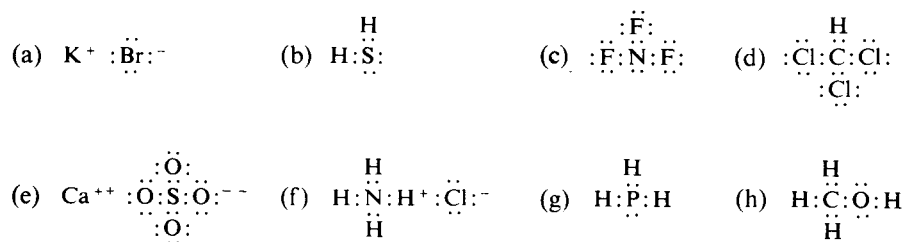
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1

Structure and Properties

1.1 Ionic: a, e, f.

In general, we expect electron-transfer—ionic bonding—between atoms that are widely separated, left-to-right, in the Periodic Table: typically, between metals on the far left and non-metals on the far right. We expect electron-sharing—covalent bonding—between atoms that are less widely separated: between S and O, for example, or N and C; and between H and almost any atom from groups III–VII. (See, too, the covalent compounds in Problem 1.2.)



1.3 (a)

	1s	2s	2p	3s	3p
Na				•	○ ○ ○
Mg				••	○ ○ ○
Al				••	• ○ ○
Si	••	••	•• •• ••	••	• • ○
P		all are like Ne			•• • • •
S	1	8			•• • • •
Cl				••	•• • • •
Ar				••	•• •• ••

(b) Elements of the same family have the same electronic configuration for their highest energy level.

(c) Metallic elements on the left of the Periodic Table lose electrons to give a 2,8 configuration; non-metallic elements on the right gain electrons to give a 2,8,8 configuration.

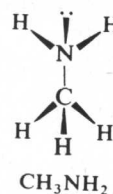
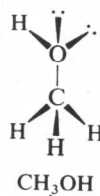
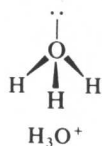
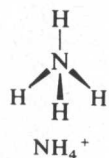
1.4 To arrive at the shape of each molecule, we see how many orbitals the central atom needs to hold not only the atoms attached to it but also any unshared pairs of electrons. If it needs four orbitals, it will use sp^3 orbitals; if three, sp^2 ; if two, sp . Following is given the shape in each case: first, if unshared pairs are included; and then, in parentheses, if only atomic nuclei are considered.

(a) Tetrahedral, like CH_4 in Figure 1.10, page 16. (*Tetrahedral.*)

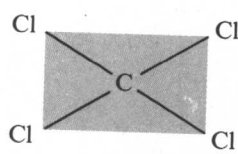
(b) Tetrahedral, like NH_3 in Figure 1.11, page 17. (*Pyramidal, with tetrahedral angles.*)

(c) Tetrahedral, like H_2O in Figure 1.13, page 19. (*Flat, with a tetrahedral angle.*)

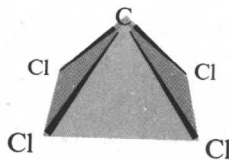
(d) Tetrahedral, like NH_3 . (*Pyramidal, with tetrahedral angles.*)



1.5 Structure (a), not (b), since in (a) the dipoles would cancel each other out.

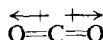


(a)



(b)

- 1.6 Linear. This is the only shape that would permit cancellation of the two carbon-oxygen dipoles.



As with BeCl_2 (Figure 1.6, page 13), this linearity stems from sp hybridization at the central atom; with CO_2 there is further overlap to give double bonds (Sec. 7.2).

- 1.7 (a) We would expect a zero dipole moment.

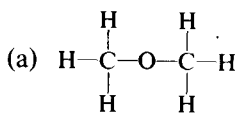
If nitrogen were sp^2 -hybridized, the molecule would be flat and symmetrical (like BF_3 , Figure 1.8, page 15), and the three bond dipoles would cancel each other out. In fact, NH_3 has $\mu = 1.46$ D. Therefore, the molecule is not flat, and not sp^2 -hybridized.

- (b) We would expect NF_3 to have a much larger dipole moment than NH_3 .

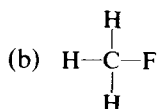
If nitrogen used p orbitals for bonding, both NH_3 and NF_3 would be pyramidal: as shown on page 24 except that the bond angles would be 90° rather than tetrahedral. The line of reasoning is the same as that on page 24—up to the point where the unshared pair of electrons is taken into consideration. Now the unshared pair would be in a $2s$ orbital *symmetrical about N*, and would provide no dipole to oppose the bond dipoles. Unopposed, the large N—F dipoles would give NF_3 a much larger dipole moment than NH_3 . In fact, NF_3 has a much smaller dipole moment than NH_3 . Therefore, the unshared pair is not in a $2s$ orbital, and the molecule is not p -hybridized.

- 1.8 Associated: d, e.

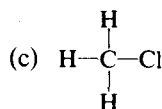
We simply draw the structure of each molecule, and look for H attached to O or N. Only if we find O—H or N—H do we expect the compound to be associated. (We see that the H's of the recurring CH_3 groups cannot be involved in hydrogen bonding.)



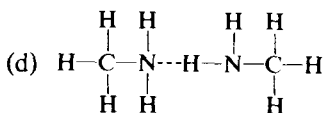
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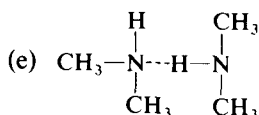
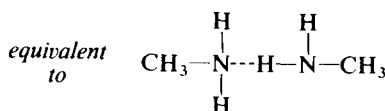
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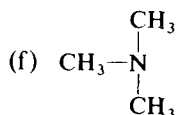
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Associated



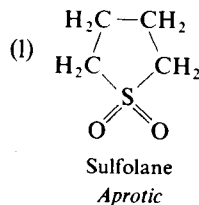
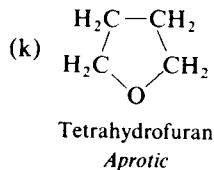
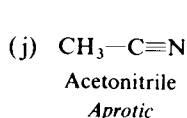
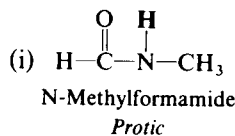
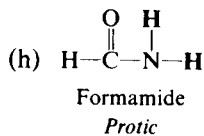
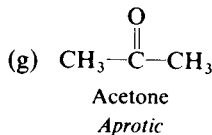
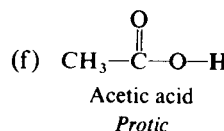
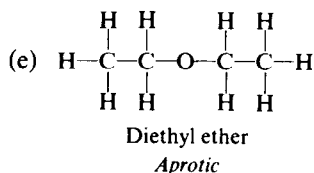
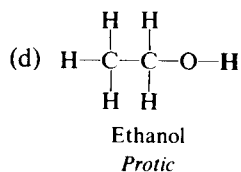
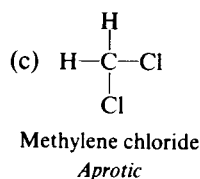
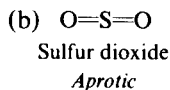
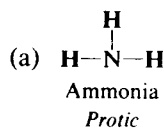
Associated



Not associated

1.9 Protic: a, d, f, h, i.

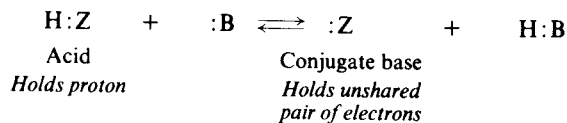
Again we draw the structure of each molecule and look for H attached to O or N. If there is an O—H or N—H grouping, the compound is protic; if not, it is aprotic.



1.10 (a) CH_3 groups are hydrocarbon, and lipophilic. Attached to the ammonium nitrogen, they make this cation lipophilic, too, and hence better solvated by non-polar solvents; when the cation enters such a solvent, it pulls the chloride ion along to balance its charge, and the salt dissolves.

(b) By increasing the size of each hydrocarbon group—to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$, for example—we could increase the lipophilic character of the cation and the solubility of the salt in non-polar solvents. (As we shall see in our discussion of *phase-transfer*, Sec. 6.29, such solubility is of great practical importance.)

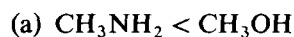
1.11 In each case we focus our attention on the atom holding the proton to be lost, that is, the atom that will hold the unshared pair of electrons in the conjugate base being formed. *The better this atom accommodates these electrons*, the greater the extent to which the conjugate base is formed, and hence, by definition, *the stronger the conjugate acid*.



We shall consider two factors that determine an atom's ability to accommodate electrons:

(i) its *electronegativity*, since by definition a more electronegative atom has a greater avidity for electrons. Among atoms of the same row of the Periodic Table, electronegativity increases as we move *to the right*.

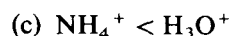
(ii) its *size*, since a bigger atom permits greater dispersal of the charge of the electrons (Sec. 1.22). Among atoms of the same family, size increases as we move *downward* in the Table.



Oxygen and nitrogen are in the same row of the Periodic Table, and oxygen is the *more electronegative*.

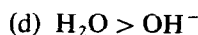
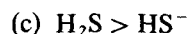
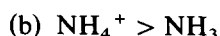
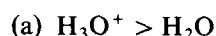


Sulfur and oxygen are in the same family of the Periodic Table, and sulfur is the *bigger*.



Again, oxygen and nitrogen are in the same row of the Periodic Table, and oxygen is the *more electronegative*.

1.12 Drawing upon our general chemical knowledge, we arrive at the following orders of acidity. (We know, for example, that H_3O^+ , not H_2O , is the strong acid in aqueous solutions of compounds like sulfuric acid.)



(e) We see that among closely related molecules where the same atom loses the proton,

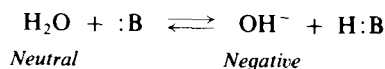
positive charge \longrightarrow increased acidity

negative charge \longrightarrow decreased acidity

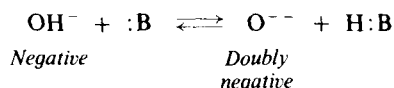
How do we account for this? Following the approach of the preceding problem, we consider the various conjugate bases being formed, and the ability of each to accommodate the electron pair—*negatively charged*, remember—left behind upon loss of the proton. This accommodation is easiest for the neutral conjugate base formed from a positively charged acid,



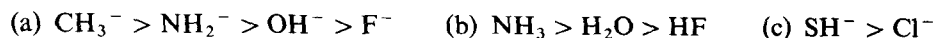
harder for the negatively charged conjugate base formed from a neutral acid,



and still harder for the doubly charged conjugate base formed from a negatively charged acid.



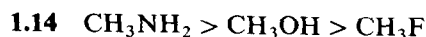
- 1.13** Again following the approach of Problem 1.11, we focus our attention on the atom holding the unshared pair of electrons in the base. *The better the atom accommodates these electrons, the less available they are for sharing, and the weaker the base.* An order of relative basicity is necessarily opposite to the order of relative acidity of the conjugate acids.



In (a), (b), and (c) the atoms of each set are in the same row of the Periodic Table, and therefore accommodation of the electron pair depends upon electronegativity: the more electronegative the element, the weaker the base.



In (d) and (e) the atoms of each set are in the same family of the Periodic Table, and therefore accommodation depends upon *size*: the bigger the atom, the weaker the base.



We apply the same approach as in the preceding problem. In this set basicity varies inversely with *electronegativity*: the more electronegative the atom, the weaker the base.

- 1.15** We approach this problem as we did Problem 1.12, above. Again we draw upon our general chemical knowledge, and arrive at the following orders of basicity. (We know, for example, that it is OH^- , not H_2O , that makes an aqueous solution of NaOH strongly basic.)



(d) We see that among closely related molecules where the same atom holds the unshared pair,

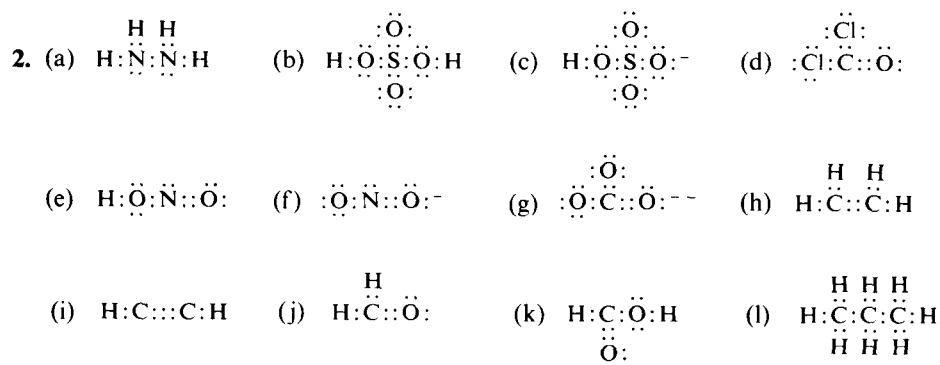
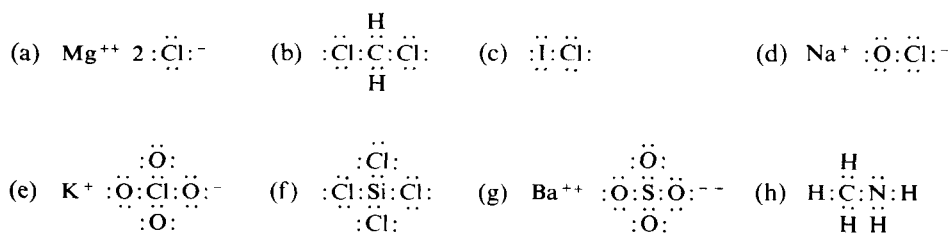
negative charge \longrightarrow increased basicity

positive charge \longrightarrow decreased basicity

To account for this, we consider the unshared pair of electrons on each base and how available they are for sharing. For a given atom, availability of electrons is clearly greatest in an electron-rich, negatively charged molecule, and least in an electron-poor, positively charged molecule.

1. Ionic: a, d, e, g.

Following the guidelines of Problem 1.1, we arrive at the following likely structures.



3. To arrive at the shape of each molecule, we follow the procedure of Problem 1.4, and see how many orbitals the central atom needs to hold both atoms and unshared pairs of electrons. Following is given the shape in each case: first, if unshared pairs are included; and then, in parentheses, if only atomic nuclei are considered.

- (a) Trigonal, like BF_3 in Figure 1.8, page 15. (*Trigonal.*)
- (b) Tetrahedral, like NH_3 in Figure 1.11, page 17. (*Pyramidal, with tetrahedral angles.*)
- (c) Trigonal, like BF_3 . (*Trigonal.*)
- (d) Tetrahedral, like H_2O in Figure 1.13, page 19. (*Flat, with a tetrahedral angle.*)
- (e) Tetrahedral, like H_2O . (*Flat, with a tetrahedral angle.*)
- (f) Tetrahedral, like H_2O . (*Flat, with a tetrahedral angle.*)
- (g) Tetrahedral, like CH_4 in Figure 1.10, page 16. (*Tetrahedral.*)