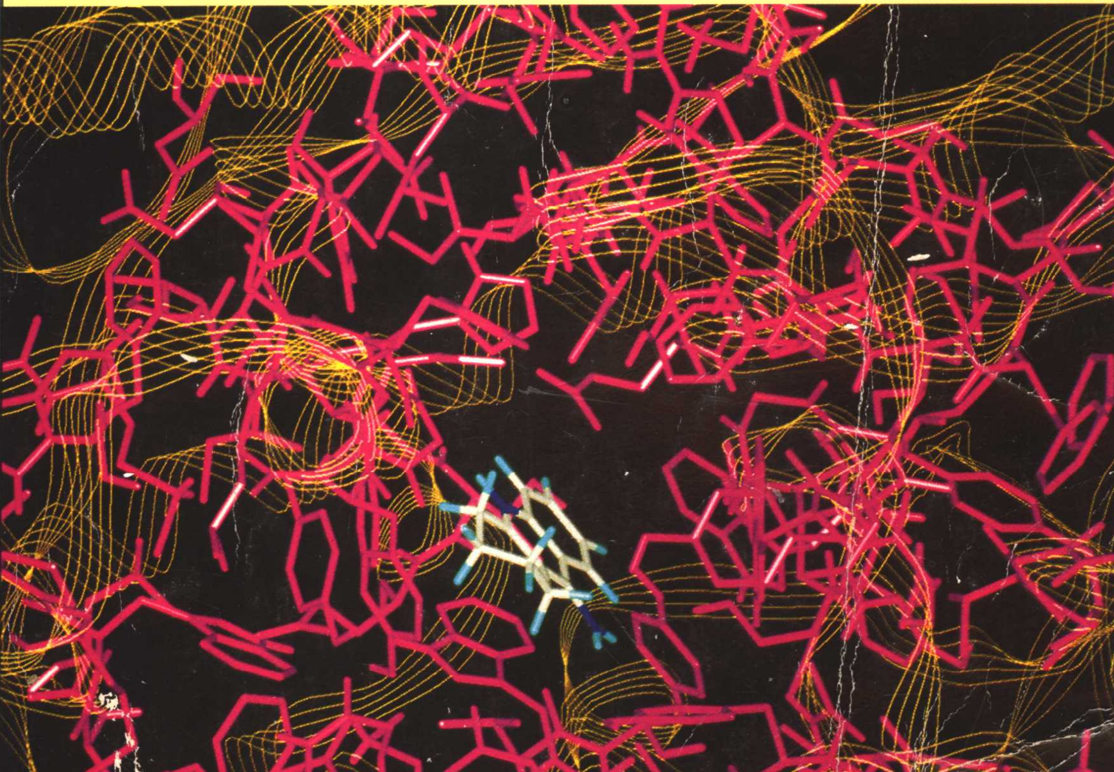
Study Guide for

ORGANIC CHEMISTRY

THIRD EDITION



SEYHAN EGE
ROBERTA KLEINMAN
MARJORIE L. C. CARTER

Study Guide for

Organic Chemistry

Structure and Reactivity

Third Edition

Seyhan N. Eğe
The University of Michigan

Roberta W. Kleinman
Lock Haven University

Marjorie L. C. Carter
Eastern Michigan University

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About the cover: Chemists deal every day with questions of structure and reactivity in their work. The picture you see on the cover was generated using molecular modeling programs and computer graphics in the laboratories of the Parke-Davis Pharmaceutical Research Division of Warner-Lambert as part of their ongoing search for more effective medications. The blue and white structure represents a molecule of tacrine (Cognex™), which was recently approved for the treatment of Altzheimer's disease. It is shown docked into the active site of acetylcholinesterase, an enzyme known to be involved in the processes of learning and memory. Scientists, in designing such medications, work with knowledge of the three-dimensional structures (shown in magenta) of the protein molecules that are the enzymes and of the drugs that complex with and inhibit the reactivity of these enzymes. In designing new and more potent drugs, chemists take into account all of the spatial and electronic properties of both the enzymes and of the drug under consideration. Computer modeling is a powerful tool that enables chemists to examine possible structures of drugs and choose the ones most likely to have the right structure and reactivity interactions and, therefore, to be active before starting the extensive experimentation work that eventually leads to clinical testing.

The chemistry discussed in this book is aimed at developing the understanding that chemists have of the structure of molecules. The book focuses on how the reactivity of such compounds is determined by their structures and how chemists use such understanding in creating new substances.

Cover image courtesy of Daniel Ortwine, Parke-Davis Pharmaceutical Research, a Division of Warner-Lambert Company.

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To the Student

The *Study Guide* that accompanies your text has been prepared to help you study organic chemistry. The textbook contains many problems designed to assist you in reviewing the chemistry that you need to know. The *Study Guide* contains the answers to these problems worked out in great detail to help you to develop the patterns of thought and work that will enable you to complete a course in organic chemistry successfully. In addition, notes that clarify points that may give you difficulty are provided in many answers.

The *Study Guide* also contains *Workbook Exercises,* created by Brian Coppola of the University of Michigan. These exercises are designed to help you review previous material and to introduce you to the problem-solving skills you will need for new material. They are found only in the *Study Guide,* and no answers are given for them. Many of the exercises can be explored with other students in your class.

Suggestions for the best way to study organic chemistry are given on pages 2 - 4 of the textbook. Before you work with the *Study Guide,* please review those pages in the text. There you will find emphasis on four things necessary for success in organic chemistry:

1. steady consistent studying,
2. working with problems as the most effective way to learn organic chemistry,
3. training your eye to look for the structural features in molecules that determine their chemical and physical properties, and
4. training your hand to draw correct structural formulas for reacting species and products.

This *Study Guide* contains two features to help you to study more effectively. The sections on Problem-Solving Skills in the textbook show you how to analyze problems in a systematic way by asking yourself questions about the structural changes in and the reactivity of the reagents shown in the problem. These same questions are used in arriving at the answers shown in the *Study Guide* for some of the problems. If you follow the reasoning shown in these answers, you will review the thinking patterns that are useful in solving problems.

The *Study Guide* also contains concept maps, which are summaries of important ideas or patterns of reactivity presented in a two-dimensional outline form. The textbook has notes in the margins telling you when a concept map appears in the *Study Guide*. The concept maps are located among the answers to the problems. The Table of Contents of the *Study Guide* on pp. iii - vi will tell you where each concept map is. The concept maps will be the most useful to you if you use them as a guide to making your own. For example, when you review your lecture notes, you will learn the essential points much more easily if you attempt to summarize the contents of the lecture in the form of a concept map. At a later time you may want to combine the contents of several lectures into a different concept map. Your maps need not look like the ones in the *Study Guide*. What is important is that you use the format to try to see relationships among ideas, reactions, and functional groups in a variety of ways.

The *Study Guide* will be most helpful to you if you make every attempt to solve each problem completely before you look at the answer. Recognition of a correct answer is much easier than being able to produce one yourself, so if you simply look up answers in the book to see whether you "know how to do the problem" or "understand" a principle, you will probably decide that you do. In truth, however, you will not have gained the practice in writing structural formulas and making the step-by-step decisions about reactivity that you will need when faced by similar questions on examinations. Work out all answers in detail, writing correct, complete formulas for all reagents and products. Build molecular models to help you draw correct three-dimensional representations of molecules. Consult the models whenever you are puzzled by questions of stereochemistry.

If you do not understand the answer to a problem, study the relevant sections of the text again, and then try to do the problem once more. The problems will tell you what you need to spend most of your time studying. As you solve the many review problems that bring together material from different chapters, your knowledge of the important reactions of organic chemistry will solidify.

We hope that the *Study Guide* will serve you as a model for the kind of disciplined care that you must take with your answers if you wish to train yourself to arrive at correct solutions to problems with consistency. We hope also that it will help you to develop confidence in your ability to master organic chemistry so that you enjoy your study of a subject that we find challenging and exciting.

Seyhan N. Eğe
Roberta W. Kleinman
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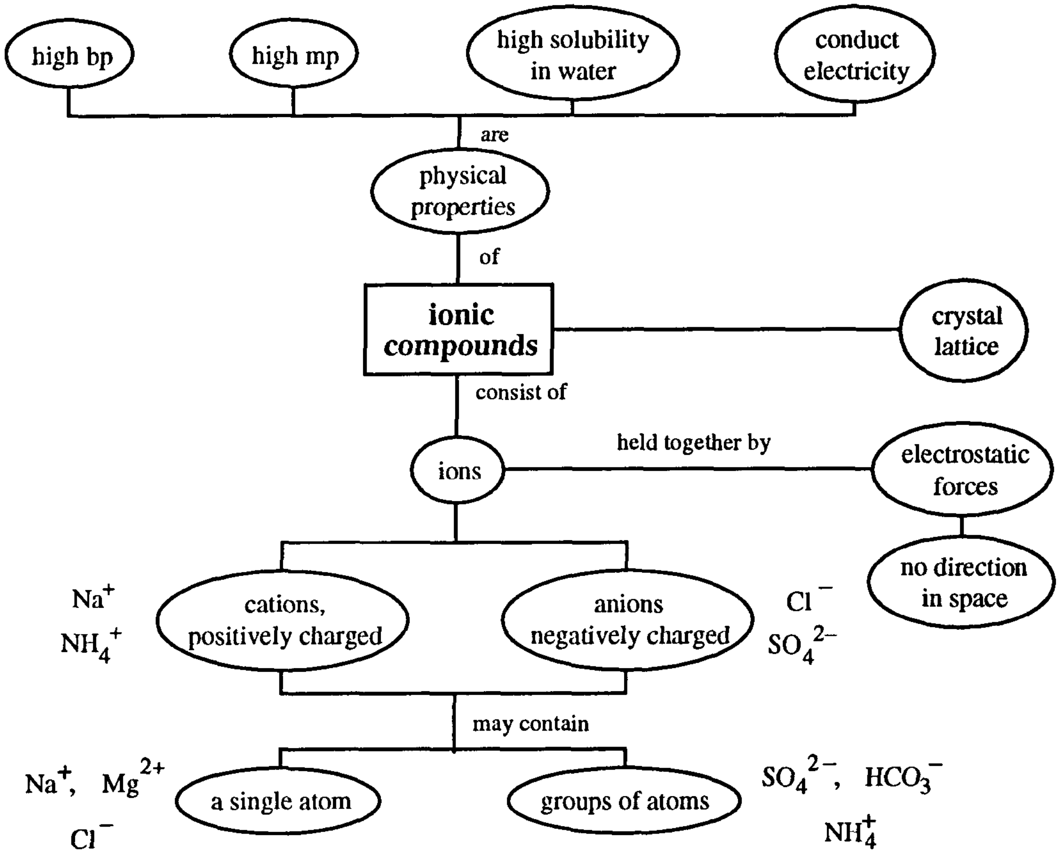
Contents

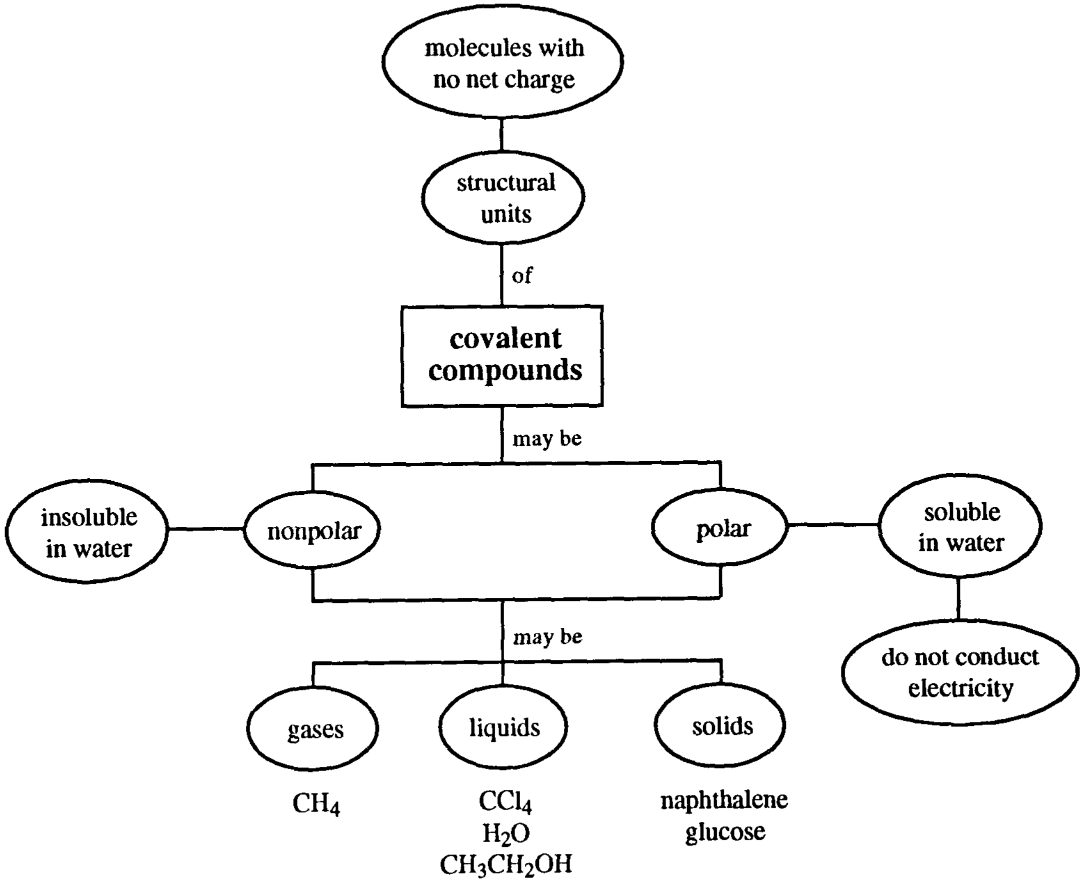
1

An Introduction to Structure and Bonding in Organic Compounds

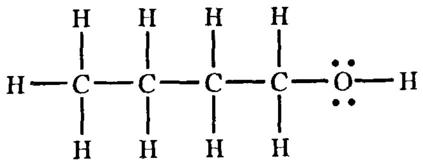
Concept Map 1.1 Ionic compounds and ionic bonding.



Concept Map 1.2 Covalent compounds.



1.1 Note: The names of the compounds shown below are given for information. You are not yet expected to know how to name the compounds, but an examination of the names to see if you recognize an emerging pattern is fun.

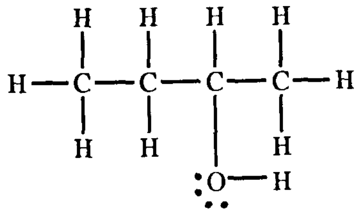


Lewis structure for 1-butanol

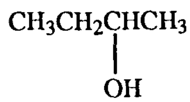
$CH_3CH_2CH_2CH_2OH$

condensed formula for 1-butanol

connectivity: four carbon atoms in a row with the oxygen atom at the end of the row



Lewis structure for 2-butanol

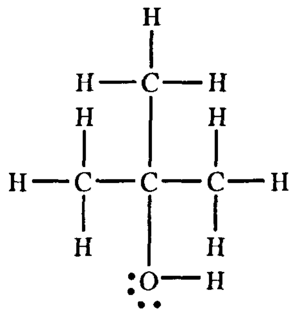


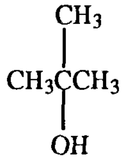
or $CH_3CH_2CHOHCH_3$

condensed formula for 2-butanol

connectivity: four carbon atoms in a row with the oxygen atom on the second carbon atom of the row

1.1 (cont)



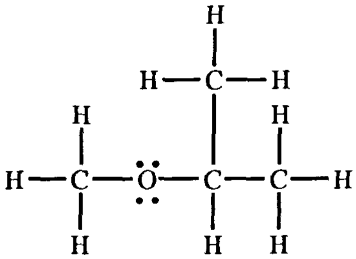


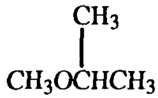
or $(CH_3)_3COH$

Lewis structure for 2-methyl-2-propanol

condensed formula for 2-methyl-2-propanol

connectivity: three carbon atoms in a row with one carbon atom and one oxygen atom on the second carbon atom of the row



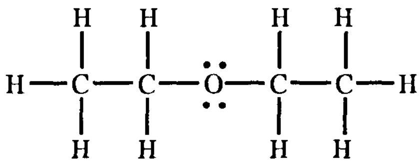


or $CH_3OCH(CH_3)_2$

Lewis structure for methyl isopropyl ether

condensed formula for methyl isopropyl ether

connectivity: one carbon atom bonded to an oxygen that is bonded to two more carbon atoms in a row, with a third carbon atom attached to the first of these carbons



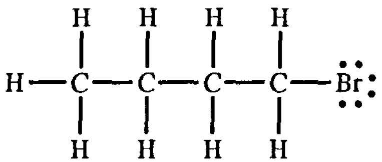
$CH_3CH_2OCH_2CH_3$

Lewis structure for diethyl ether

condensed formula for diethyl ether

connectivity: two carbon atoms in a row bonded to an oxygen atom that is bonded to two other carbon atoms in a row

1.2 The names (and the connectivities) of the compounds in this problem are related to some of those in Problem 1.1. See if you can find the pattern.



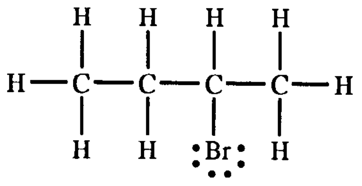
$CH_3CH_2CH_2CH_2Br$

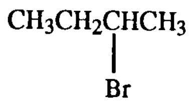
Lewis structure for 1-bromobutane

condensed formula for 1-bromobutane

connectivity: four carbon atoms in a row with the bromine atom at the end of the row

1.2 (cont)

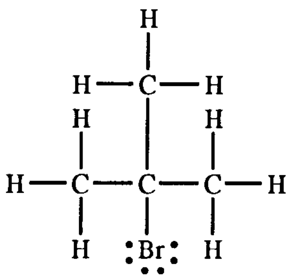


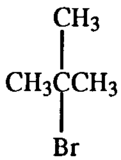
 or $CH_3CH_2CHBrCH_3$

Lewis structure for 2-bromobutane

condensed formula for 2-bromobutane

connectivity: four carbon atoms in a row with the bromine atom on the second carbon atom of the row

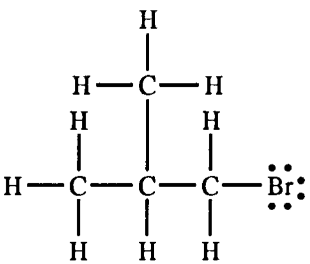


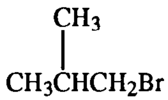
 or $(CH_3)_3CBr$

Lewis structure for 2-bromo-2-methylpropane

condensed formula for 2-bromo-2-methylpropane

connectivity: three carbon atoms in a row with the bromine atom and a carbon atom on the second carbon atom of the row



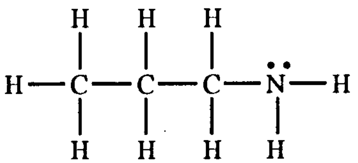
 or $(CH_3)_2CHCH_2Br$

Lewis structure for 1-bromo-2-methylpropane

condensed formula for 1-bromo-2-methylpropane

connectivity: three carbon atoms in a row with the bromine atom at the end of the row and a carbon atom on the second carbon atom of the row

1.3



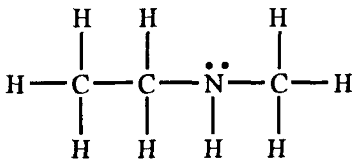
$CH_3CH_2CH_2NH_2$

Lewis structure for propylamine

condensed formula for propylamine

connectivity: three carbon atoms in a row with the nitrogen atom at the end of the row

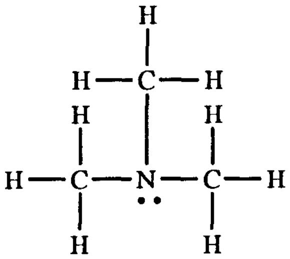
1.3 (cont)

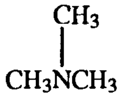


$CH_3CH_2NHCH_3$

Lewis structure for methylethylamine — condensed formula for methylethylamine

connectivity: two carbon atoms in a row attached to a nitrogen atom that is bonded to one other carbon atom



 or $(CH_3)_3N$

Lewis structure for trimethylamine — condensed formula for trimethylamine

connectivity: a nitrogen atom with three single carbon atoms bonded to it

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Workbook Exercises

In most chemical reactions, molecules undergo changes in the connectivity, that is, the bonding, of their atoms. Learning how to identify these changes rapidly is a skill you should master.

EXERCISE I. Identify these features in the following chemical reactions:

(1) bonds broken

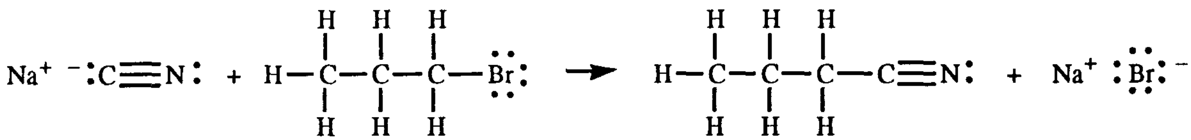
(2) bonds formed

(3) redistribution of bonding and nonbonding electrons

EXAMPLE

SOLUTION

While you are becoming comfortable with molecular structures, it is a good idea to use complete Lewis structures to follow the changes in connectivity. You should also examine the formal charges and electron configurations of the atoms involved in those changes.

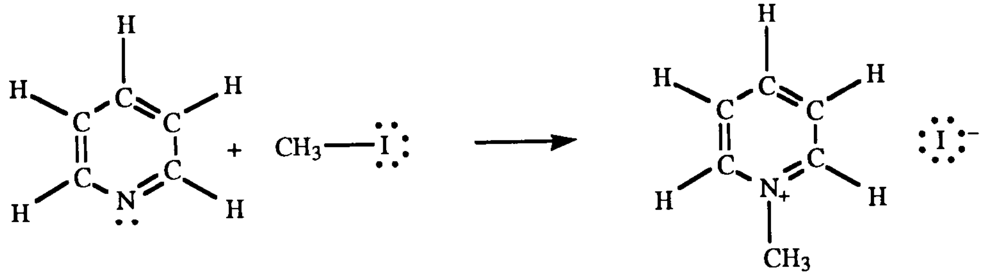


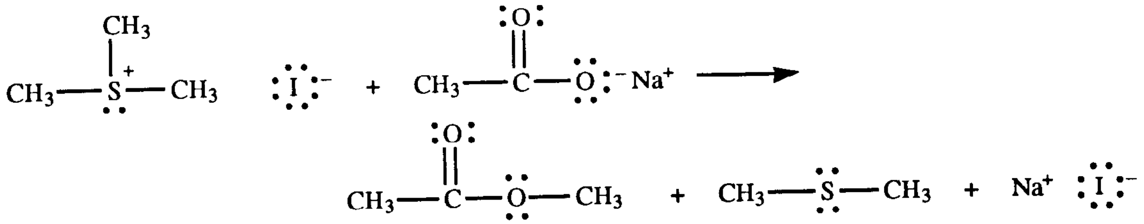
Workbook Exercises (cont)

One bond is broken: the 2-electron C—Br bond breaks, and this electron pair becomes the fourth nonbonding electron pair on the bromide ion that forms. One bond is formed: the nonbonding electron pair on the carbon atom of cyanide ion (CN^-) is used to form the new C—C bond.

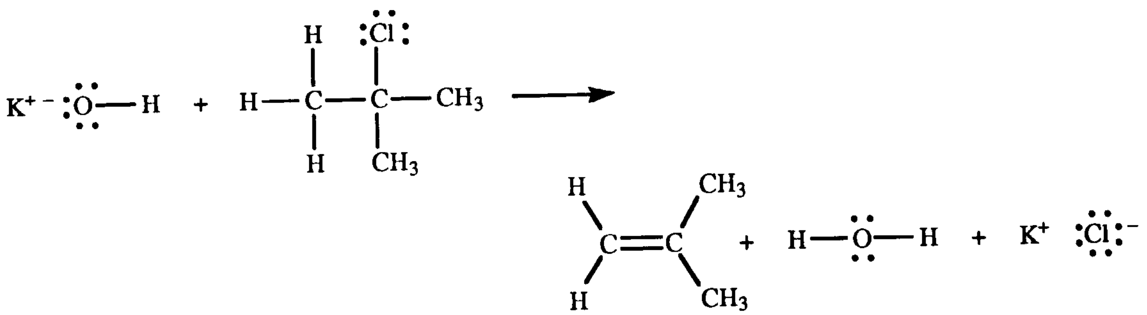
EXERCISE I. Identify the bonds broken, the bonds formed, and the way electrons have been redistributed in the processes of chemical change for the following reactions.

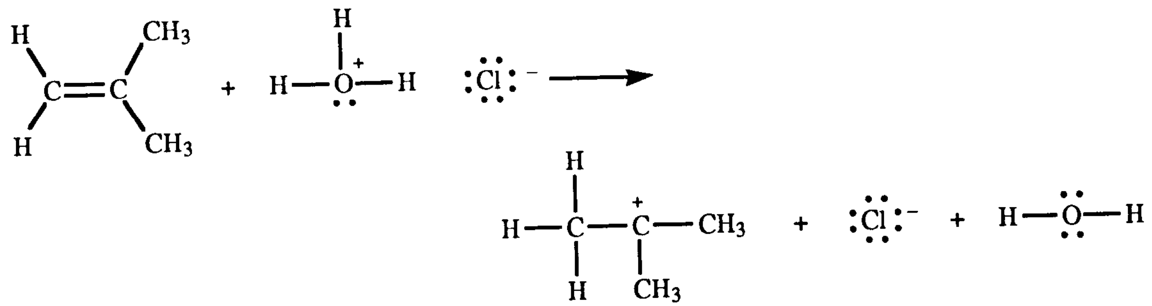
1. $(CH_3)_2CHCH_2\ddot{O}H$ + Na^+ $H:^-$ ⟶ $(CH_3)_2CHCH_2\ddot{O}:^-$ Na^+ + H—H

2. 

3. 

The next two examples involve double bonds, introduced in Section 1.5 of the text. Can you also describe these changes?

4. 

5. 

Workbook Exercises (cont)

EXERCISE II. Complete each of the equations by providing the structure of the molecule that will balance the chemical equation. In a balanced equation, there must be an equal number of each kind of atom on both sides of the equation. The overall charge must also be the same on both sides of a chemical reaction equation. All of the atoms in the compounds in these exercises have closed shell configurations.

EXAMPLE

$$Li^+ \; ^-{:}\ddot{\underset{..}{S}}H \; + \; (CH_3)_2CH\ddot{\underset{..}{Cl}}{:} \longrightarrow \textbf{A} \; + \; Li^+ \; {:}\ddot{\underset{..}{Cl}}{:}^-$$

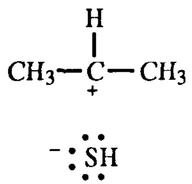
SOLUTION

As in Exercise I, we can identify some of the bonding changes. From this information, and the fact that the equation must balance, we determine the structure of the unknown substance **A**.

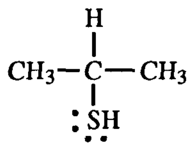
What we see: the C—Cl bond breaks, and the electron pair from the single bond becomes the fourth nonbonding electron pair of chloride ion on the right side of the equation. The unknown compound **A** must (a) incorporate the atoms from the left hand side of the equation that are not shown on the right, (b) have an overall neutral charge in order to keep the charges balanced, and (c) be comprised of atoms with closed shell configurations.

So, compound **A** needs to include (a) the SH atoms derived from the ionic compound LiSH, and (b) the atoms from $(CH_3)_2CHCl$, except for chloride ion which appears as a product. The product ion, Cl^-, must come from the uncharged molecule $(CH_3)_2CHCl$ because there is no other source of chlorine atoms on the left hand side of the equation. Although we cannot identify the structure of A with certainty at this point, we can account for the atoms from $(CH_3)_2CHCl$ that remain when the chloride ion, Cl^-, is removed. Perhaps only temporarily, we can imagine the presence of a positively charged fragment, $CH_3-\overset{H}{\underset{+}{C}}-CH_3$, that comes from removing Cl^- from the uncharged starting compound. In our imagination, the fragments we can use to make A are the cation, $CH_3-\overset{H}{\underset{+}{C}}-CH_3$, and the anion, $^-{:}\ddot{\underset{..}{S}}H$. There are two possible ways to create a compound from these fragments:

the first way gives us an ionic compound:



the second way gives us a covalent compound:



Is there a way to decide between these two possible structures for A? Or are they both acceptable answers? When solving an open-ended problem such as this one, either in the homework or on an examination, it is important to check the assumptions and information given in the problem. In this case, rereading the question tells us that "All of the atoms in these compounds have closed shell configurations." Therefore, the covalent structure is the only one that satisfies this criterion. In the ionic structure, the positively charged carbon has an open shell.

EXERCISE II. Complete each of the following equations, as demonstrated in the example above.

1. $CH_3CH_2\ddot{\underset{..}{Br}}{:} \; + \; \textbf{B} \longrightarrow CH_3CH_2\overset{+}{N}H_3 \; + \; {:}\ddot{\underset{..}{Br}}{:}^-$