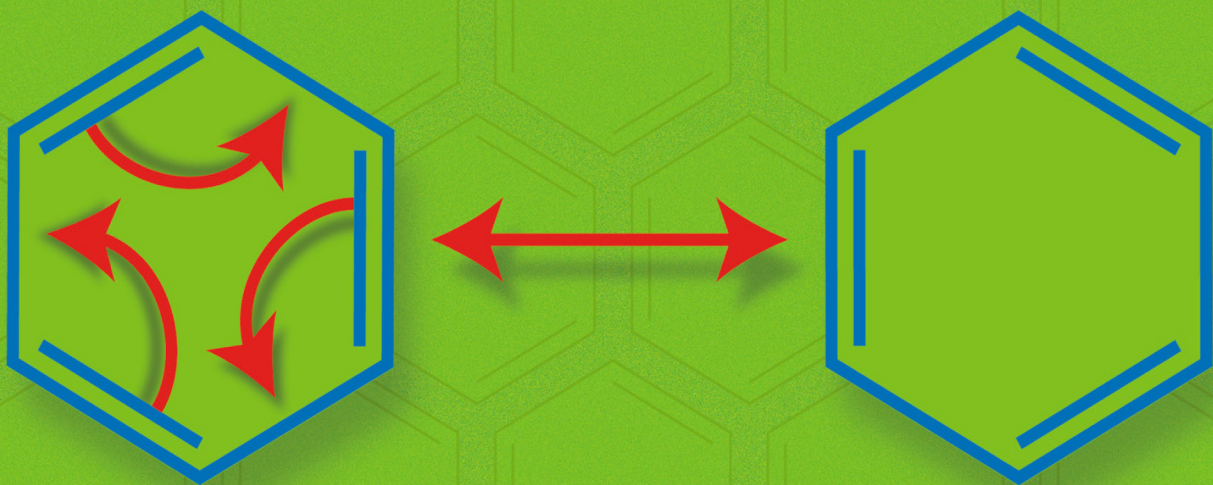


Pushing Electrons

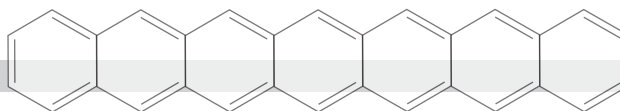
A Guide for Students of Organic Chemistry



Weeks
4e



FOURTH EDITION



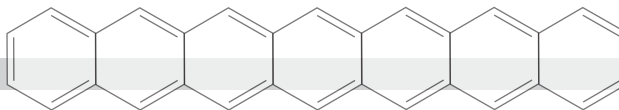
Pushing Electrons

A GUIDE FOR STUDENTS OF
ORGANIC CHEMISTRY

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FOURTH EDITION



Pushing Electrons

A GUIDE FOR STUDENTS OF
ORGANIC CHEMISTRY

Daniel P. Weeks, Ph.D.

Northwestern University

Arthur H. Winter, Ph.D.

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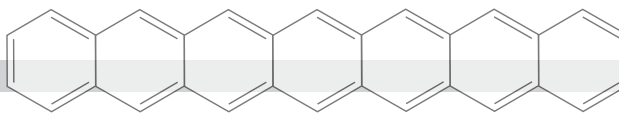
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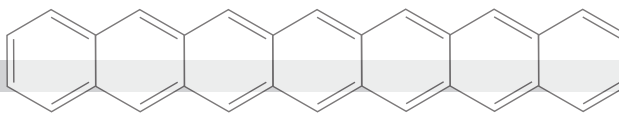
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Preface

Among the factors that set organic chemistry apart from the other traditional divisions of chemistry are the endless variety of structure, the strong dependence on the resonance theory, and the emphasis on mechanisms. As students become more facile with structure and more adroit at writing resonance structures and mechanisms, organic chemistry changes from a bewildering array of facts to a unified science. Newly encountered reactions can be understood from previously learned principles.

At the introduction of resonance or mechanisms, the professor begins using little arrows that resemble fishhooks (\curvearrowright , \curvearrowleft). Using these arrows, electrons are moved around molecules and appear—as if by wizardry—precisely where the professor needs them. The penchant for moving electrons has earned organic chemists the pejorative *electron pusher* that, like the 18th century British expression *Yankee Doodle*, we wear proudly.

We have observed that students avoid pushing electrons. They find it difficult, therefore, to write resonance structures and lose a powerful tool to explain reactivity. Many students never become comfortable with bond-making and bond-breaking steps in organic mechanisms. With this low-tech, pencil-and-paper program, a student can learn to push electrons with the same wizardry as the professor.

While working through this book, the student will learn to construct Lewis structures of organic molecules and functional groups. The functional groups will be learned early and in a way that minimizes the necessity for memorization. Then a systematic method is presented whereby all the possible resonance structures for a molecule, ion, or radical can be generated by beginning with one Lewis structure and moving electrons.

Chapter 3 demonstrates the individual bond-making and bond-breaking steps in reaction mechanisms. In Chapter 4 students' newly acquired ability to push electrons is used to construct complete mechanisms. Chapters 5 and 6 describe electron-pushing skills applied to the reactions of biochemistry and polymerization. The programmed approach of this book emphasizes repetition and active participation in learning how to push electrons.

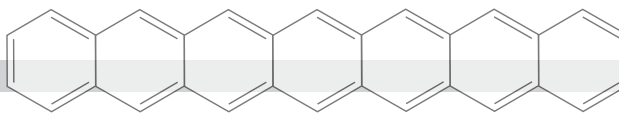
For this edition, all Lewis structures have been reviewed to correct bond angles and other concerns. Revisions have been made throughout for clarity and efficacy; Chapter 6, new to this edition, presents the use of transition metals in organic synthesis.

Acknowledgments

In the production of three editions of the book, Dan Weeks received help from Dr. Joyce C. Brockwell and Professor Emeritus Charles D. Hurd (Northwestern University), Dr. Rebecca Dickstein (Drexel University), Dr. Kenneth Turnbull (Wright State University), and Dr. Darrell J. Woodman (University of Washington). While retirement to rural western Virginia has its advantages, Dan Weeks needed access to a chemistry library and vigorous chemistry faculty in order to write the third edition; he found both at Virginia Polytechnic Institute and State University (Virginia Tech). Professor Richard Gandour, Chemistry Department Head, provided a generous welcome. As always, Dan Weeks is grateful to his late publisher John Vondeling and his development editor Sandi Kiselica for their encouragement and patience in the production of the first three editions.

For the latest edition we are indebted to Peter McGahey and Christopher Simpson of Cengage Learning. We also received valuable advice from Philip Albinak (Ball State University), Peter Bell (Tarleton State University), Nathan Hershberger (The City College of New York), Deborah Lieberman (University of Cincinnati), Jason Locklin (University of Georgia), Barbara Mayer (California State University, Fresno), and Daniel Turner (Ohio State University).

DANIEL P. WEEKS
ARTHUR H. WINTER
NOVEMBER 2012



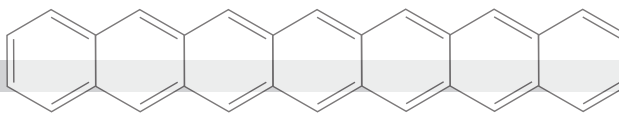
To the Professor

Students will be better at organic chemistry if they master the skills in *Pushing Electrons*. The book is a supplement. It knows its place. It is short, methodical, and repetitious. A student will complete *Pushing Electrons* in 12 to 16 hours and have the rest of the time for important things such as listening to you, asking questions, and studying the main text.

The approach is methodical; the pace is slow. Strong students will race through certain sections, but even they will benefit. We tell them in the text, “you can never be too skilled at pushing electrons.” Weaker students will appreciate that Dan Weeks still holds a grudge against his calculus professors who skipped steps.

The repetition used in teaching students how to write Lewis structures and how properly to push electrons has an additional benefit. Students become comfortable writing and rewriting organic structures, a useful skill when taking an exam. The book may not eliminate pentavalent carbon but it should reduce the frequency of its appearance. The structures in this book, except for rings and larger structures in the last chapters, show all carbons and hydrogens. We assert that the early introduction of line-angle structures does students great harm.

Assign Chapter 1, Lewis Structures, right away. Chapters 2 and 3 are relatively independent of one another; assign them as you see fit. It is not necessary for students to complete Chapter 2 before beginning Chapter 3. Although a chapter may be interrupted, it should be done from beginning to end. Chapter 4 describes strategies for dealing with mechanism problems. We suggest that you assign parts of it as your students encounter mechanism problems of increasing difficulty. Once again, you may interrupt Chapter 4 but assign it from beginning to end. Chapter 5 should be considered optional depending on whether or not your course contains biochemistry. The new Chapter 6 adds a brief treatment of the use of transition metals in organic synthesis. You are the best judge of whether or not to use it.



To the Student

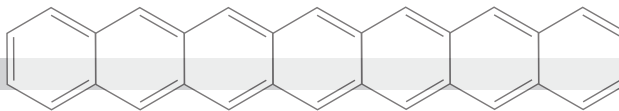
We have three instructions.

- Supply an answer wherever a line appears under a blank space. Actually, in Chapter 4 only blank spaces are provided, but by that time you will know what is required. The correct answer will be a word, a number, a structure, some arrows, or—in Chapter 4—a mechanism.
- Don't look up the correct answers until you have made a serious try at doing it yourself.
- If you plan to just look up the right answers and transcribe them, return the book and get your money back.

This program uses two effective learning devices, no matter what textbook is used in your course: active involvement and repetition. You will participate actively in the learning process. Because so much of the academic experience consists of just receiving information, it should be refreshing to work through a program using your own wits. You will see an example of an operation and then carry it out several times as the supporting material is gradually removed. The approach is methodical. Some of you will find that you can accelerate your trip through certain sections. But the program has been written in the hope that none of you will ever feel abandoned. Expect to spend a total of 12 to 16 hours to complete the entire book.

We hope your professor will assign appropriate sections of the book as the course proceeds. Failing that, do Chapter 1 right away. Then, start Chapters 2 and 3 (they are relatively independent of each other) before your course gets to that material. If you start to feel lost, put it aside for a while and then pick up where you left off. Begin Chapter 4 when you need some help with solving mechanism problems. Chapters 5 and 6 are for courses where some biochemistry and polymer chemistry is introduced toward the end. From time to time during the course, we think you will find *Pushing Electrons* useful for review. This is especially true of Chapter 3, the backbone of the book.

One last thing. **You will be using a pencil** just like you will during an exam. You will benefit from the practice.



Glossary

Boldfaced numbers refer to the page on which the term first appears.

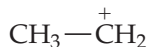
Aliphatic One of two broad classes of organic compounds. The other is *aromatic*. Aliphatic compounds are composed of chains of carbon atoms. A subgroup within this class is the alicyclic compounds that contain rings of carbon atoms but are similar to open-chain compounds in chemical and physical properties. Actually, the most sensible definition of aliphatic compounds is “compounds that are not aromatic.” **14**

Aromatic One of two broad classes of organic compounds. The other is *aliphatic*. Benzene, compounds containing a benzene ring, and compounds similar to benzene in chemical properties constitute the aromatic compounds. **14**

Carbanion An ion in which a negative charge resides on a carbon atom. **29**

Carbocation An ion in which a positive charge resides on a carbon atom. Carbocations are classified as primary, secondary, or tertiary according to the following scheme. **29**

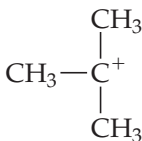
Primary: The carbon atom with the positive charge is *directly* attached to only one other carbon atom and two hydrogen atoms. For example,



Secondary: The carbon atom with the positive charge is directly attached to two other carbon atoms and one hydrogen atom. For example,



Tertiary: The carbon atom with the positive charge is directly attached to three other carbon atoms and no hydrogen atoms. For example,



The order of stability of carbocations is tertiary > secondary > primary.

Decarboxylation A reaction in which a carboxylic acid loses carbon dioxide. 152

Double bond The combination of a sigma bond and a pi bond between two atoms. The carbon—carbon double bond is written C=C. In this notation there is no convention regarding which line represents the sigma and which the pi bond. The presence of a double bond makes a compound unsaturated. 7

Electron-attracting groups, and electron-releasing groups Various groups of atoms found in organic compounds are electron attracting or releasing, relative to the carbon atom to which they are attached. The presence of these groups can have a marked effect on chemical reactivity. Some electron-releasing groups are —NH_2 , —OCH_3 , and —CH_3 . Some electron-attracting groups are —NO_2 , —COOH , —F , —Cl , —Br , and —CN . 118, 119

Electrophile The word comes from the Greek meaning “electron lover.” Electrophiles are chemical entities (atoms, ions, radicals, or molecules) that seek electrons. Electrophiles are electron-poor. They are designated as E or E+. When an electrophile reacts with some electron-rich center on an organic molecule, the process is called electrophilic attack. 97

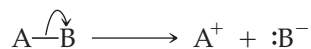
Formal charge A Lewis structure is, after all, only a graphic representation of a molecular structure. As useful as they are, Lewis structures are not entirely descriptive of a molecule. The formal charge is the charge that would be on an atom in a molecule if the Lewis structure were an entirely accurate representation of the molecule. In one sense, formal charge is simply electron bookkeeping. However, the location of formal charge on a Lewis structure is always revealing of the chemistry of the molecule. 18

Free radical A chemical species having at least one unpaired valence electron. 31

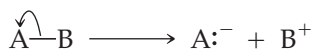
Functional group One can think of organic compounds as being composed of two parts: a hydrocarbon backbone and a functional group. The latter is an atom or group of atoms that confers some distinct chemical or physical property. The functional group is the site of chemical reactions. Thus, molecules with the same functional group undergo similar chemical reactions despite having quite different hydrocarbon backbones. 20

Grignard reagent A reagent formed by reaction of an alkyl halide with magnesium in an ether solvent. These reagents are extremely useful and versatile intermediates for synthesizing organic compounds. The actual structure of the Grignard reagent is rather complex. It is expedient, however, to consider it an ion pair, as this text does. 87

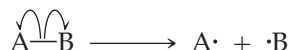
Heterolytic cleavage (heterolysis) The breaking of a bond so that the electrons that formed the bond are distributed unevenly between the two fragments. Heterolysis results in an anion and a cation. 78



or



The counterpart of heterolysis is *homolysis*, in which the electrons are distributed evenly between the two fragments. The result is a pair of radicals.



Metabolism The sum total of all biochemical reactions that take place in an organism.

Nucleophile The word comes from the Greek, meaning “nucleus lover.” Nucleophiles are chemical entities (ions or molecules) that seek an electron-poor center. Nucleophiles are electron-rich. They are designated as Nu or Nu⁻. When a nucleophile reacts with some electron-poor center of an organic molecule, the process is called *nucleophilic attack*. 82


Pi bonds and pi electrons Bonds that are the result of lateral (side to side) overlap of atomic p-orbitals. Pi bonds are weaker than sigma bonds. Pi bonds are always found in combination with a sigma bond. Therefore, single bonds are never pi bonds. Pi electrons are the electrons in pi bonds. 45, 52, 80

Protonation The combination of a proton (hydrogen ion) with some organic base to give the conjugate acid of that base. 155

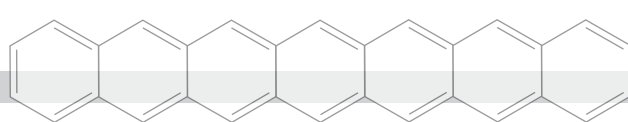


Regiochemistry The study of reactions in which one direction of bond making or bond breaking is preferred over all others.

Saturated Compounds that contain only single bonds cannot add other reagents. Thus, they are called *saturated*. 1



C H A P T E R 1



Lewis Structures

In a perfect world there would be no need for this chapter at the beginning of a course in organic chemistry. The skills described here are taught in general chemistry. Skip this chapter if you feel entirely confident that you are able to write Lewis structures correctly and are comfortable with the concepts of ions, radicals, multiple bonding, and formal charge. On the other hand, these skills are vital to organic chemists and a little review never hurt anyone.

The distinguished American chemist, Gilbert Newton Lewis (1875–1946), was the first to propose that atoms share a pair of electrons to form a covalent bond. Lewis electron-dot formulas are familiar to all students of introductory chemistry. Lewis used dots to denote all valence electrons in chemical formulas. We will use the current convention that denotes a pair of shared electrons (a covalent bond) as a dash connecting the atoms and shows only the unshared electrons as dots.

Using Lewis's notation together with a judicious application of the octet rule allows us to write useful chemical formulas. The most important requirement for the formation of a stable compound is that the atoms achieve a closed shell, noble gas configuration. For all but the very light elements, this means eight electrons. The light elements (H, Li, Be) require two electrons, the configuration of helium. A few compounds such as borane (BH_3), boron trifluoride (BF_3), and aluminum chloride (AlCl_3), which are important to elementary organic chemistry, do not conform to the octet rule.

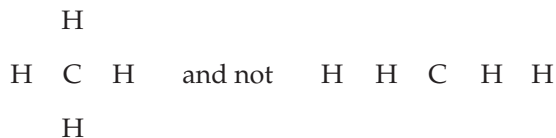
Molecules and Functional Groups

Saturated Groups

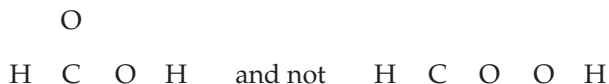
Proper Lewis structures for **saturated** compounds can be written by following this brief set of rules.

RULE 1

Write the molecular skeleton. Historically, the correct skeleton of each functional group was deduced from experiment. Most of that has been done, however, and we shall assume that you know, or will know shortly, that methane's skeleton is



and formic acid's molecular skeleton is



which is how it is often written to save space. In your initial study of organic chemistry you must be careful to not let space-saving notation mislead you about structure.

RULE 2

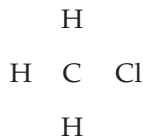
Assume that all bonds are covalent. This assumption is not always accurate, but it works most of the time, especially for organic compounds. As your experience increases, you will learn when to use ionic bonds.

RULE 3

Count the available valence electrons. Each atom in a compound brings into the union a certain number of valence electrons. The number is determined by the atom's group in the periodic table.

1. Hydrogen is a Group I element and each hydrogen will contribute 1 valence electron. Carbon is a Group IV (Roman numeral) element and each carbon will contribute 4 (number) electrons. Every oxygen atom in a compound will contribute 6 valence electrons.

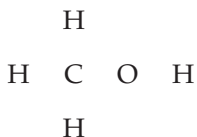
Chloromethane has the molecular formula CH_3Cl . Its skeleton is



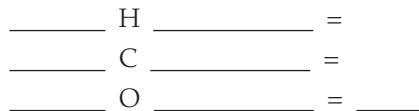
and the number of valence electrons may be determined as follows. There are three hydrogen atoms, each of which contributes 1 valence electron; the single carbon contributes 4 electrons; and the single chlorine atom contributes 7 electrons, making a total of 14. A convenient tabular form of this calculation is

$$\begin{array}{r} 3 \quad \text{H} \quad 1 \times 3 = \quad 3 \\ 1 \quad \text{C} \quad 4 \times 1 = \quad 4 \\ 1 \quad \text{Cl} \quad 7 \times 1 = \quad 7 \\ \hline 14 \end{array}$$

2. Methanol has the molecular formula CH_4O . Its skeleton is



Each of four hydrogen atoms contributes ____ valence electron, the carbon atom contributes ____, and the oxygen atom contributes ____, making a total of ____.

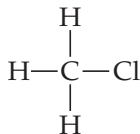


RULE 4

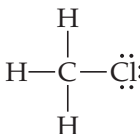
Add electrons to the skeleton by making single bonds between the atoms that are bonded and then by providing each atom with a complement of eight electrons (hydrogen requires only two electrons).

3. The skeleton of chloromethane is

The central carbon atom is bonded to each of the other atoms by a shared electron pair (represented by a straight line, —) giving



Now, each hydrogen has two electrons and the carbon atom has eight. However, chlorine must be provided with **unshared electrons** (represented by pairs of dots, ••) to complete its octet, thus,



4. Methanol's skeleton is

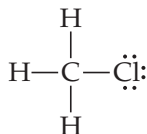
Connecting all bonded atoms by means of an electron pair (single bond) gives

and completing the octet of oxygen with two pairs of dots gives

RULE 5

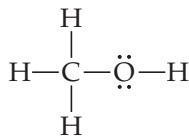
Count the electrons in the Lewis structure and compare the result with the number derived from Rule 3. If the two numbers are the same, the Lewis structure is correct.

5. The structure for chloromethane is



It contains 14 valence electrons. The number of available valence electrons in chloromethane is _____. The Lewis structure is correct.

6. The structure for methanol is

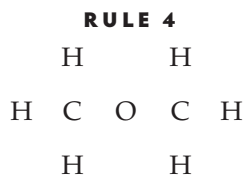
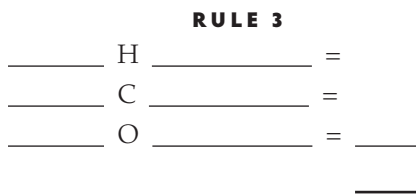


It contains _____ valence electrons. The number of available valence electrons is _____. The structure is _____ (correct, incorrect).

EXERCISES

Using the method outlined above, derive the Lewis structures for the following compounds. The unbonded skeletons are provided.

7. Dimethyl ether ($\text{C}_2\text{H}_6\text{O}$)



RULE 5

No. of electrons in structure _____

No. of valence electrons _____

Structure is _____ (correct, incorrect)

8. Methylamine (CH_5N)**RULE 3**

_____ H _____ =
 _____ C _____ =
 _____ N _____ = _____

=====

RULE 5

No. of electrons in structure _____

No. of valence electrons _____

Structure is _____

9. Methanethiol (CH_4S)**RULE 3**

_____ H _____ =
 _____ C _____ =
 _____ S _____ = _____

=====

RULE 5

No. of electrons in structure _____

No. of valence electrons _____

Structure is _____

10. Methylal ($\text{C}_3\text{H}_8\text{O}_2$)**RULE 3**

_____ H _____ =
 _____ C _____ =
 _____ O _____ = _____

=====

RULE 5

No. of electrons in structure _____

No. of valence electrons _____

Structure is _____

RULE 4

```

  H   H
H   C   N
  H   H

```

RULE 4

```

  H
H   C   S   H
  H

```

RULE 4

```

  H   H   H
H   C   O   C   O   C   H
  H   H   H

```

Unsaturated Groups

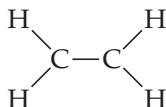
11. When the compound in question is **unsaturated**, the application of Rule 5 will show that the number of valence electrons in the trial structure is larger than the number of available valence electrons. In such cases the trial structure cannot be correct. It must be modified to contain the proper number of electrons. The skeleton of ethylene (C_2H_4) is



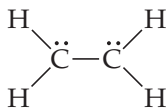
Each of 4 hydrogen atoms will contribute _____ electron and each of _____ carbon atoms will contribute _____ electrons. The total number of available valence electrons is _____.

$$\begin{array}{r} \underline{4} \quad \text{H} \quad \underline{1 \times 4} = \underline{4} \\ \underline{2} \quad \text{C} \quad \underline{4 \times 2} = \underline{8} \\ \hline \underline{12} \end{array}$$

12. Adding electrons to the skeleton by making single bonds between all bonded atoms gives



Each hydrogen atom now has a pair of electrons, but each carbon has only 6 electrons. Adding a pair of electrons to each carbon gives the trial structure

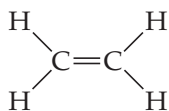


The number of electrons in the trial structure is _____. Since this number exceeds the number of available valence electrons, the structure is incorrect.

RULE 6

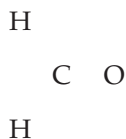
When the number of electrons in the trial structure is larger than the number of available valence electrons, the structure may be corrected by introducing one or more multiple bonds.

13. This is done by removing an unshared pair from each of two adjacent atoms and adding one electron pair as a second bond between the atoms. Each such operation reduces the number of electrons in the trial structure by two. Removing the unshared pairs of electrons on the carbon atoms and adding a second carbon—carbon bond gives



a structure in which there are four electrons involved in a **double bond** between the carbon atoms. The trial structure now contains ____ electrons and is correct.

14. Formaldehyde has the skeleton



Each of ____ hydrogen atoms will contribute ____ electron, the carbon atom, ____ electrons, and the oxygen, ____ electrons. The total number of valence electrons is ____.

$$\begin{array}{r}
 \underline{\hspace{1cm}} \text{ H} \quad \underline{\hspace{1cm}} = \\
 \underline{\hspace{1cm}} \text{ C} \quad \underline{\hspace{1cm}} = \\
 \underline{\hspace{1cm}} \text{ O} \quad \underline{\hspace{1cm}} = \underline{\hspace{1cm}}
 \end{array}$$

=====

Adding single bonds to the skeleton gives



and providing the carbon atom and the oxygen atom with an octet of electrons gives

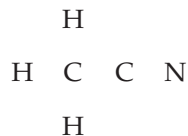


The number of electrons in the trial structure is ____ . The structure is _____ (correct, incorrect). Since the trial structure is incorrect, the pair of unshared electrons on the carbon atom and one of the pairs of unshared electrons on the oxygen atom are removed. Adding a second carbon—oxygen bond gives



The trial structure now contains ____ electrons and is _____ (correct, incorrect).

15. The skeleton of acetonitrile is



Each of ____ hydrogens will contribute ____ electron, each of ____ carbons will contribute ____ electrons, and the nitrogen will contribute ____ electrons. The total number of valence electrons is ____.

$$\underline{\hspace{2cm}} \text{ H } \underline{\hspace{2cm}} =$$

$$\underline{\hspace{2cm}} \text{ C } \underline{\hspace{2cm}} =$$

$$\underline{\hspace{2cm}} \text{ N } \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$$

=====

Adding single bonds to the skeleton gives

and providing the carbon and nitrogen atoms with octets gives

The number of electrons in the trial structure is _____. The trial structure is ____ (correct, incorrect). Removing one unshared pair of electrons from carbon and one pair from nitrogen and adding a second carbon—nitrogen bond gives

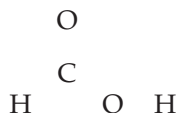
The structure now contains ____ electrons and is ____ (correct, incorrect). Performing the same operation again gives

The trial structure now contains ____ electrons and is ____ (correct, incorrect). Thus, you continue to remove pairs of unshared electrons from adjacent atoms and add multiple bonds (add unsaturation) until the number of electrons in the trial structure is equal to the number of available valence electrons.

* * * * *

Sometimes, you must decide where a multiple bond is best added.

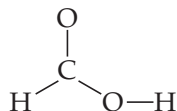
16. Formic acid has the skeleton



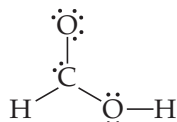
The number of available valence electrons is ____.

$$\begin{array}{r} \underline{\hspace{1cm}} \text{H} \underline{\hspace{1cm}} = \\ \underline{\hspace{1cm}} \text{C} \underline{\hspace{1cm}} = \\ \underline{\hspace{1cm}} \text{O} \underline{\hspace{1cm}} = \underline{\hspace{1cm}} \end{array} \quad \underline{\hspace{1cm}} \underline{\hspace{1cm}} \underline{\hspace{1cm}}$$

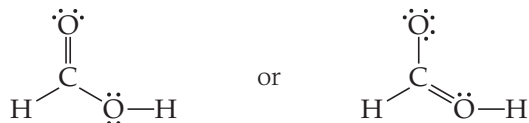
Filling in the skeleton with single bonds gives



and adding the appropriate unshared pairs gives



The number of electrons in the structure is ____, which is 2 too many electrons. This structure can be corrected by removing two unshared pairs and making one double bond. However, the double bond could be placed between the carbon atom and either one of the two oxygens. Thus,



The correct choice is the first structure and is made by observing that both oxygen atoms in the first structure have the appropriate valence of two. The second structure is less acceptable since it requires that the oxygen atoms have the unfamiliar valences of one and three respectively. We shall see later that the second structure is less acceptable also because it contains charge separation.