

Schaum's
题解精萃

有机化学

ORGANIC CHEMISTRY

影印版

Estelle K. Meislich Herbert Meislich Joseph Sharefkin

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Estelle K. Meislich, Ph.D.

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内容简介

Schaum's 丛书是由麦格劳-希尔(McGraw-Hill)国际出版公司出版的著名的系列教学辅助用书,涵盖了高等教育各类各门学科和课程。每本书都汇集了该门学科课程中的精髓内容,并对基本理论和基本概念作了简明精炼的归纳和总结,还提供了由美国众多经验丰富的资深教师和学者推荐、讲解透彻的精选例题和形式多样的各类习题。

本书根据 Schaum's 系列丛书《有机化学 3000 习题解答》原文影印出版。可供在校本科生、研究生以及社会各类科技人员参考使用。

图字: 01-1999-3837

3000 SOLVED PROBLEMS IN ORGANIC CHEMISTRY

International Editions 1994

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图书在版编目(CIP)数据

Schaum's 题解精萃. 有机化学: 英文/ (美) 迈斯林
(Meislich, E. K.) 等著. —北京: 高等教育出版社,
2000.6

ISBN 7-04-008760-X

I. S... II. 迈... III. 有机化学-高等学校-解题-
英文 IV. G642.3-44

中国版本图书馆 CIP 数据核字(2000)第 26685 号

Schaum's 题解精萃 有机化学
Estellek. Meislich Herbert Meislich Joseph sharefkin

出版发行 高等教育出版社
社 址 北京市东城区沙滩后街 55 号
电 话 010-64054588
网 址 <http://www.hep.edu.cn>

邮政编码 100009
传 真 010-64014048

经 销 新华书店北京发行所
印 刷 国防工业出版社印刷厂

开 本 850×1168 1/16
印 张 43.5
字 数 1 200 000

版 次 2000 年 6 月第 1 版
印 次 2000 年 6 月第 1 次印刷
定 价 49.00 元

本书如有缺页、倒页、脱页等质量问题,请到所购图书销售部门联系调换。

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出版说明

随着我国高等教育改革形势的发展,高等教育的人才培养模式及教学形式和教学方法正在发生重大变化,一个拓宽专业口径,实行弹性学习制度,允许分阶段完成学业,横向沟通、纵向衔接的教育体制正在逐步构建形成。为了促进高等教育的改革,活跃高等学校的教学工作,扩大学生的眼界,我们组织出版了这套“Schaum's 题解精萃”。

“Schaum's 丛书”是由麦格劳-希尔(McGraw-Hill)国际出版公司出版的著名的系列教学辅助用书,目前已出版了约 700 多个品种,涵盖了高等教育各类各门学科和课程。本套丛书的特点是:每本书都汇集了该门学科课程中的精髓内容,并对基本理论和基本概念作了简明精炼的归纳和总结;同时,还提供了由美国众多经验丰富的资深教师和学者推荐、讲解透彻的精选例题和形式多样的各类习题约 2000—4000 个。本套书在美国高等学校中颇具权威性,多年来持续畅销,目前在世界范围销售超过 3000 万册。

我们从“Schaum's 丛书”中经精心挑选,组合成“Schaum's 题解精萃”,以原版影印的形式介绍到国内,意在使学生在使用本书的同时,了解、熟悉相关学科和课程的英语专业词汇,提高英语专业阅读的速度和水平,锻炼使用英语学习、解题的能力。因为,当今时代,熟练掌握英语已成为 21 世纪人才必备的基本素质和能力。“Schaum's 题解精萃”第一批影印书内容涉及理工科各基础学科,今后我们将陆续影印出版该系列其他学科的图书。

本套书可供高等学校的理工科学生在学习各学科课程的同时,进行辅助学习和各类习题训练,有助于提高学生巩固学科基本知识和解题的综合能力,同时也可适用于各科教师在教学和辅导中参考。本套书同时还可作为在校本科生、研究生以及社会各类科技人员参加各类国际资格证书考试、国外留学考试(如 GRE)等的适用参考书。

我们相信,本套书的出版,将会对我国高等院校的学生、教师们提供丰富多彩、形式多样、卓有成效的参考资料。

出版者

2000 年 4 月

第 18 章

本章主要介绍了几种常用的排序算法，包括冒泡排序、选择排序、插入排序、快速排序、归并排序、堆排序等。这些算法在面试中经常出现，也是程序员必须掌握的基本技能。

本章首先介绍了冒泡排序，这是一种最简单的排序算法，通过多次比较和交换相邻元素，将最大的元素“冒泡”到数组的末尾。接着介绍了选择排序，通过每次选择最小的元素放到数组的起始位置。然后介绍了插入排序，将每个元素插入到已排序部分的适当位置。快速排序是本章的重点，它是一种高效的排序算法，通过选择一个基准元素，将数组分成两部分，分别递归排序。归并排序也是一种高效的排序算法，通过递归地将数组分成两半，然后合并成有序数组。最后介绍了堆排序，利用堆数据结构实现的排序算法。

本章还介绍了一些排序算法的变种和优化，如桶排序、计数排序、基数排序等。这些算法在某些特定场景下非常高效。最后，本章还介绍了一些排序算法的时间复杂度和空间复杂度，帮助读者理解不同算法的适用场景。

本章内容对于面试准备非常有帮助，建议读者熟练掌握本章介绍的排序算法，并能灵活运用。

本章小结

本章主要介绍了

TO THE STUDENT

Organic chemistry is best learned by solving problems—as many as is practical. This book provides you with 3000 opportunities. In each chapter the problems are presented in sequence to best develop your understanding of the theories and practice of this basic, very logical science. The authors do not just present the answers. Rather we make clear the thought processes you should go through to get the correct answers. Attempt the problems first before resorting to the answers. By challenging yourself first, you will solidify your understanding. Some problems, especially those involving syntheses, may have several solutions and you may find more than one approach given. If your solution is different but correct—don't fret, more power to you!

Most textbooks used today have a consistent underlying sequencing of topics, albeit with significant variations. The order of chapters in 3000 Solved Problems is an attempt to conform with most textbooks. However, you may have to resort to the Table of Contents to find a particular subject. The very thorough index should also prove helpful.

We would like to send our thanks and appreciation to Ms. Maurcen Walker and Mr. Nick Monti for their careful and thorough proofreading.

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CHAPTER 1

Structure and Properties

DEFINITIONS

1.1 What is (a) organic and (b) inorganic chemistry?

/// (a) With a few exceptions (i.e., carbonate salts and CO_2) *organic chemistry* is the study of carbon compounds. (b) *Inorganic chemistry* is the study of all other compounds.

1.2 What is the origin of the term *organic chemistry*?

/// Prior to 1828, most carbon compounds had been found only in living matter and it was believed that their natural synthesis required a *vital force*. It was concluded that inanimate and living (organic) matter had different origins and were therefore completely different. In that year, Friedrich Wöhler converted the inorganic ammonium isocyanate $[(\text{NH}_4)^+(\text{N}=\text{C}=\text{O})^-]$ to the known organic compound urea $[\text{O}=\text{C}(\text{NH}_2)_2]$, and the definitions of organic and inorganic chemistry changed.

1.3 What are the important differences between organic and inorganic compounds?

/// In general, organic compounds

- (1) react more slowly and require higher temperatures for reaction;
- (2) undergo more complex reactions and produce more side products;
- (3) have lower melting and boiling points and are generally insoluble in water;
- (4) are less stable and therefore often decompose on heating to compounds of lower energy content;
- (5) are classified into families of compounds such as alcohols, which have similar reactive groups and chemical properties; and
- (6) are far more numerous than inorganic compounds.

1.4 Account for the large number of organic compounds.

/// Carbon is in group IV of the periodic table and forms bonds with almost every other element (other than the noble gases). Carbon atoms bond to each other in single and multiple bonds, forming both long chains as well as ring compounds. Also, carbon compounds with identical molecular formulas but with different structural formulas are called *isomers*.

1.5 What are the three important classes of organic compounds?

- ///
1. *Aliphatic* compounds with C's bonded in chains are called *acyclic* to distinguish them from *cyclic* compounds, which have C's bonded in rings (not circular).
 2. *Aromatic* compounds, originally so named because of their pleasant odors, include derivatives of the parent hydrocarbon benzene (C_6H_6) and other ring systems with unusual stability.
 3. *Heterocyclics* are compounds with rings having at least one element other than C in the ring.

CHEMICAL BONDS

1.6 Why is it important to know about chemical bonds between atoms in a molecule?

/// Since chemical reactions occur by breaking and making bonds, their energies and rates depend on the strength of these bonds.

1.7 What are the two important types of chemical bonds observed in organic molecules?

- ///
- (1) *Covalent bonds*, in which an electron pair is shared between the two atoms, $\text{A}:\text{B}$, and
 - (2) *Ionic bonds*, formed by transfer of one or more e^- 's to form a positive cation and negative anion, i.e., $\text{A}^+:\text{B}^-$. Metallic (left side of the periodic table) elements usually form ionic bonds with nonmetallic (H and those on right side of the periodic table) elements. Nonmetallic elements form covalent bonds to each other and to themselves. All organic compounds have covalent bonds but some also have ionic bonds.

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- 1.8 Specify the type of chemical bond in the compounds (a) Li_2O , (b) PH_3 , (c) N_2O , and (d) CaF_2 .

// (a) Ionic, (b) covalent, (c) covalent, and (d) ionic.

- 1.9 Predict the type of chemical bond in the following molecules from their physical properties:

	(a) Cl_2	(b) NaCl	(c) ICl	(d) H_2O
Melting Point:	$-101.6\text{ }^\circ\text{C}$	$800.4\text{ }^\circ\text{C}$	$27.2\text{ }^\circ\text{C}$	$0\text{ }^\circ\text{C}$
Boiling Point:	$34.6\text{ }^\circ\text{C}$	$1413\text{ }^\circ\text{C}$	$97\text{ }^\circ\text{C}$	$100\text{ }^\circ\text{C}$
Unit Particles:	molecules	ions	molecules	molecules

// (a) Covalent, (b) ionic, (c) covalent, and (d) covalent.

- 1.10 Explain the difference in melting point (mp) and boiling point (bp) of the covalent and ionic compounds in Problem 1.9.

// Melting and boiling require separation of the particles comprising the solid and liquid states, respectively. The ionic salt is a three-dimensional array of alternating cations (Na^+) and anions (Cl^-). Its mp and bp are high because the strong electrostatic forces of attraction between the oppositely charged ions must be overcome, and this requires considerable energy (high temperatures). In covalent compounds like H_2O , each H is covalently bonded to the O to give a discrete molecule, H_2O . In (a) and (c) the discrete particles are the molecules Cl_2 and ICl , respectively. These molecules are the unit particles that must be separated from each other during melting and boiling, and these processes require less energy (lower temperatures).

- 1.11 Can it be concluded from the answer in Problem 1.10 that covalent bonds are necessarily *weaker* than ionic bonds?

// No; covalent bonds are not broken when molecules are separated during melting and/or boiling. Breaking covalent bonds may require high temperatures (see Problem 1.12).

- 1.12 The mp of SiO_2 , sand, is $1710\text{ }^\circ\text{C}$, and its bp is $2650\text{ }^\circ\text{C}$. (a) Describe the bonding in SiO_2 . (b) Why are its mp and bp so high?

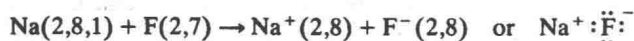
// (a) The relative positions of the elements in the periodic table indicate that the Si—O bond is covalent. (b) Each Si is bonded to four O atoms, and each O is bonded to two Si atoms in a three-dimensional array. There are no individual molecules of SiO_2 . The entire grain of solid is considered a giant single molecule, often called a *network covalent* substance, with the empirical formula SiO_2 . During melting and boiling, covalent bonds *between* atoms are broken. Much more energy is required to break covalent bonds than to separate molecules from each other.

- 1.13 Both diamond and graphite, two different crystalline allotropic forms of carbon, have extremely high mp's ($> 3500\text{ }^\circ\text{C}$). Diamond is very hard while graphite is soft and slippery—it is used as a lubricant. Explain in terms of bonding.

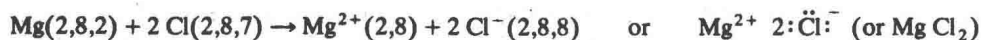
// The high mp's point to a network covalent structure for both substances. The C to C bonds in graphite extend in sheets, two-dimensionally, with only weak forces of attraction between the sheets. Thus the layers can slide past each other easily, making graphite feel soft and slippery. The C to C bonds in diamond extend in three dimensions. Cracking a diamond crystal requires the rupture of a large number of stable C—C bonds, a process that takes much energy. Hence, diamond is the hardest known substance.

- 1.14 How does the Lewis–Langmuir octet rule explain the formation of chemical bonds?

// Individual atoms lose, gain, or share e^- 's to attain electronic configurations (stable outer shells with eight e^- 's) of the nearest noble gas. In ionic bonding an e^- is transferred to form a cation and an anion: $\text{A} \cdot + \cdot \ddot{\text{B}} : \rightarrow \text{A}^+ + : \ddot{\text{B}} :^-$. For example, $\text{Na} \cdot$ transfers the lone e^- in its outer (valence) shell to $: \ddot{\text{F}} \cdot$ with seven e^- 's in its outer shell, leaving both cation and anion with outer shells of eight (an octet) e^- 's.



Octets are also formed by transferring more than one e^- .



Noble gas configurations are attained during covalent bonding by sharing of e^- pairs, with each e^- having an opposite spin as required by the Pauli Exclusion Principle: $: \ddot{\text{Cl}} \cdot + \cdot \ddot{\text{Cl}} : \rightarrow : \ddot{\text{Cl}} : \ddot{\text{Cl}} :$.

- 1.15 (a) What is a *coordinate covalent bond* (dative bond)? (b) Once formed, how does it differ from a typical covalent bond?

// (a) In a coordinate covalent bond, the pair of e^- 's are furnished by one atom (the donor) for sharing with the acceptor atom:

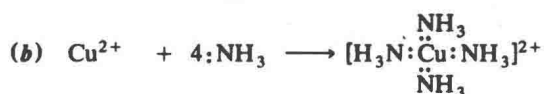
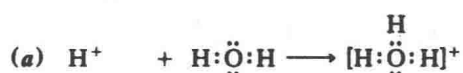


(b) Although it differs in mode of formation, once formed it is a typical covalent bond.

- 1.16 Identify donor and acceptor species in the formation of coordinate covalent bonds in the following:

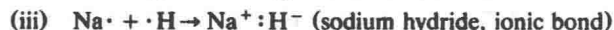
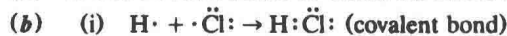


// acceptor donor



- 1.17 (a) Does the octet rule apply to H and Li? (b) Diagram the formation of (i) $\text{HCl}_{(g)}$, (ii) LiBr , and (iii) NaH .

// (a) H and Li form bonds to attain the stable *duet* of the noble gas He.



- 1.18 For the second period elements Be, B, C, N, O, and F give: (a) the number of e^- 's in the outer shell, (b) the number of covalent bonds formed, and (c) formulas of H compounds.

	Be	B	C	N	O	F
(a)	2	3	4	5	6	7
(b)	2	3	4	3	2	1
(c)	BeH_2	BH_3	CH_4	NH_3	H_2O	HF

- 1.19 What are some of the exceptions to the octet rule?

// In addition to H and Li (Problem 1.17) Be and B form less than four bonds in many of their compounds, thus lacking an octet. The octet rule also does not apply to higher atomic number elements in the third and higher periods such as S, Si, and P, which can acquire more than eight e^- 's.

- 1.20 How many e^- 's make up (a) a single, (b) a double, and (c) a triple bond?

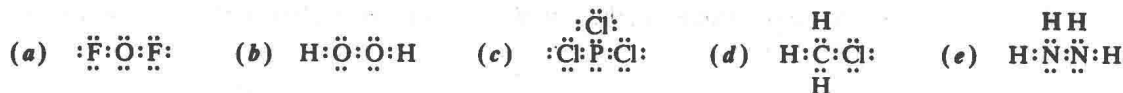
// (a) Two (one pair), (b) four (2 pairs), and (c) six (3 pairs).

- 1.21 Write *electron-dot* structures for the following covalent compounds: (a) F_2O , (b) H_2O_2 , (c) PCl_3 , (d) CH_3Cl , and (e) N_2H_4 (hydrazine).

// Electron-dot structures show all bonding and unshared valence e^- 's. First write the *skeleton* of the molecule, showing the bonding arrangement of the atoms. In molecules with three or more atoms there is at least one central atom, which has the highest covalency. If there is more than one multivalent atom in the molecule [as in (b) and (e)], bond them to each other to get the skeleton; then bond the univalent atoms (H, F, Cl) to them in order to satisfy their normal multivalencies. In their bonded state, second period elements should have eight

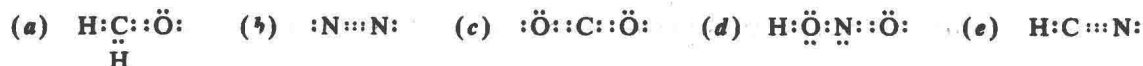
4 // CHAPTER 1

e^- 's, but not more. (Exceptions are Be and B which may have less than eight.) The number of e^- 's in the Lewis structure should equal the sum of the valence e^- 's of all the individual atoms.



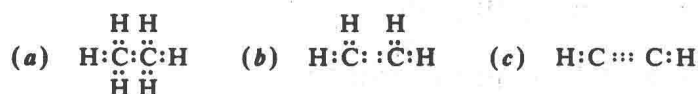
- 1.22 Provide electron-dot structures for the following multiple-bonded compounds: (a) H_2CO , (b) N_2 , (c) CO_2 , (d) HONO , and (e) HCN .

// If the number of univalent atoms available for bonding to the multivalent atoms is insufficient for achieving normal covalencies, form multiple bonds (Problem 1.20).



- 1.23 Provide electron-dot structures for the compounds whose molecular formulas are: (a) C_2H_6 , (b) C_2H_4 , and (c) C_2H_2 .

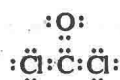
// Carbon is tetravalent (Problem 1.18) and can form single and multiple bonds.



- 1.24 (a) Write an electron-dot structure for phosgene, COCl_2 . (b) Why are all the following structures incorrect?



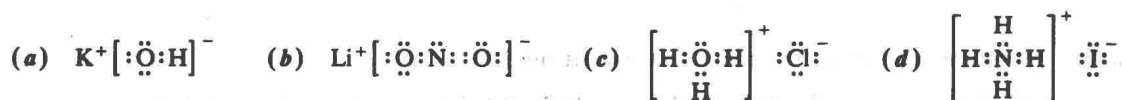
// (a) The central atom C has the highest covalence. To satisfy the tetravalency of C and divalency of O, a double bond between them is required:



- (b) The total number of valence e^- 's that must appear in the electron-dot structure is 24; 14 (two Cl's) + 4(C) + 6(O). In (i), C and O do not have their normal covalencies. Structures (ii) and (iii) are rejected because they each show only 22 e^- 's. Also, in (ii) O has four rather than two bonds, and in (iii) and (iv) one Cl has two bonds. (iv) is also rejected because O has 10 e^- 's, yet it cannot have more than an octet.

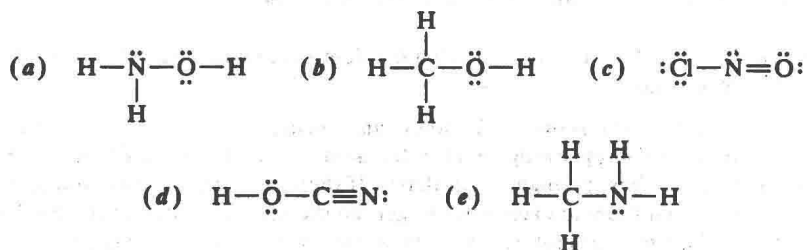
- 1.25 Write electron-dot structures for the ionic compounds that also have covalent bonds: (a) K^+OH^- , (b) Li^+NO_2^- , (c) $\text{H}_3\text{O}^+\text{Cl}^-$, (d) NH_4^+I^- .

// Add an e^- for each $-$ charge in the anion and subtract one for each $+$ charge in the cation.

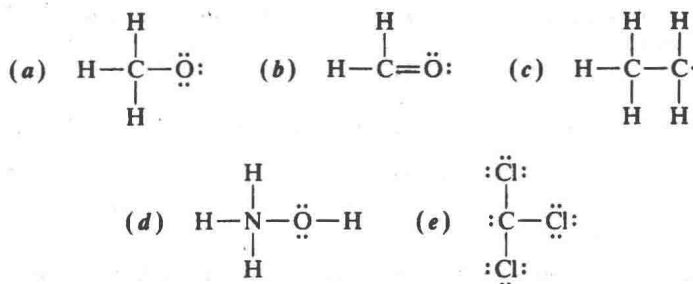


- 1.26 Draw Lewis structures for (a) hydroxylamine, H_2NOH , (b) methanol, CH_3OH , (c) ClNO , (d) HOCN , and (e) CH_3NH_2 .

// In Lewis structures a dash represents a shared electron-pair. Unshared outer shell (valence) e^- 's are also shown.



1.27 Determine the positive or negative charge, if any, on:

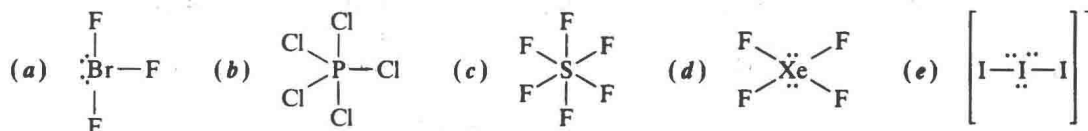


▮ The charge on a species is numerically equal to the total number of valence electrons of the unbonded atoms, minus the total number of electrons shown (as bonds or dots) in the Lewis structure.

- (a) The sum of the valence electrons (six for O, four for C, and three for three H's) is 13. The electron-dot formula shows 14 e^- 's. The net charge is $13 - 14 = -1$ and the species is the methoxide anion, $\text{CH}_3\ddot{\text{O}}^-$.
- (b) There is no charge on the formaldehyde molecule, because the 12 e^- 's in the structure equals the number of valence electrons; i.e., six for O, four for C, and two for H's.
- (c) This species is neutral, because there are 13 e^- 's shown in the formula and 13 valence electrons: eight from two C's and five from five H's.
- (d) There are 15 valence electrons: six from O, five from N, and four from four H's. The Lewis dot structure shows 14 e^- 's. It has a charge of $15 - 14 = +1$ and is the hydroxylammonium cation, $[\text{H}_3\text{NOH}]^+$.
- (e) There are 25 valence electrons, 21 from three Cl's and four from C. The Lewis dot formula shows 26 e^- 's. It has a charge of $25 - 26 = -1$ and is the trichloromethide anion, CCl_3^- .

1.28 Give Lewis structures for: (a) BrF_3 , (b) PCl_5 , (c) SF_6 , (d) XeF_4 , and (e) I_3^- .

▮ In these molecules the central atom is surrounded by more than eight e^- 's. This *octet expansion* requires *d* orbitals, and is therefore only possible for elements below the second period. To determine the number of electron pairs in the valence shell of the central atom, add the number of e^- 's contributed by it (its group number) to one e^- for each covalent bond and divide by 2. For anions, add the negative charge as well.

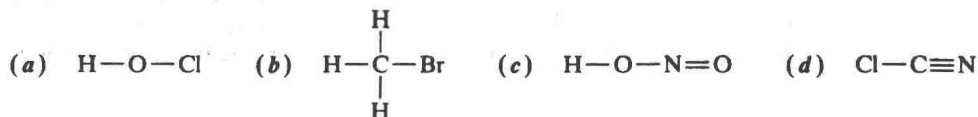


The number of e^- pairs are: (a) $(7 + 3)/2 = 5$; (b) $(5 + 5)/2 = 5$; (c) $(6 + 6)/2 = 6$; (d) $(8 + 4)/2 = 6$; (e) $(7 + 2 + 1)/2 = 5$. (The three unshared pairs of e^- 's on univalent halogens are omitted.)

STRUCTURAL FORMULAS AND ISOMERS

1.29 Write structural formulas for: (a) HOCl , (b) CH_3Br , (c) HONO , and (d) ClCN .

▮ Structural formulas omit the outer unshared e^- 's of Lewis structures.

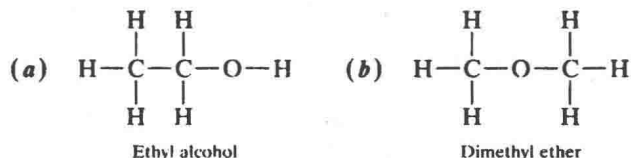


1.30 (a) Write two structures with the molecular formula CHNO . (b) What are these structures called?

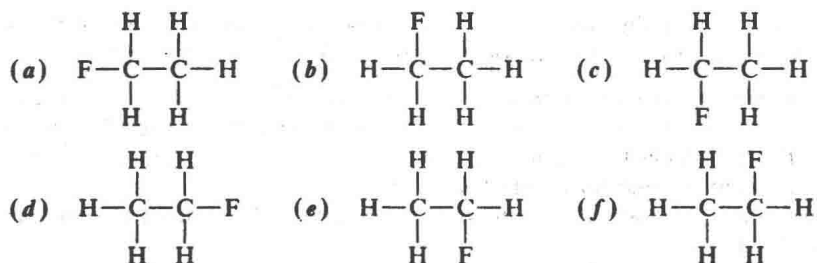
▮ (a) Two structural formulas can be written with different skeletons corresponding to the compounds: $\text{H}-\text{O}-\text{C}\equiv\text{N}$ (cyanic acid) and $\text{H}-\text{N}=\text{C}=\text{O}$ (isocyanic acid). (b) Different compounds with the same molecular formulas are called *isomers*. Because in this case they differ in the order of arrangement of the atoms, they are *structural isomers*. They can be interconverted only by breaking bonds and forming new ones to other atoms.

- 1.31 Write two isomeric structures with the molecular formula C_2H_6O .

/// The three atoms with the largest covalencies (C, C, O) can be bonded to each other in two ways, resulting in the two structures:



- 1.32 (a) Do the following structural formulas for C_2H_5F represent different compounds? Explain. (b) Illustrate your answer with the so-called *sawhorse* structures.



/// No. There is only *one* compound C_2H_5F . Rotation about the C—C single bond brings the F to the different positions depicted in (a)–(c), and structures (d)–(f) are arrived at by turning structures (a)–(c) through 180° in the plane of the paper. (b) See Fig. 1-1. In the three-dimensional *sawhorse* (wedge) structure a dotted line is a bond projecting below the plane of the paper and away from the viewer, and a darkened wedge is a bond projecting above the plane and toward the viewer. By rotating about the C—C bond, structures (a)–(f) appear.

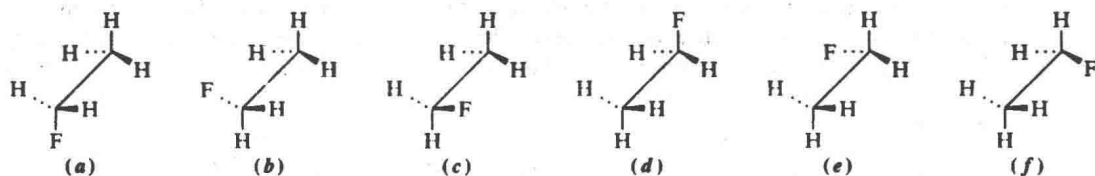
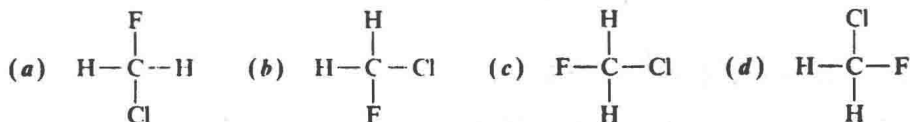


Fig. 1-1

- 1.33 Which, if any, of the structures (a)–(d) are isomers?



/// None. They are all two-dimensional representations of one compound which is three-dimensional. The four single bonds of C are directed away from each other towards the corners of an imaginary tetrahedron, with C in the center, as illustrated in Fig. 1-2(a). (The dotted lines show the imaginary tetrahedron.) The angles separating any two atoms with C at the apex is 109.5° . Figures 1-2(b) and (c) illustrate different ways of depicting the spatial

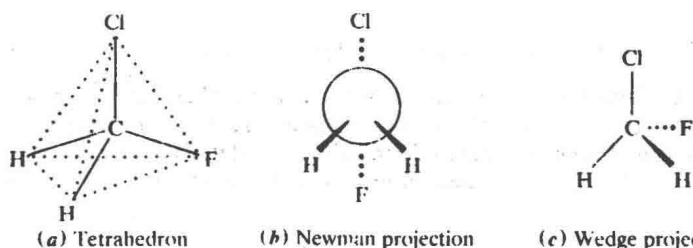
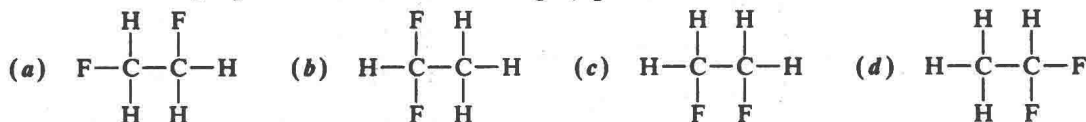


Fig. 1-2

relationship about a *tetrahedral* C. Structures (a)–(d) appear to be different; they do not accurately represent the space-filling molecule.

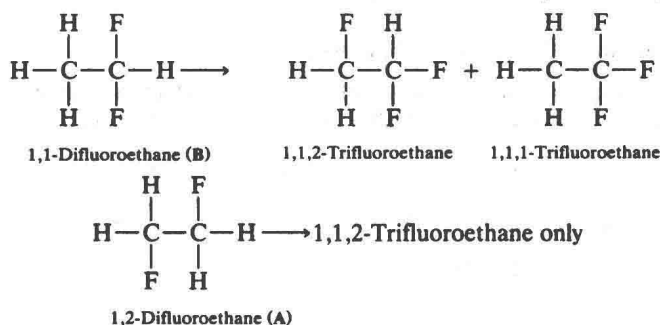
- 1.34 Which of the following represent the two isomers of $C_2H_4F_2$?



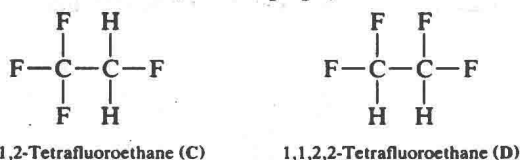
Structures (a) and (c) represent one isomer (A), with an F on each C while (b) and (d) represent a second isomer (B) with both F's on the same C.

- 1.35 Explain how the introduction of a third F to form $C_2H_3F_3$ can help establish the structures of the two isomers in Problem 1.34.

A affords *one* trifluoro product while B gives *two* trifluorides. The products from this *substitution method* also prove the structures of the two difluoro isomers inasmuch as these are predicted by deduction.



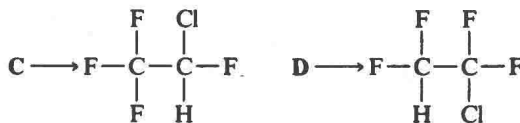
- 1.36 Give structural formulas for the isomers of a compound $C_2H_2F_4$.



- 1.37 Can the isomers in Problem 1.36 be distinguished by substituting (a) an F and (b) a Cl? Explain.

(a) No. Both isomers form the only possible pentafluoroethane, E, $\begin{array}{c} \text{F} \quad \text{F} \\ | \quad | \\ \text{F}-\text{C}-\text{C}-\text{F} \\ | \quad | \\ \text{F} \quad \text{H} \end{array}$.

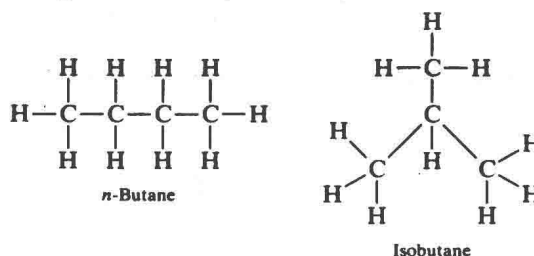
(b) Yes, different compounds are formed as shown:



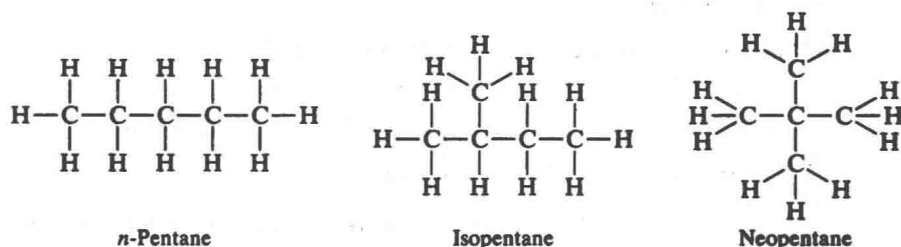
- 1.38 Derive all structural formulas for the isomers of (a) C_3H_8 , (b) C_4H_{10} , and (c) C_5H_{12} .

(a) There is only one possible structure: $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$.

(b) The four C's can lie in a straight (unbranched) or branched chain.



(c) The three isomers of pentane are:

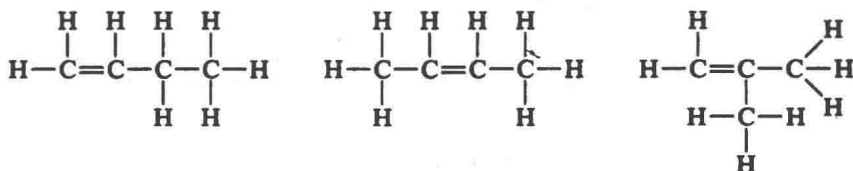


1.39 Write *condensed* structural formulas for the pentane isomers in Problem 1.38c.

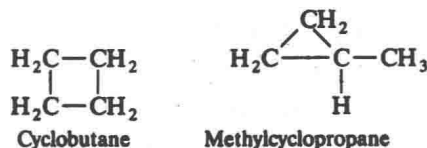
// In condensed structural formulas parentheses are used for identical groups of atoms. *n*-Pentane, $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$; isopentane $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$; neopentane $(\text{CH}_3)_4\text{C}$.

1.40 Write structural formulas for all the C_4H_8 isomers.

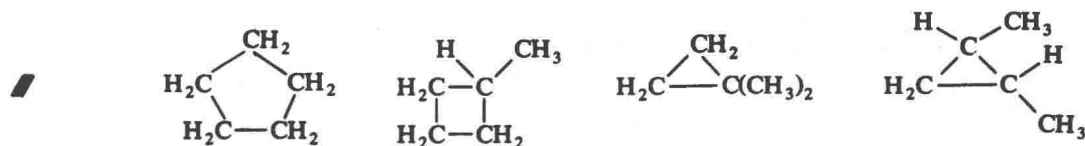
// There are two less H's in C_4H_8 than in C_4H_{10} from which it is deduced that the isomers have either a double bond or a cyclic structure. The double bond structures (alkenes) are:



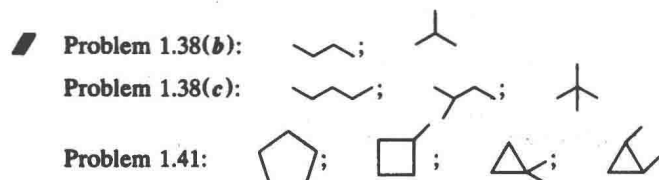
Two cyclic structures are possible: one is a four-C ring and the other is a three-C ring with an attached fourth C.



1.41 Give structural formulas for cyclic compounds having the molecular formula C_5H_{10} .



1.42 Draw simplified line or *carbon skeleton* structures for the compounds in Problems 1.38(b), 1.38(c), and 1.41.



1.43 Write the following line structures as (i) structural and (ii) condensed structural formulas.

