

ORGANIC CHEMISTRY

Graham Solomons

Craig Fryhle

Scott Snyder

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PERIODIC TABLE OF THE ELEMENTS

	1 IA																		18 VIIIA
1 H Hydrogen 1.0079	2 IIA											13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 He Helium 4.0026		
3 Li Lithium 6.941	4 Be Beryllium 9.0122											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180		
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29		
55 Cs Cesium 132.91	56 Ba Barium 137.33	* La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)		
87 Fr Francium (223)	88 Ra Radium (226)	# Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut (284)	114 Fl Flerovium (289)	115 Uup (288)	116 Lv Livermorium (293)	117 Uus (294)	118 Uuo (294)		

Atomic number → **6**
 Symbol → **C**
 Name (IUPAC) → **Carbon**
 Atomic mass → **12.011**

IUPAC recommendations →
 Chemical Abstracts Service group notation →

*Lanthanide Series

	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97				

Actinide Series

	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)				

TABLE 3.1 RELATIVE STRENGTH OF SELECTED ACIDS AND THEIR CONJUGATE BASES

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	HSbF ₆	< -12	SbF ₆ ⁻	Weakest base
	HI	-10	I ⁻	
	H ₂ SO ₄	-9	HSO ₄ ⁻	
	HBr	-9	Br ⁻	
	HCl	-7	Cl ⁻	
	C ₆ H ₅ SO ₃ H	-6.5	C ₆ H ₅ SO ₃ ⁻	
	(CH ₃) ₂ OH ⁺	-3.8	(CH ₃) ₂ O	
	(CH ₃) ₂ C=OH ⁺	-2.9	(CH ₃) ₂ C=O	
	CH ₃ OH ₂ ⁺	-2.5	CH ₃ OH	
	H ₃ O ⁺	-1.74	H ₂ O	
	HNO ₃	-1.4	NO ₃ ⁻	
	CF ₃ CO ₂ H	0.18	CF ₃ CO ₂ ⁻	
	HF	3.2	F ⁻	
	C ₆ H ₅ CO ₂ H	4.21	C ₆ H ₅ CO ₂ ⁻	
	C ₆ H ₅ NH ₃ ⁺	4.63	C ₆ H ₅ NH ₂	
	CH ₃ CO ₂ H	4.75	CH ₃ CO ₂ ⁻	
	H ₂ CO ₃	6.35	HCO ₃ ⁻	
	CH ₃ COCH ₂ COCH ₃	9.0	CH ₃ COCHCOCH ₃ ⁻	
	NH ₄ ⁺	9.2	NH ₃	
	C ₆ H ₅ OH	9.9	C ₆ H ₅ O ⁻	
	HCO ₃ ⁻	10.2	CO ₃ ²⁻	
	CH ₃ NH ₃ ⁺	10.6	CH ₃ NH ₂	
	H ₂ O	15.7	HO ⁻	
	CH ₃ CH ₂ OH	16	CH ₃ CH ₂ O ⁻	
	(CH ₃) ₃ COH	18	(CH ₃) ₃ CO ⁻	
	CH ₃ COCH ₃	19.2	⁻ CH ₂ COCH ₃	
	HC≡CH	25	HC≡C ⁻	
	C ₆ H ₅ NH ₂	31	C ₆ H ₅ NH ⁻	
	H ₂	35	H ⁻	
	(i-Pr) ₂ NH	36	(i-Pr) ₂ N ⁻	
	NH ₃	38	⁻ NH ₂	
	CH ₂ =CH ₂	44	CH ₂ =CH ⁻	
Weakest acid	CH ₃ CH ₃	50	CH ₃ CH ₂ ⁻	Strongest base

Increasing acid strength

Increasing base strength



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ORGANIC CHEMISTRY

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WILEY



In memory of my beloved son, John Allen Solomons. TWGS

For my family. CBF

For Cathy, who has always inspired me. SAS

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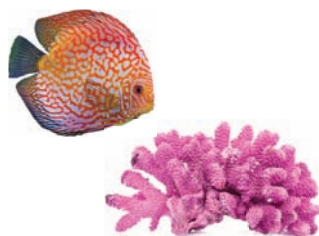
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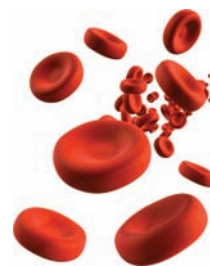
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[PREFACE]

“IT’S ORGANIC CHEMISTRY!”

That’s what we want students to exclaim after they become acquainted with our subject. Our lives revolve around organic chemistry, whether we all realize it or not. When we understand organic chemistry, we see how life itself would be impossible without it, how the quality of our lives depends upon it, and how examples of organic chemistry leap out at us from every direction. That’s why we can envision students enthusiastically exclaiming “It’s organic chemistry!” when, perhaps, they explain to a friend or family member how one central theme—organic chemistry—pervades our existence. We want to help students experience the excitement of seeing the world through an organic lens, and how the unifying and simplifying nature of organic chemistry helps make many things in nature comprehensible.

Our book makes it possible for students to learn organic chemistry well and to see the marvelous ways that organic chemistry touches our lives on a daily basis. Our book helps students develop their skills in critical thinking, problem solving, and analysis—skills that are so important in today’s world, no matter what career paths they choose. The richness of organic chemistry lends itself to solutions for our time, from the fields of health care, to energy, sustainability, and the environment. After all, it’s organic chemistry!

Guided by these goals, and by wanting to make our book even more **accessible to students** than it has ever been before, we have brought many changes to this edition.

NEW TO THIS EDITION

With this edition we bring Scott Snyder on board as a co-author. We’re very excited to have Scott join our team. Scott brings a rich resource of new perspectives to the book, particularly in the arena of complex molecule synthesis. Scott has infused new examples and applications of exciting chemistry that help achieve our goals. In addition to adding his perspectives to the presentation of core chemistry throughout the book, Scott’s work is manifest in most of this edition’s chapter openers and in all of the chapter closers, couched in a new feature called “Why do these topics matter?”.

“Why do these topics matter?” is a new feature that bookends each chapter with a teaser in the opener and a captivating example of organic chemistry in the closer. The chapter opener seeks to whet the student’s appetite both for the core chemistry in that chapter as well as a prize that comes at the end of the chapter in the form of a “Why do these topics matter?” vignette. These new closers consist of fascinating nuggets of organic chemistry that stem from research relating to medical, environmental, and other aspects of organic chemistry in the world around us, as well as the history of the science. They show the rich relevance of what students have learned to applications that have direct bearing on our lives and wellbeing. For example, in Chapter 6, the opener talks about the some of the benefits and drawbacks of making substitutions in a recipe, and then compares such changes to the nucleophilic displacement reactions that similarly allow chemists to change molecules and their properties. The closer then shows how exactly such reactivity has enabled scientists to convert simple table sugar into the artificial sweetener Splenda which is 600 times as sweet, but has no calories!

Laying the foundation earlier Certain tools are absolutely key to success in organic chemistry. Among them is the ability to draw structural formulas quickly and correctly. In this edition, we help students learn these skills even sooner than ever before by moving coverage of structural formulas and the use curved arrows earlier in the text (Section 3.2). We have woven together instruction about Lewis structures, covalent bonds, and dash structural formulas, so that students build their skills in these areas as a coherent unit, using organic examples that include alkanes, alkenes, alkynes, and alkyl halides. One could say that it’s a “use organic to teach organic” approach.

CHAPTER

6

Ionic Reactions

NUCLEOPHILIC SUBSTITUTION AND
ELIMINATION REACTIONS OF ALKYL HALIDES

Not all substitutions are a good thing; for instance, we wouldn't want to accidentally use salt in place of the needed amount of sugar in a batch of chocolate chip cookies. But with some substitutions, we get something even better: organic chemistry that is often the case, since nucleophilic substitution reactions (which we will learn about in this chapter) allow the conversion of functional groups within a given molecule into entirely different functional groups, leading to new compounds with distinct properties. Moreover, nature utilizes a number of specific substitution reactions that are required for life.

IN THIS CHAPTER WE WILL CONSIDER:

- what groups can be replaced (i.e., substituted) or eliminated
- the various mechanisms by which such processes occur
- the conditions that can promote such reactions

[WHY DO THESE TOPICS MATTER?] At the end of the chapter, we will show an example where just a few substitution reactions can convert table sugar into a sweetener that has no calories—a sugar substitute that is not salty but is in fact 600 times sweeter than sugar itself!

photo credit: (sugar bowl) Sylvie Szlazi Photography/Getty Images (salt pouring) Tom Gill/Getty Images (sugar pouring) Tom Gill/Getty Images



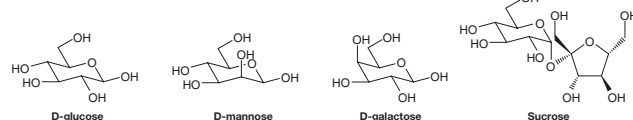
WHY DO THESE TOPICS MATTER?

New opening vignettes prepare the students and foreshadow the relevance of chapter content, asking the question “Why do these topics matter?” Closing vignettes answer the question by relating real world or historical aspects of organic chemistry.

[WHY Do These Topics Matter?]

SUBSTITUTING THE CALORIES OF TABLE SUGAR

As we shall see in more detail in Chapter 24, simple carbohydrates, or monosaccharides, can exist in the form of a six-membered ring system with a chair conformation. The name carbohydrate derives from “hydrated carbon” since most carbon atoms have an H and OH attached. In the examples below, the structural differences of the monosaccharides glucose, mannose, and galactose are based on the change of one or more chirality centers through what we could formally consider to be an inversion reaction. As such, all of these carbohydrates are diastereomers of each other. Based on what you already know about torsional strain from Chapter 4, it should come as no surprise that D-glucose is the most common monosaccharide; D-glucose has the least strain because all of its substituents are in equatorial positions. All other six-carbon sugars have at least one axial group, and thus possess some 1,3-diaxial strain. Standard table sugar, or sucrose, is a disaccharide, since it combines a molecule of D-glucose with the slightly less common carbohydrate called D-fructose.



All carbohydrates taste sweet, though not equally so. D-Fructose, for example, tastes approximately 1.5 times sweeter than the same amount of simple table sugar, while D-glucose is only about 0.75 times as sweet. Irrespective of their individual degrees of sweetness, however, it is the fact that they are all sweet that lets us perceive their presence in foods whether they are found naturally or have been added (often from corn syrup or cane sugar) to create a more unique flavor profile. Either way, their

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Getting to the heart of the matter quicker Acid-base chemistry, and electrophiles and nucleophiles are at the heart of organic chemistry. Students cannot master the subject if they do not have a firm and early grasp of these topics. In this edition, we cut to the chase with these topics earlier in Chapter 3 than ever before, providing a streamlined and highly efficient route to student mastery of these critical concepts.

Improving a core area: substitution reactions All organic instructors know how important it is for their students to have a solid understanding of substitution reactions. This is one reason our text has proven its lasting value. In this edition we have even further enhanced the presentation of substitution reactions in several ways, including a revised introduction of S_N1 reactions (Section 6.10) through the classic hydrolysis experiments of Hughes, and a newly organized presentation of solvent effects on the rate of substitution reactions.

Striking a strong balance of synthetic methods Students need to learn methods of organic synthesis that are useful, as environmentally friendly as possible, and that are placed in the best overall contextual framework. In this edition we incorporate the Swern oxidation (Section 12.4), long held as a useful oxidation method and one that provides a less toxic alternative to chromate oxidations in some cases. We also restore coverage of the Wolff-Kishner reduction (Section 16.8C) and the Baeyer-Villiger oxidation (Section 16.12), two methods whose importance has been proven by the test of time. The chemistry of radical reactions has also been refocused and streamlined by reducing thermochemistry content and by centralizing the coverage of allylic and benzylic radical substitutions (including NBS reactions) in one chapter (Sections 10.8 and 10.9), instead of distributing it between two, as before. The addition of sulfuric acid to alkenes and the Kolbe reaction have been deleted from the text, since these have little practical use in the laboratory. Toward the inclusion of modern, though mechanistically complex, methods of organic synthesis, we introduce catalytic oxidation methods (e.g., Sharpless and others) in special boxes, and provide coverage of transition metal organometallic reactions (Heck, Suzuki, and others) in Special Topic G.

Maintaining an eye for clarity With every edition we improve the presentation of topics, reactions, and diagrams where the opportunity arises. In this edition some examples include improved discussion and diagrams regarding endo and exo Diels-Alder transition states, the effect of diene stereochemistry in Diels-Alder reactions (Section 13.10B), and improved mechanism depictions for aromatic sulfonation and thionyl chloride substitution.

Resonating with topics in spectroscopy The authors have incorporated new figures to depict shielding and deshielding of alkenyl and alkynyl hydrogens by magnetic anisotropy, and clarified the discussion of shielding and deshielding in NMR chemical shifts (no longer invoking the terms upfield and downfield). The discussion of chlorine and bromine isotopic signatures in mass spectra has been enhanced, and presentation of mass spectrometer designs has been refocused.

Showing how things work A mechanistic understanding of organic chemistry is key to student success in organic chemistry. Mechanisms have always been central to the book, and in this edition the authors have added a mechanistic framework for the Swern and chromate alcohol oxidations (Section 12.4) by presenting elimination of the carbinol hydrogen and a leaving group from oxygen as the common theme.

TRADITIONAL PEDAGOGICAL STRENGTHS

Solved Problems Knowing “where to begin” to solve organic chemistry problems is one of the greatest challenges faced by today’s students. By modeling problem solving strategies, students begin to understand the patterns inherent in organic chemistry and learn to apply that knowledge to new situations. In this edition we have added even more Solved Problems. Now over 165 Solved Problems guide students in their strategies for problem solving. Solved Problems are **usually paired with a related Practice Problem**.

Practice Problems Students need ample opportunities to practice and apply their new found strategies for solving organic chemistry problems. We’ve added to our rich array of in-text Practice Problems to provide students with even more opportunities to check their progress as they study. If they can work the practice problem, they should move on. If not, they should review the preceding presentation.

SOLVED PROBLEMS

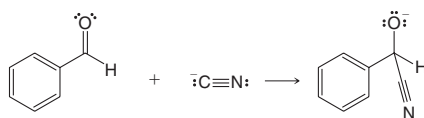
model problem solving strategies.

PRACTICE PROBLEMS

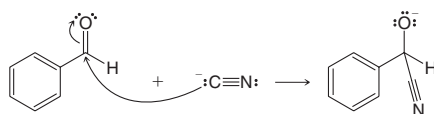
provides opportunities to check progress.

SOLVED PROBLEM 3.3

Identify the electrophile and the nucleophile in the following reaction, and add curved arrows to indicate the flow of electrons for the bond-forming and bond-breaking steps.



STRATEGY AND ANSWER: The aldehyde carbon is electrophilic due to the electronegativity of the carbonyl oxygen. The cyanide anion acts as a Lewis base and is the nucleophile, donating an electron pair to the carbonyl carbon, and causing an electron pair to shift to the oxygen so that no atom has more than an octet of electrons.

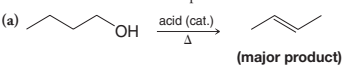
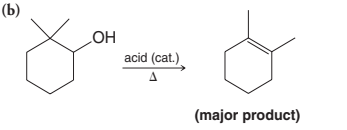


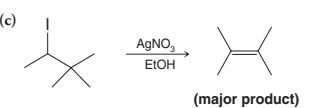
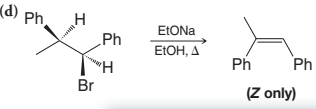
PRACTICE PROBLEM 3.4

Use the curved-arrow notation to write the reaction that would take place between dimethylamine ($\text{CH}_3)_2\text{NH}$ and boron trifluoride. Identify the Lewis acid, Lewis base, nucleophile, and electrophile and assign appropriate formal charges.

End-of-Chapter Problems As athletes and musicians know, practice makes perfect. The same is true with organic chemistry. The End of Chapter problems, categorized by topic, provide essential practice for students and help them build mastery of both concepts and skills presented throughout the chapter. Many of the End of Chapter problems are cast in a visual format using structures, equations, and schemes. In addition, we still provide **Challenge Problems** and **Learning Group Problems** to address myriad teaching goals and styles. Learning Group Problems engage students in synthesizing information and concepts from throughout a chapter. They can be used to facilitate collaborative learning in small groups, and can serve as a culminating activity that demonstrates student mastery over an integrated set of principles. Supplementary material provided to instructors includes suggestions about how to orchestrate the use of learning groups.

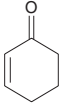
7.44 Provide a mechanistic explanation for each of the following reactions:

(a)  (b) 

(c)  (d) 

INDEX OF HYDROGEN DEFICIENCY

7.45 What is the index of hydrogen deficiency (IHD) (degree of unsaturation) for each of the following molecules?

(a)  (b) $C_6H_8Br_4$

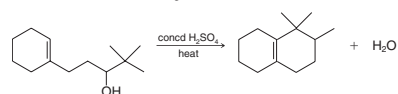
7.46 Caryophyllene, a compound found in oil of cloves, has the molecular formula $C_{15}H_{24}$. Caryophyllene is synthesized by the hydrogenation of β -phyllylene with an excess of hydrogen in the presence of a platinum catalyst produces a compound with the molecular formula $C_{15}H_{26}$. How many (a) double bonds and (b) rings does a molecule of caryophyllene have?

END-OF-CHAPTER

PROBLEMS are grouped and labeled by topic. Students and instructors can more easily select problems for specific purposes.

LEARNING GROUP PROBLEMS

- (a) Synthesize (3*S*,4*R*)-3,4-dibromo-1-cyclohexylpentane (and its enantiomer, since a racemic mixture will be formed) from ethyne, 1-chloro-2-cyclohexylethane, bromomethane, and any other reagents necessary. (Use ethyne, 1-chloro-2-cyclohexylethane, and bromomethane as the sole sources of carbon atoms.) Start the problem by showing a retrosynthetic analysis. In the process, decide which atoms of the target molecule will come from which atoms of the starting reagents. Also, bear in mind how the stereospecificity of the reactions you employ can be used to achieve the required stereochemical form of the final product.
 - Explain why a racemic mixture of products results from this synthesis.
 - How could the synthesis be modified to produce a racemic mixture of the (3*R*,4*R*) and (3*S*,4*S*) isomers instead?
- Write a reasonable and detailed mechanism for the following transformation:



A Mechanism for the Reaction Understanding mechanisms and the ability to recognize patterns among them is a key component in determining student success in organic chemistry. We provide A Mechanism for the Reaction boxes that show step-by-step details about how reactions take place so that students have the tools to understand rather than memorize organic reactions.

A MECHANISM FOR THE REACTION

Stepped out reactions with just the right amount of detail provides the tools for students to understand rather than memorize reaction mechanisms

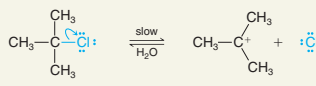
[A MECHANISM FOR THE REACTION — Mechanism for the S_N1 Reaction]

Reaction

$$CH_3-C(CH_3)_2-Cl + 2 H_2O \rightarrow CH_3-C(CH_3)_2-OH + H_3O^+ + :Cl^-$$

Mechanism

Step 1

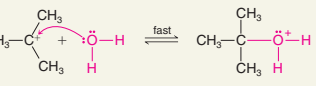


Aided by the polar solvent, a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the 3° carbocation intermediate and a chloride ion. Although not shown here, the ions are solvated (and stabilized) by water molecules.

Free energy diagram for Step 1: The energy profile shows a single high energy barrier (Transition state 1) leading to a local minimum (the carbocation intermediate). $\Delta G^\ddagger_{(1)}$ is much larger than $\Delta G^\ddagger_{(2)}$ or $\Delta G^\ddagger_{(3)}$, hence this is the slowest step.

Step 2

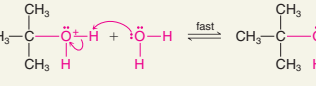


A water molecule acting as a Lewis base donates an electron pair to the carbocation (a Lewis acid). This gives the cationic carbon eight electrons.

The product is a tert-butyl oxonium ion (or protonated tert-butyl alcohol).

Free energy diagram for Step 2: The energy profile shows a lower energy barrier (Transition state 2) leading to a local minimum (the oxonium ion intermediate).

Step 3



A water molecule acting as a Brønsted base accepts a proton from the tert-butyl oxonium ion.

The products are tert-butyl alcohol and a hydronium ion.

Free energy diagram for Step 3: The energy profile shows a very low energy barrier (Transition state 3) leading to the final products.

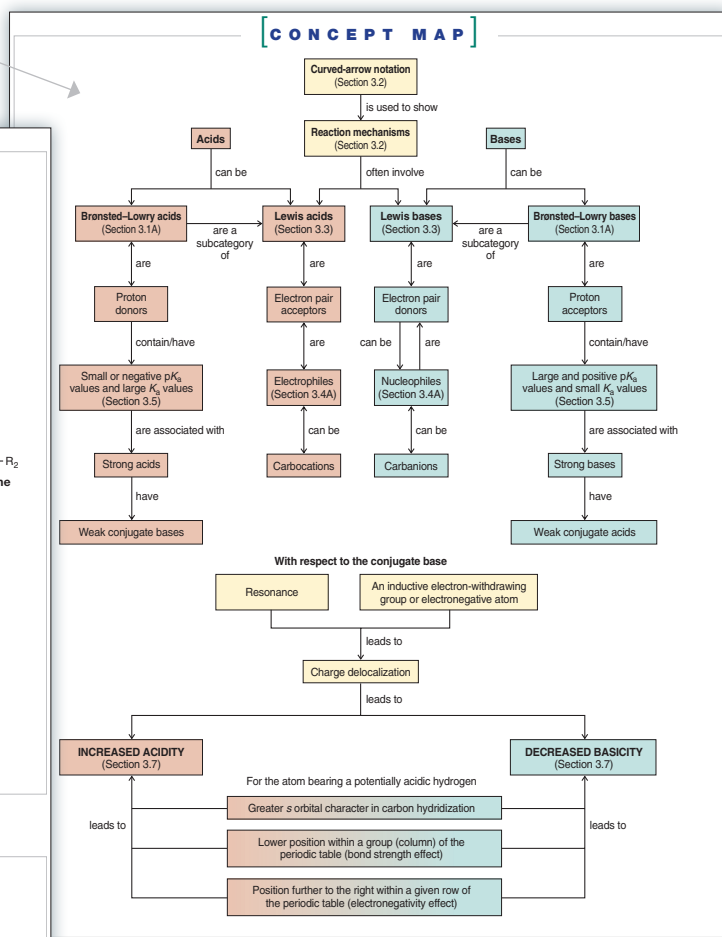
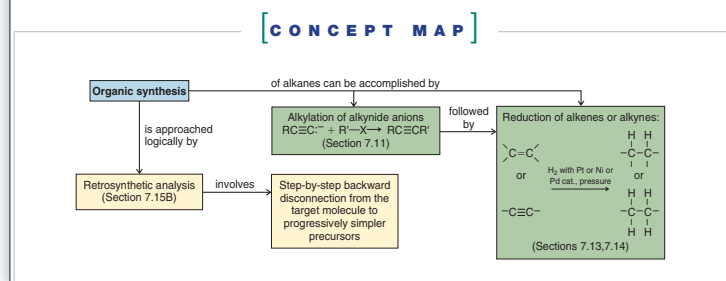
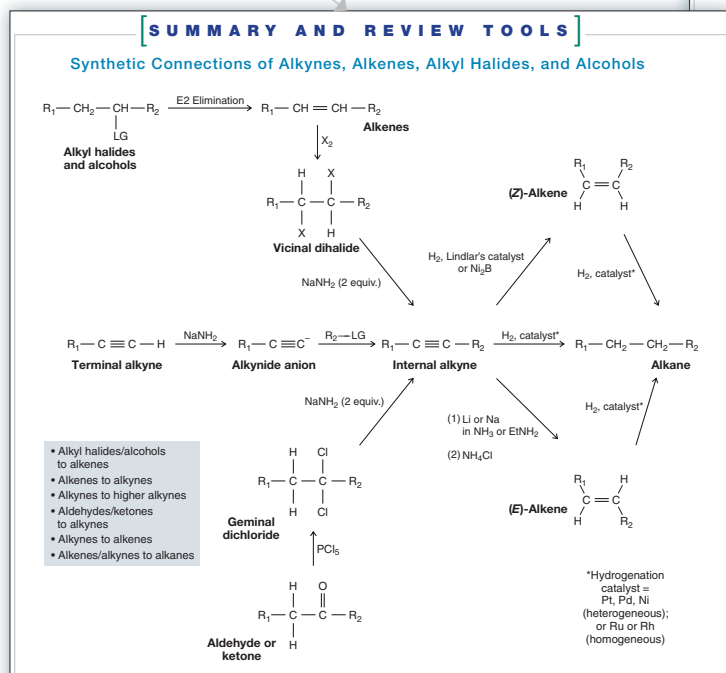
Key Ideas as Bullet Points The amount of content covered in organic chemistry can be overwhelming to students. To help students focus on the most essential topics, key ideas are emphasized as bullet points in every section. In preparing bullet points, we have distilled appropriate concepts into simple declarative statements that convey core ideas accurately and clearly. No topic is ever presented as a bullet point if its integrity would be diminished by oversimplification, however.

“How to” Sections Students need to master important skills to support their conceptual learning. “How to” Sections throughout the text give step-by-step instructions to guide students in performing important tasks, such as using curved arrows, drawing chair conformations, planning a Grignard synthesis, determining formal charges, writing Lewis structures, and using ^{13}C and ^1H NMR spectra to determine structure.

The Chemistry of . . . Virtually every instructor has the goal of showing students how organic chemistry relates to their field of study and to their everyday life experience. The authors assist their colleagues in this goal by providing boxes titled “The Chemistry of . . .” that provide interesting and targeted examples that engage the student with chapter content.

Summary and Review Tools At the end of each chapter, Summary and Review Tools provide visually oriented roadmaps and frameworks that students can use to help organize and assimilate concepts as they study and review chapter content. Intended to accommodate diverse learning styles, these include Synthetic Connections, Concept Maps, Thematic Mechanism Review Summaries, and the detailed Mechanism for the Reaction boxes already mentioned. We also provide Helpful Hints and richly annotated illustrations throughout the text.

SUMMARY AND REVIEW TOOLS Visually oriented study tools accommodate diverse learning styles.





COVERAGE

Throughout the book, we have streamlined or reduced content to match the modern practice of organic chemistry, and we have provided new coverage of current reactions, while maintaining our commitment to an appropriate level and breadth of coverage.

- Chapters on carbonyl chemistry that are organized to emphasize mechanistic themes of nucleophilic addition, acyl substitution, and reactivity at the α -carbon.
- Presentation of the important modern synthetic methods of the Grubbs, Heck, Sonogashira, Stille, and Suzuki transition metal catalyzed carbon-carbon bond-forming reactions in a practical and student-oriented way that includes review problems and mechanistic context (Special Topic G).

ORGANIZATION — An Emphasis on the Fundamentals

So much of organic chemistry makes sense and can be generalized if students master and apply a few fundamental concepts. Therein lays the beauty of organic chemistry. If students learn the essential principles, they will see that memorization is not needed to succeed.

Most important is for students to have a solid understanding of structure—of hybridization and geometry, steric hindrance, electronegativity, polarity, formal charges, and resonance—so that they can make intuitive sense of mechanisms. It is with these topics that we begin in Chapter 1. In Chapter 2 we introduce the families of functional groups—so that students have a platform on which to apply these concepts. We also introduce intermolecular forces, and infrared (IR) spectroscopy—a key tool for identifying functional groups. Throughout the book we include calculated models of molecular orbitals, electron density surfaces, and maps of electrostatic potential. These models enhance students' appreciation for the role of structure in properties and reactivity.

We begin our study of mechanisms in the context of acid-base chemistry in Chapter 3. Acid-base reactions are fundamental to organic reactions, and they lend themselves to introducing several important topics that students need early in the course: (1) curved arrow notation for illustrating mechanisms, (2) the relationship between free-energy changes and equilibrium constants, and (3) the importance of inductive and resonance effects and of solvent effects.

In Chapter 3 we present the first of many “A Mechanism for the Reaction” boxes, using an example that embodies both Brønsted-Lowry and Lewis acid-base principles. All throughout the book, we use boxes like these to show the details of key reaction mechanisms. All of the Mechanism for the Reaction boxes are listed in the Table of Contents so that students can easily refer to them when desired.

A central theme of our approach is to emphasize the relationship between structure and reactivity. This is why we choose an organization that combines the most useful features of a functional group approach with one based on reaction mechanisms. Our philosophy is to emphasize mechanisms and fundamental principles, while giving students the anchor points of functional groups to apply their mechanistic knowledge and intuition. The structural aspects of our approach show students what organic chemistry is. Mechanistic aspects of our approach show students how it works. And wherever an opportunity arises, we show them what it does in living systems and the physical world around us.

In summary, our writing reflects the commitment we have as teachers to do the best we can to help students learn organic chemistry and to see how they can apply their knowledge to improve our world. The enduring features of our book have proven over the years to help students learn organic chemistry. The changes in our 11th edition make organic chemistry even more accessible and relevant. Students who use the in-text learning aids, work the problems, and take advantage of the resources and practice available in *WileyPLUS* (our online teaching and learning solution) will be assured of success in organic chemistry.

TEACHING AND LEARNING RESOURCES

WILEYPLUS FOR ORGANIC CHEMISTRY— A Powerful Teaching and Learning Solution



WileyPLUS is an innovative, research-based online environment for effective teaching and learning. WileyPLUS builds student confidence because it takes the guesswork out of studying by providing students with a clear roadmap: what to do, how to do it, if they did it right. Students will take more initiative so instructors will have greater impact on their achievement in the classroom and beyond.

Breadth of Depth of Assessment: Four unique silos of assessment are available to instructors for creating online homework and quizzes and are designed to enable and support problem-solving skill development and conceptual understanding

WILEYPLUS ASSESSMENT FOR ORGANIC CHEMISTRY

REACTION EXPLORER	MEANINGFUL PRACTICE OF MECHANISMS AND SYNTHESIS PROBLEMS (A DATABASE OF OVER 100,000 QUESTIONS)
IN CHAPTER/EOC ASSESSMENT	90-100% OF REVIEW PROBLEMS AND END OF CHAPTER (EOC) QUESTIONS ARE CODED FOR ONLINE ASSESSMENT
CONCEPT MASTERY	PRE-BUILT CONCEPT MASTERY ASSIGNMENTS (FROM DATABASE OF OVER 25,000 QUESTIONS)
TEST BANK	RICH TESTBANK CONSISTING OF OVER 3,000 QUESTIONS

Reaction Explorer Students ability to understand mechanisms and predict synthesis reactions greatly impacts their level of success in the course. Reaction Explorer is an interactive system for **learning and practicing reactions, syntheses** and **mechanisms** in organic chemistry with advanced support for the automatic generation of random problems and curved arrow mechanism diagrams.

MECHANISM EXPLORER:

valuable practice with reactions and mechanisms

SYNTHESIS EXPLORER:

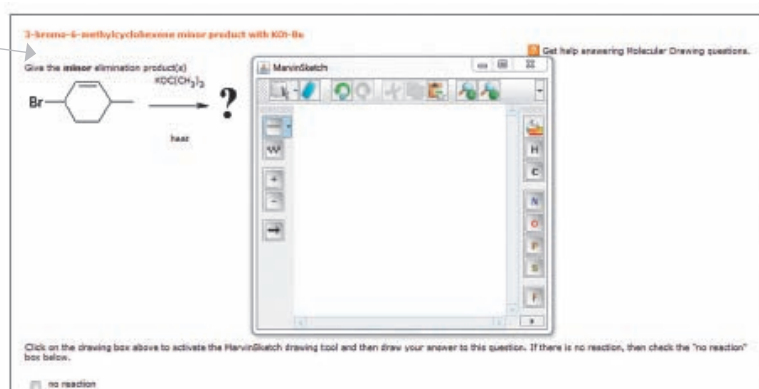
meaningful practice with single and multi-step synthesis

The image displays two screenshots from the WileyPLUS interface. The left screenshot, titled "Mechanism Step Sketch and Submission", shows a chemical reaction step where a methyl bromide cation ($\text{H}_3\text{C}-\text{Br}^+$) reacts with a cyanide ion ($:\text{N}\equiv\text{C}^-$). Below the reaction is a "Submitted Mechanism Steps" table with columns for "Reactant / Intermediate" and "Product / Intermediate". The overall reaction is shown as $\text{H}_3\text{C}-\text{Br} + \text{N}\equiv\text{C}^- + \text{Na}^+ \xrightarrow{\text{Mix Reactants, Aprotic}} \text{N}\equiv\text{C}-\text{CH}_3$. The right screenshot, titled "Synthesis Explorer", shows a multi-step synthesis problem. It includes a "Reactants" section with $\text{Br}-\text{CH}_3$ and $\text{H}_3\text{C}-\text{CH}_2-\text{Br}$, a "Reagents" section with instructions: "1. Mix Reactants in DMSO or THF (solvent) (2. H_2O (Aqueous workup))" and "Mix Reactants in Alcohol (solvent)", and a "Target Product" section with a nitrile structure. A "Pathway" section at the bottom shows a sequence of boxes for "Select a Reactant", "Select a Reagent", and "Apply Reaction to Generate Product(s)".

End of Chapter Problems. Approximately 90% of the end of chapter problems are included in *WileyPLUS*. Many of the problems are algorithmic and feature structure drawing/assessment functionality using MarvinSketch, with immediate answer feedback and video question assistance. A subset of these end of chapter problems is linked to **Guided Online tutorials** which are stepped-out problem-solving tutorials that walk the student through the problem, offering individualized feedback at each step.

Prebuilt concept mastery assignments Students must continuously practice and work organic chemistry in order to master the concepts and skills presented in the course. Prebuilt concept mastery assignments offer students ample opportunities for practice, covering all the major topics and concepts within an organic chemistry course. Each assignment is organized by topic and features **feedback for incorrect answers**. These assignments are drawn from a unique database of over 25,000 questions, over half of which require students to draw a structure using MarvinSketch.

PREBUILT CONCEPT MASTERY ASSIGNMENTS



WHAT DO STUDENTS RECEIVE WITH WILEYPLUS?

- The complete digital textbook, saving students up to 60% off the cost of a printed text.
- Question assistance, including links to relevant sections in the online digital textbook.
- Immediate feedback and proof of progress, 24/7.
- Integrated, multi-media resources that address students' unique learning styles, levels of proficiency, and levels of preparation by providing multiple study paths and encourage more active learning.

WILEYPLUS STUDENT RESOURCES

NEW Chapter 0 General Chemistry Refresher. To ensure students have mastered the necessary prerequisite content from general chemistry, and to eliminate the burden on instructors to review this material in lecture, *WileyPLUS* now includes a complete chapter of core general chemistry topics with corresponding assignments. Chapter 0 is available to students and can be assigned in *WileyPLUS* to ensure and gauge understanding of the core topics required to succeed in organic chemistry.

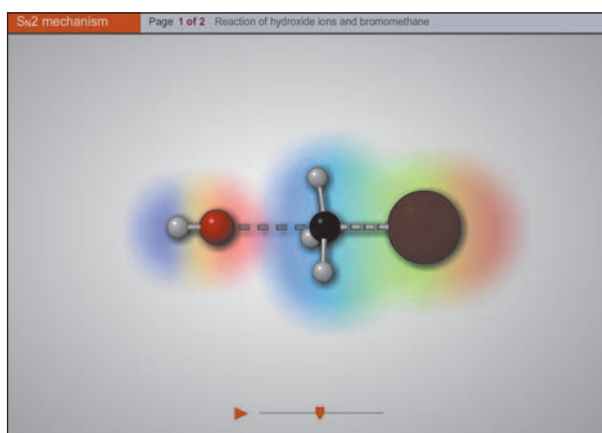
NEW Prelecture Assignments. Preloaded and ready to use, these assignments have been carefully designed to assess students prior to their coming to class. Instructors can assign these pre-created quizzes to gauge student preparedness prior to lecture and tailor class time based on the scores and participation of their students.



Video Mini-Lectures, Office Hour Videos, and Solved Problem Videos In each chapter, several types of video assistance are included to help students with conceptual understanding and problem solving strategies. The video mini-lectures focus on challenging concepts; the office hours videos take these concepts and apply them to example problems, emulating the experience that a student would get if she or he were to attend office hours and ask for assistance in working a problem. The Solved Problem videos demonstrate good problem solving strategies for the student by walking through in text solved problems using audio and a whiteboard. The goal is to illustrate good problem solving strategies.

Skill Building Exercises are animated exercises with instant feedback to reinforce the key skills required to succeed in organic chemistry.

3D Molecular Visualizations use the latest visualization technologies to help students visualize concepts with audio. Instructors can assign quizzes based on these visualizations in *WileyPLUS*.




WHAT DO INSTRUCTORS RECEIVE WITH WILEYPLUS?

- Reliable resources that reinforce course goals inside and outside of the classroom.
- The ability to easily identify students who are falling behind by tracking their progress and offering assistance easily, even before they come to office hours. *WileyPLUS* simplifies and automates such tasks as student performance assessment, creating assignments, scoring student work, keeping grades, and more.
- Media-rich course materials and assessment content that allow you to customize your classroom presentation with a wealth of resources and functionality from PowerPoint slides to a database of rich visuals. You can even add your own materials to your *WileyPLUS* course.

ADDITIONAL INSTRUCTOR RESOURCES

All Instructor Resources are available within *WileyPLUS* or they can be accessed by contacting your local Wiley Sales Representative. Many of the assets are located on the book companion site, www.wiley.com/college/solomons

Test Bank Authored by Robert Rossi, of Gloucester County College, Jeffrey Allison, of Austin Community College, and Gloria Silva, of Carnegie Mellon University, the Test Bank for this edition has been completely revised and updated to include over 3,000 short answer, multiple choice, and essay/drawing questions. The Test Bank files, along with a software tool for managing and creating exams, are available online.



PowerPoint Lecture Slides PowerPoint Lecture Slides have been prepared by Professor William Tam, of the University of Guelph, Dr. Phillis Chang, and Gary Porter, of Bergen Community College. The PowerPoint slides include additional examples, illustrations, and presentations that help reinforce and test students' grasp of organic chemistry concepts. An additional set of PowerPoint slides features the illustrations, figures, and tables from the text. All PowerPoint slide presentations are customizable to fit your course.

Personal Response System (“Clicker”) Questions A bank of questions is available for anyone using personal response system technology in their classroom. The clicker questions are also available in a separate set of PowerPoint slides.

Digital Image Library Images from the text are available online in JPEG format. Instructors may use these images to customize their presentations and to provide additional visual support for quizzes and exams.

ADDITIONAL STUDENT RESOURCES

Study Guide and Solutions Manual (978-1-118-14790-0)

The Study Guide and Solutions Manual for *Organic Chemistry, Eleventh Edition*, authored by Jon Antilla, of the University of South Florida, Robert Johnson, of Xavier University, Craig Fryhle, Graham Solomons, and Scott Snyder **contains explained solutions to all of the problems in the text.** The Study Guide also contains:

- An introductory essay “Solving the Puzzle—or—Structure is Everything” that serves as a bridge from general to organic chemistry
- Summary tables of reactions by mechanistic type and functional group
- A review quiz for each chapter
- A set of hands-on molecular model exercises
- Solutions to the problems in the Special Topics sections (many of the Special Topics are only available within *WileyPLUS*)

MOLECULAR VISIONS™ MODEL KITS

We believe that the tactile and visual experience of manipulating physical models is key to students' understanding that organic molecules have shape and occupy space. To support our pedagogy, we have arranged with the Darling Company to bundle a special ensemble of Molecular Visions™ model kits with our book (for those who choose that option). We use Helpful Hint icons and margin notes to frequently encourage students to use hand-held models to investigate the three-dimensional shape of molecules we are discussing in the book.

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[ABOUT THE AUTHORS]

T. W. GRAHAM SOLOMONS did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor Emeritus. In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been in the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, and the *Journal of Heterocyclic Chemistry*. He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 30 years and have been translated into French, Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, Turkish, and Italian. He and his wife Judith have a daughter who is a building conservator and a son who is a research biochemist.

CRAIG BARTON FRYHLE is Chair and Professor of Chemistry at Pacific Lutheran University. He earned his B.A. degree from Gettysburg College and Ph.D. from Brown University. His experiences at these institutions shaped his dedication to mentoring undergraduate students in chemistry and the liberal arts, which is a passion that burns strongly for him. His research interests have been in areas relating to the shikimic acid pathway, including molecular modeling and NMR spectrometry of substrates and analogues, as well as structure and reactivity studies of shikimate pathway enzymes using isotopic labeling and mass spectrometry. He has mentored many students in undergraduate research, a number of who have later earned their Ph.D. degrees and gone on to academic or industrial positions. He has participated in workshops on fostering undergraduate participation in research, and has been an invited participant in efforts by the National Science Foundation to enhance undergraduate research in chemistry. He has received research and instrumentation grants from the National Science Foundation, the M J. Murdock Charitable Trust, and other private foundations. His work in chemical education, in addition to textbook coauthorship, involves incorporation of student-led teaching in the classroom and technology-based strategies in organic chemistry. He has also developed experiments for undergraduate students in organic laboratory and instrumental analysis courses. He has been a volunteer with the hands-on science program in Seattle public schools, and Chair of the Puget Sound Section of the American Chemical Society. His passion for climbing has led to ascents of high peaks in several parts of the world. He resides in Seattle with his wife, where both enjoy following the lives of their two daughters as they unfold in new places.

SCOTT A. SNYDER is Associate Professor of Chemistry at Columbia University. He grew up in the suburbs of Buffalo NY and was an undergraduate at Williams College, where he graduated summa cum laude in 1999, before pursuing his doctoral studies at The Scripps Research Institute under the tutelage of K. C. Nicolaou as an NSF, Pfizer, and Bristol-Myers-Squibb predoctoral fellow. While there, he co-authored the graduate textbook *Classics in Total Synthesis II* with his doctoral mentor. Scott was then an NIH postdoctoral fellow in the laboratories of E. J. Corey at Harvard University before assuming his current position in 2006. His research interests lie in the arena of natural products total synthesis, especially in the realm of unique polyphenols and halogenated materials, and to date he has trained more than 60 students at the high school, undergraduate, graduate, and postdoctoral levels and co-authored more than 40 research and review articles. Scott has received a number of awards and honors, including a Camille and Henry Dreyfus New Faculty Award, Amgen New Faculty and Young Investigator Awards, Eli Lilly New Faculty and Grantee Awards, a Bristol-Myers Squibb Unrestricted Grant Award, an NSF CAREER Award, an Alfred P. Sloan Foundation Fellowship, a DuPont Young Professor Award, and an Arthur C. Cope Scholar Award from the American Chemical Society. He has also received recognition for his teaching through a Cottrell Scholar Award from the Research Corporation for Science Advancement and a Columbia Presidential Teaching Award. He is a member of the international advisory board for *The Chemical Record* and the editorial board of *Chirality*. He lives north of New York City with his wife Cathy where he enjoys gardening, cooking, and watching movies.



[TO THE STUDENT]

Contrary to what you may have heard, organic chemistry does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

1. Keep up with your work from day to day—never let yourself get behind.

Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. The lecture, then, will be much more helpful because you will already have some understanding of the assigned material. Your time in class will clarify and expand ideas that are already familiar ones.

2. Study material in small units, and be sure that you understand each new section before you go on to the next.

Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept.

3. Work all of the in-chapter and assigned problems.

One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. You should also carefully study the Solved Problems. If you understand a Solved Problem and can work the related in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the end of the chapter, as well. Do all of your problems in a notebook and bring this book with you when you go to see your instructor for extra help.

4. Write when you study.

Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting material in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions

are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the number of pages of paper that you fill with your own writing in studying during the term.

5. Learn by teaching and explaining.

Study with your student peers and practice explaining concepts and mechanisms to each other. Use the Learning Group Problems and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.

6. Use the answers to the problems in the Study Guide in the proper way.

Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.

7. Use molecular models when you study.

Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. When you need to see the three-dimensional aspect of a particular topic, use the Molecular Visions™ model set that may have been packaged with your textbook, or buy a set of models separately. An appendix to the *Study Guide* that accompanies this text provides a set of highly useful molecular model exercises.

8. Make use of the rich online teaching resources in WileyPLUS

and do any online exercises that may be assigned by your instructor.