Organic Chemistry

FIFTH EDITION

Maitland Jones, Jr., Steven A. Fleming

Thomas A. Gray

THE SAGE COLLEGES

Ekaterina N. Kadnikova

GUSTAVUS ADOLPHUS COLLEGE

Alan J. Kennan

COLORADO STATE UNIVERSITY



W • W • NORTON & COMPANY • NEW YORK • LONDON

W.W. Norton & Company has been independent since its founding in 1923, when William Warder Norton and Mary D. Herter Norton first published lectures delivered at the People's Institute, the adult education division of New York City's Cooper Union. The Nortons soon expanded their program beyond the Institute, publishing books by celebrated academics from America and abroad. By midcentury, the two major pillars of Norton's publishing program—trade books and college texts—were firmly established. In the 1950s, the Norton family transferred control of the company to its employees, and today—with a staff of four hundred and a comparable number of trade, college, and professional titles published each year—W.W. Norton & Company stands as the largest and oldest publishing house owned wholly by its employees.

Copyright © 2014, 2010 by W. W. Norton & Company, Inc.

All rights reserved. Printed in the United States of America

Associate Editor, Digital Media: Jennifer Barnhardt Project Editor: Carla Talmadge Production Manager: Eric Pier-Hocking Assistant Emedia Editor: Paula Iborra Composition by Westchester Publishing Services Manufacturing by Sterling Pierce

ISBN 978-0-393-93661-2

W. W. Norton & Company, Inc., 500 Fifth Avenue, New York, NY 10110 wwnorton.com

W. W. Norton & Company, Ltd., Castle House, 75/76 Wells Street, London W1T 3QT

 $1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 0$

CONTENTS

Pre	eface	v
Chapter 1 A	toms and Molecules; Orbitals and Bonding	1
Chapter 2 A	lkanes	28
Chapter 3 A	lkenes and Alkynes	59
Chapter 4 St	ereochemistry	90
Chapter 5 R	ings	126
Chapter 6 Su ar	ubstituted Alkanes: Alkyl Halides, Alcohols, Amines, Ethers, Thiols, and Thioethers	154
Chapter 7 Su	ubstitution Reactions: The SN2 and SN1 Reactions	182
Chapter 8 El	limination Reactions: The E1 and E2 Reactions	208
Chapter 9 A	nalytical Chemistry: Spectroscopy	240
Chapter 10 El	lectrophilic Additions to Alkenes	280
Chapter 11 M	lore Additions to pi Bonds	319
Chapter 12 Ra	adical Reactions	361
Chapter 13 D	ienes and the Allyl System: 2p Orbitals in Conjugation	398
Chapter 14 A	romaticity	435
Chapter 15 Su	ubstitution Reactions of Aromatic Compounds	465
Chapter 16 Ca	arbonyl Chemistry 1: Addition Reactions	506
Chapter 17 Ca	arboxylic Acids	557
Chapter 18 De	erivatives of Carboxylic Acids: Acyl Compounds	598
Chapter 19 Ca	arbonyl Chemistry 2: Reactions at the alpha Position	639
Chapter 20 Ca	arbohydrates	697
Chapter 21 Sp	pecial Topic: Bioorganic Chemistry	721

Chapter 22 Special Topic: Amino Acids and Polyamino Acids (Peptides and Proteins)	740
Chapter 23 Special Topic: Reactions Controlled by Orbital Symmetry	758
Chapter 24 Special Topic: Intramolecular Reactions and Neighboring Group Participation	784

PREFACE

When was the last time you were pleased with the consistency and quality of the assessment supplements that come with introductory texts? If you are like most professors, you probably find that these assessment packages do not always meet your needs. To address this issue, Norton has collaborated with Valerie Shute (Florida State University) and Diego Zapata-Rivera (Educational Testing Services) to develop a methodology for delivering high-quality, valid, and reliable assessment supplements through our test banks and extensive suite of support materials.

WHY A NEW APPROACH?

In evaluating the test banks that accompany introductory texts, we found four substantive problem areas associated with the questions:

- 1. Test questions were misclassified in terms of type and difficulty.
- 2. The prevalence of low-level and factual questions misrepresented the goals of the course.
- 3. Topics were unevenly distributed: Trivial topics were tested via multiple items, while important concepts were not tested at all.
- 4. Links to course topics were too general, thus preventing diagnostic use of the item information.

STUDENT COMPETENCIES AND EVIDENCE-CENTERED DESIGN

In December 2007, we conducted a focus group with the brightest minds in educational testing to create a new model for assessment. A good assessment tool needs to (a) define what students need to know and the level of knowledge and skills expected, (b) include test items

that assess the material to be learned at the appropriate level, and (c) enable instructors to accurately judge students' mastery of the material—what they know, what they don't know, and to what degree—based on the assessment outcomes. Accurate assessments of student mastery allow instructors to focus on areas where students need the most help.

HOW DOES IT WORK?

The test bank authors listed the learning objectives from each chapter that they believed are the most important for students to learn. The author then developed questions designed to test students' knowledge of a particular learning objective. By asking students questions that vary in both type and level of difficulty, instructors can gather different types of evidence, which will allow them to more effectively assess how well students understand specific concepts.

Six Question Types:

- 1. Remembering questions—test declarative knowledge, including textbook definitions and relationships between two or more pieces of information. Can students recall or remember the information in the same form it was learned?
- 2. Understanding questions—pose problems in a context different from the one in which the material was learned, requiring students to draw from their declarative and/or procedural understanding of important concepts. Can students explain ideas or concepts?
- 3. Applying questions—ask students to draw from their prior experience and use critical-thinking skills to take part in qualitative reasoning about the real world. Can students use learned information in another task or situation?

- 4. Analyzing questions—test students' ability to break down information and see how different elements relate to each other and to the whole. Can students distinguish among the different parts?
- 5. Evaluating questions—ask students to assess information as a whole and frame their own argument. Can students justify a stand or decision?
- 6. Creating questions—pose questions or objectives that prompt students to put elements they have learned together into a coherent whole to generate new ideas. Can students create a new product or point of view based on data?

Three Difficulty Levels:

- 1. Easy questions—require a basic understanding of the concepts, definitions, and examples.
- 2. Medium questions—direct students to use critical thinking skills, to demonstrate an understanding of core concepts independent of specific textbook examples, and to connect concepts across chapters.
- 3. Difficult questions—ask students to synthesize textbook concepts with their own experience, making analytical inferences about biological topics and more.

Each question measures and explicitly links to a specific competency and is written with clear, concise, and grammatically correct language that suits the difficulty level of the specific competency being assessed. To ensure the validity of the questions, no extraneous, ambiguous, or confusing material is included, and no slang expressions are used. In developing the questions, every effort has been made to eliminate bias (e.g., race, gender, cultural, ethnic, regional, handicap, age) to require specific knowledge of material studied, not of general knowledge or experience. This ensures accessibility and validity.

KEY TO THE QUESTION METADATA

Each question in the Test Bank is tagged with five pieces of information designed to help instructors create the most ideal mix of questions for their quiz or exam. These tags are:

- **ANS:** This is the correct answer for each question. Or, in the case of some short answer questions, a possible correct answer to the given question.
- **DIF:** This is the difficulty assigned to the problem. Problems have been classified as Easy, Medium, or Difficult.
- **REF:** This is the section in the textbook from which a question is drawn.
- **OBJ:** This is the learning objective that the question is designed to test.
- **MSC:** This is the knowledge type (see above) the question is designed to test.

LEARNING OBJECTIVES

Understand properties of atomic orbitals Multiple Choice: 1 Short Answer: 6, 24

Evaluate trends in IP, EA in periodic table Multiple Choice: 2

Determine atomic orbital structure Multiple Choice: 3

Apply rules for quantum numbers Multiple Choice: 4, 5 Short Answer: 7

Understand the rules for quantum mechanics Multiple Choice: 6 Short Answer: 1, 2, 5

Apply rules and properties for atomic orbitals Short Answer: 3

Construct electronic configuration using rules for quantum mechanics Short Answer: 8

Derive nodes based on quantum numbers Multiple Choice: 7–9

Apply rules for Lewis structures Multiple Choice: 10, 16

Determine polarity based on 3D structure, bond dipoles Multiple Choice: 11 Short Answer: 14

Determine a dipole moment from a structure Multiple Choice: 12, 17 Calculate formal charge Multiple Choice: 13–15, 18

Analyze resonance forms for stability Multiple Choice: 19

Identify resonance structures Multiple Choice: 20–24

Construct molecular orbital diagrams Multiple Choice: 25 Short Answer: 21–23

Apply rules for molecular orbital construction Multiple Choice: 26–30, 32

Identify types of bond cleavage Multiple Choice: 31 Short Answer: 26

Understand Lewis acids and bases Multiple Choice: 33 Short Answer: 28–31

Apply rules and properties for atomic orbitals Short Answer: 3

Draw Lewis structures Short Answer: 9–13

Draw resonance forms Short Answer: 15, 17, 18, 20

Analyze resonance forms Short Answer 16, 19

Apply thermodynamics of bond formation Short Answer: 25, 27

MULTIPLE CHOICE

- 1. Which of the following statements about atomic orbitals is *false*?
 - a. A 1s orbital is spherically symmetrical.
 - b. An atomic orbital may contain zero, one, or two electrons.
 - c. A 2s orbital and a 2p orbital are equal in energy.
 - d. A $2p_x$ orbital and a $2p_y$ orbital are equal in energy.
 - e. A 2p orbital is not spherically symmetrical.

ANS: C DIF: Easy REF: 1.1

OBJ: Understand properties of atomic orbitals

MSC: Remembering

- 2. Which of the following statements is true?
 - a. Ionization potential decreases going across a row left to right.
 - b. Ionization potential increases going down a group.
 - c. Electron affinity increases going across a row left to right.
 - d. Electron affinity increases going down a group.
 - e. Atoms with high ionization potentials have correspondingly high electron affinities.

ANS: CDIF: EasyREF: 1.2OBJ: Evaluate trends in IP, EA in periodic tableMSC: Remembering

3. What is the total number of occupied *p* orbitals in a neutral phosphorus atom?

a.	2		d.	9
b.	3		e.	12
c.	6			
AN	IS: C	DIF: Easy	REF:	1.2

	-)		
OBJ:	Determine	e atomic orbita	1 structure	MSC:	Analyzing

4. Which one of the following sets of quantum numbers is impossible?

a. $n = 1, l = 0,$	$m_l = 0, s = +\frac{1}{2}$	d.	$n = 2, l = 1, m_l = -1, s = -\frac{1}{2}$
b. $n = 1, l = 1,$	$m_l = 0, s = +\frac{1}{2}$	e.	$n = 3, l = 0, m_l = 0, s = -\frac{1}{2}$
c. $n = 2, l = 1,$	$m_l = 1, s = +\frac{1}{2}$		
ANS: B OBJ: Apply ru	DIF: Easy es for quantum numbers	REF: MSC:	1.2 Applying

5. Which of these sets of quantum numbers would define an electron in the 5d subshell?

a. $n = 5; l = 2,$	$m_l = -3, s = \frac{1}{2}$	d. $n = 5; l = 2, m_l = -2, s =$	1
b. $n = 5; l = 2,$	$m_l = -2, s = \frac{1}{2}$	e. $n = 5; l = 1, m_l = 0, s = -$	-1/2
c. $n = 5; l = 4,$	$m_l = -2, s = -\frac{1}{2}$		
ANS: B	DIF: Easy	REF: 1.2	
OBJ: Apply rul	les for quantum numbers	MSC: Applying	

6.	The rule or principle that states that the electroni will have the lowest energy is called	ic state with the greatest number of unpaired spins
	a. the Pauli principle	d. Hund's rule
	b. the aufbau principle e	e. the octet rule
	c. the Heisenberg uncertainty principle	
	ANS: D DIF: Easy REF	F: 1.2
	OBJ: Understand the rules for quantum mechan	nics MSC: Remembering
7	<i>d</i> -orbitals have two nodal planes. How many sol	<i>herical</i> nodes will a 5 <i>d</i> orbital contain?
7.	a 1	d 4
	b. 2 e	e. 5
	c. 3	
	ANS: B DIF: Difficult REF	F: 1.2
	OBJ: Derive nodes based on quantum numbers	MSC: Analyzing
8.	 Which of the following statements accurately deta. a. There are zero nodes in a 2s orbital. b. A 2s orbital has one spherical node. c. A 2s orbital has one nodal plane. d. A 2s orbital has one spherical node and one e. A 2s orbital has two spherical nodes. 	escribes the node(s) in a 2 <i>s</i> orbital? nodal plane.
	ANS: B DIF: Medium REF OBJ: Derive nodes based on quantum numbers	F: 1.2 MSC: Analyzing
9.	 Which of the following statements accurately defa. a. There are zero nodes in a 2p orbital. b. A 2p orbital has one spherical node. c. A 2p orbital has one nodal plane. d. A 2p orbital has one spherical node and one e. A 2p orbital has two spherical nodes. 	escribes the node(s) in a $2p$ orbital? e nodal plane.

ANS:CDIF:MediumREF:1.2OBJ:Derive nodes based on quantum numbers

MSC: Analyzing

10. Which of the Lewis structures shown below is *incorrect*?



- ANS: DDIF: MediumREF: 1.3OBJ: Apply rules for Lewis structuresMSC: Analyzing
- 11. Indicate which of the species shown are expected to have a net dipole moment.



ANS: A DIF: Difficult REF: 1.3 OBJ: Determine polarity based on 3D structure, bond dipoles MSC: Analyzing

4 • CHAPTER 1

12. Which of the following Lewis structures shows an *incorrectly* drawn bond dipole?



ANS: ADIF: EasyREF: 1.3OBJ: Determine a dipole moment from a structureMSC: Analyzing

13. In which of the following Lewis structures does the nitrogen atom have a formal charge of 1+?



ANS: B DIF: Easy REF: 1.3 OBJ: Calculate formal charge MSC: Applying



15. Which of the following Lewis structures contains an oxygen atom with a 1+ formal charge?



- 16. Which of the following structures is the best Lewis structure for hypochlorous acid, HOCl?
 - a. HHH<t



17. Which of the following molecules has a net dipole moment?



ANS: ADIF: MediumREF: 1.3OBJ: Determine a dipole moment from a structureMS

MSC: Applying

- 18. In which of the following structures does the carbon atom have a formal charge that is not zero?
 - a. $H \longrightarrow N \equiv C \longrightarrow \ddot{O}$: b. $H \longrightarrow \ddot{N} = C = \ddot{O}$ c. $H \longrightarrow \ddot{N} = C \longrightarrow \ddot{O}$: d. $H \longrightarrow \ddot{N} \longrightarrow \ddot{C} \longrightarrow \ddot{O}$: e. Both c and d

ANS: C DIF: Medium REF: 1.3 OBJ: Calculate formal charge MSC: Applying

19. Which of the following resonance forms would be expected to be the most important contributor for the anionic species?



ANS: A DIF: Easy OBJ: Identify resonance structures REF: 1.4 MSC: Remembering 21. Which two of the following structures are *equivalent* resonance contributors?



22. Which of the following pairs are *not* related as resonance structures?



ANS: C DIF: Medium OBJ: Identify resonance structures

REF: 1.4 MSC: Analyzing

23. Which of the following pairs are related as resonance structures? All nonzero formal charges are shown.



ANS: B DIF: Medium OBJ: Identify resonance structures

REF: 1.4 MSC: Analyzing

24. Which of the structures shown is not related to Structure A as a resonance contributor?



REF: 1.4 MSC: Analyzing

MSC: Applying

25. In the orbital interaction diagram for ground state H₂, how many electrons occupy the antibonding molecular orbital?

a.	0			d.	3
b.	1			e.	4
c.	2				
AN OB	S: J:	A DIF: Construct molecular	Easy orbital diagram	REF: s	1.5

26.	How many molecular orbitals are generated from combining one $2p$ orbital on carbon and one $2p$ orbital on oxygen?
	a. 0 d. 3
	b. 1 e. 4 c. 2
	ANS: CDIF: EasyREF: 1.5OBJ:Apply rules for molecular orbital constructionMSC: Applying
27.	How many antibonding molecular orbitals are generated from combining one $2p$ orbital on nitrogen and one $2p$ orbital on carbon?
	a. 0 d. 3
	b. 1 e. 4 c. 2
	ANS: B DIF: Easy REF: 1.5
	OBJ: Apply rules for molecular orbital construction MSC: Applying
28.	 A certain orbital interaction diagram has four bonding molecular orbitals and four antibonding molecular orbitals. How many atomic orbitals were mixed to create all these orbitals? a. 2 b. 4 c. 8 d. 16 e. It cannot be determined from the information given.
	ANS: CDIF: EasyREF: 1.5OBJ:Apply rules for molecular orbital constructionMSC: Applying
29.	 Which of the following statements about the molecular orbital diagram for H₂⁻ is <i>false</i>? a. There are two atomic orbitals that mix to produce molecular orbitals. b. There is one bonding molecular orbital. c. There is one antibonding molecular orbital. d. All bonding orbitals are occupied. e. All antibonding orbitals are unoccupied.
	ANS: EDIF: MediumREF: 1.5OBJ: Apply rules for molecular orbital constructionMSC: Applying
30.	Which of the following molecular orbitals is the highest in energy? (All were generated by the mixing of four $2p$ orbitals.)
	b. $\bigcup_{i=1}^{n} \bigcup_{j=1}^{n} \bigcup_{i=1}^{n} \bigcup_{j=1}^{n} \bigcup_{j=1}^{n} \bigcup_{j=1}^{n} \bigcup_{i=1}^{n} \bigcup_{j=1}^{n} \bigcup$

- c.
- d.

e. All four orbitals shown are equal in energy.

ANS: CDIF: DifficultREF: 1.5OBJ: Apply rules for molecular orbital constructionMSC: Applying

31. Each of the chemical events shown represents a mechanistic step in a reaction you will learn this semester. Which of the following pictures represents the heterolytic cleavage of a carbon–oxygen bond?



ANS: C DIF: Medium REF: 1.6 OBJ: Identify types of bond cleavage MSC: Analyzing

- 32. Which of these orbital interactions would be expected to form a covalent bond with the highest BDE?
 - a. H atom 1s with H⁺ cation 1s

b.

He atom 1s with He atom 1s

- d. H^+ cation 1s with He⁺ cation 1s
- e. H^+ cation 1s with He atom 1s
- c. He atom 1s with H atom 1s

ANS: E DIF: Difficult REF: 1.6 OBJ: Apply rules for molecular orbital construction

MSC: Applying

- 33. Which of the following statements is true about Lewis acids and bases?
 - a. Lewis acids are also called nucleophiles.
 - b. A Lewis base always accepts a proton from a Lewis acid.
 - c. The interaction between a Lewis acid and a Lewis base leads to a covalent bond.
 - d. A Lewis base accepts an electron pair from a Lewis acid.
 - e. Homolytic bond cleavage leads to the formation of a Lewis acid/base pair.

ANS:	C DIF	:	Easy	REF:	1.7
OBJ:	Understand Lewis	ac	ids and bases	MSC:	Remembering

SHORT ANSWER

1. State the Heisenberg uncertainty principle.

ANS:

It is not possible to determine simultaneously both the position and momentum of an electron.

DIF: Easy REF: 1.1 OBJ: Understand the rules for quantum mechanics MSC: Remembering

2. Explain what is meant by the term quantized as it applies to the energy of an electron.

ANS:

A property such as the energy of an electron is quantized when it is restricted to certain values.

DIF: Medium REF: 1.1 OBJ: Understand the rules for quantum mechanics MSC: Remembering

3. What is the relationship between the principal quantum number *n* and the number of nodes in an orbital?

ANS:

The number of nodes in an orbital is one less than the principal quantum number *n*.

DIF: Easy REF: 1.2 OBJ: Apply rules and properties for atomic orbitals MSC: Applying

4. Write the lowest-energy electron configuration for a neutral, ground-state oxygen atom.

ANS: $1s^22s^22p_x^22p_y^{-1}2p_z^{-1}$

DIF:	Easy	REF:	1.2	OBJ:	Write electron configurations
MSC:	Creating				

5. A student wrote the following electron configuration for a ground state, neutral nitrogen atom: $1s^22s^22p_x^22p_y^1$. Explain why the configuration does not describe the lowest energy state of a ground-state nitrogen atom and provide the lowest-energy electron configuration for nitrogen.

ANS:

Nitrogen has seven electrons (Z = 7). The student violated Hund's rule by pairing two electrons in the same p orbital instead of placing an unpaired electron in each of the three available p orbitals, as Hund's rule states that for a given electron configuration, the state with the greatest number of parallel spins has the lowest energy. The lowest-energy electron configuration is $1s^22s^22p_x^{-1}2p_y^{-1}2p_z^{-1}$.

DIF:	Medium	REF: 1.2	OBJ:	Understand the rules for quantum mechanics
MSC:	Applying			