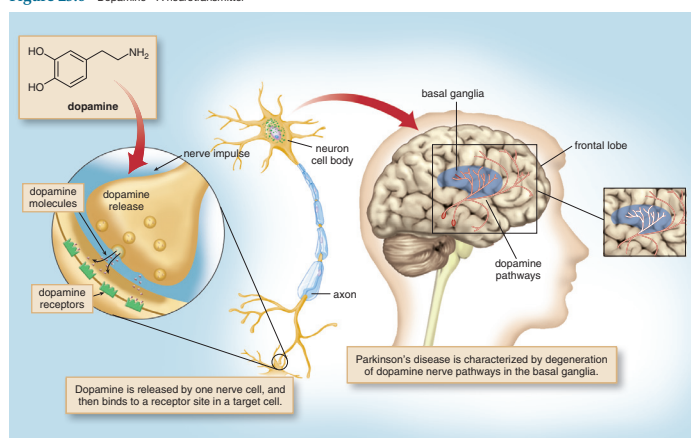


A guide to Organic Chemistry

Illustrations

902 CHAPTER 25 Amines

Figure 25.6 Dopamine—A neurotransmitter



Cocaine, amphetamines, and several other addicting drugs increase the level of dopamine in the brain, which results in a pleasurable "high." With time, the brain adapts to increased dopamine levels.

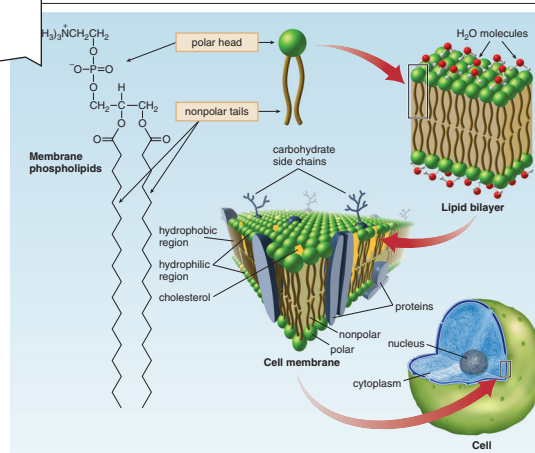
affects brain processes that control movement and emotions, so proper dopamine levels are necessary to maintain an individual's mental and physical health. For example, when dopamine-producing neurons die, the level of dopamine drops, resulting in the loss of motor control symptomatic of Parkinson's disease.

Understanding the neurochemistry of these compounds has led to the synthesis and availability of several useful drugs. **Fentanyl** is a common narcotic pain reliever used in surgical procedures.

Micro-to-macro illustrations

At key points throughout the text, photos and illustrations are combined. These "micro-to-macro" illustrations reveal the underlying molecular structures that give rise to macroscopic properties of common phenomena.

3.8 Application: The Cell Membrane 101

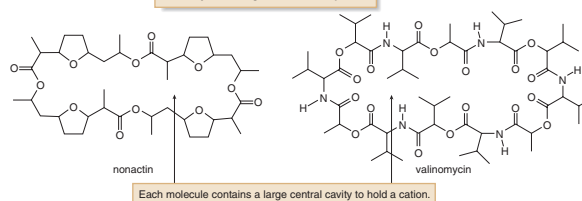


Phospholipids contain an ionic or polar head, and two long nonpolar hydrocarbon tails. In an aqueous environment, phospholipids form a lipid bilayer, with the polar heads oriented toward the aqueous exterior and the nonpolar tails forming a hydrophobic interior. Cell membranes are composed largely of this lipid bilayer.

"The artwork depicting intermolecular forces in Chapter 3 is the best that I have ever seen. I think these renderings will be a tremendous aid to the students' understanding of these often difficult to grasp concepts."

S. Todd Deal
Georgia Southern University

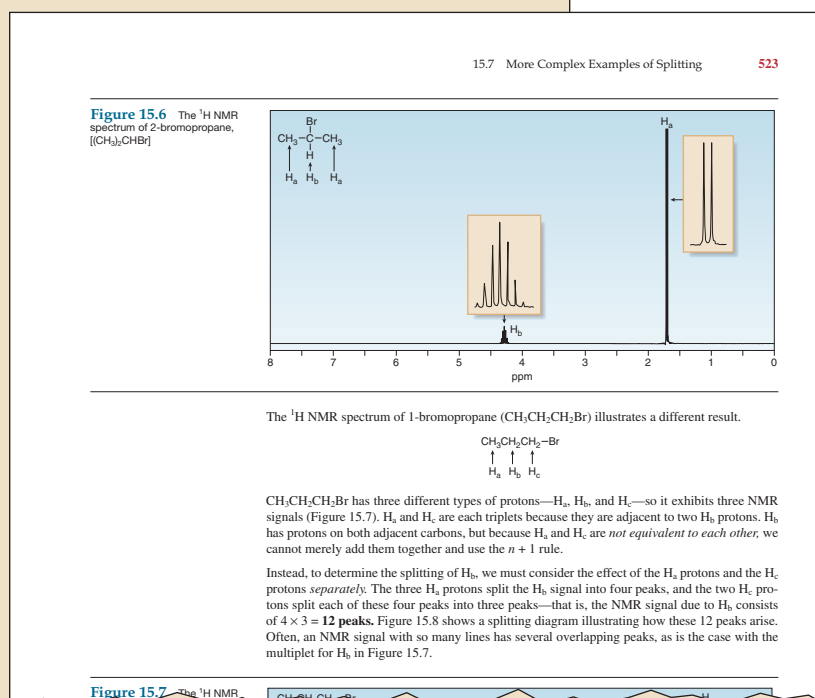
Naturally occurring antibiotic ionophores



Several synthetic ionophores have also been prepared, including one group called **crown ethers**. **Crown ethers** are cyclic ethers containing several oxygen atoms that bind specific cations depending on the size of their cavity. Crown ethers are named according to the general format *x-crown-y*, where *x* is the total number of atoms in the ring and *y* is the number of oxygen atoms. For example, 18-crown-6 contains 18 atoms in the ring, including 6 O atoms. This crown ether binds potassium ions. Sodium ions are too small to form a tight complex with the O atoms, and larger cations do not fit in the cavity.

Spectra

Over 100 spectra created specifically for *Organic Chemistry*, are presented throughout the text. The spectra are color-coded by type and generously labeled.



Mechanisms

Curved arrow notation is used extensively to help students follow the movement of electrons in reactions. Where appropriate, mechanisms are presented in parts to promote a better conceptual understanding.

Figure 14.3 Mass spectrum of 2-chloropropane $[(\text{CH}_3)_2\text{CHCl}]$

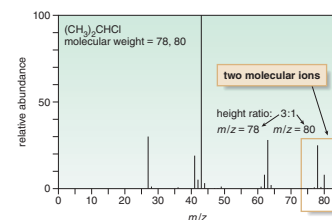
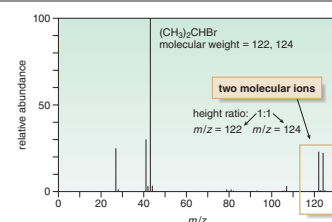


Figure 14.4 Mass spectrum of 2-bromopropane $[(\text{CH}_3)_2\text{CHBr}]$



When the molecular ion consists of two peaks (M and $M + 2$) in a 1:1 ratio, a Br atom present in the molecule.

molecular ions would you expect for compounds having each of the following molecular formulas: (a) $\text{C}_4\text{H}_9\text{Cl}$; (b) $\text{C}_3\text{H}_7\text{F}$; (c) $\text{C}_6\text{H}_5\text{Br}$; (d) $\text{C}_4\text{H}_9\text{N}$?

Mass Spectrometry

Using the molecular ion to determine the molecular weight of an organic compound is a valuable, recent advance that has greatly expanded the information obtained from mass

"I truly like the way Chapter 15 TEACHES students about NMR and how to interpret spectra. For example, showing students how and HOW NOT to draw alkenes is exactly what they need to see."

Robert E. Maleczka, Jr.
Michigan State University

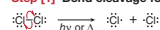


MECHANISM 13.1

Radical Halogenation of Alkanes

Initiation

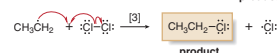
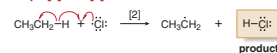
Step [1] Bond cleavage forms two radicals.



- The reaction begins with homolysis of the weakest bond in the starting materials using energy from light or heat.
- Thus, the Cl—Cl bond ($\Delta H^\circ = 58$ kcal/mol), which is weaker than either the C—C or C—H bond in ethane ($\Delta H^\circ = 88$ and 98 kcal/mol, respectively), is broken to form two chlorine radicals.

Propagation

Steps [2] and [3] One radical reacts and a new radical is formed.

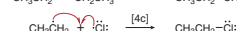
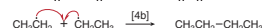


Repeat Steps [2], [3], [2], [3], again and again.

- The $\cdot\text{Cl}$ radicals are highly reactive (they lack an octet of electrons), so they abstract a hydrogen atom from ethane (Step [2]). This forms H—Cl and leaves one unpaired electron on carbon, generating the ethyl radical ($\text{CH}_3\text{CH}_2\cdot$).
- $\text{CH}_3\text{CH}_2\cdot$ is highly reactive, so it can abstract a chlorine atom from Cl_2 (Step [3]), forming $\text{CH}_3\text{CH}_2\text{Cl}$ and a new chlorine radical ($\cdot\text{Cl}$).
- The $\cdot\text{Cl}$ radical formed in Step [3] is a reactant in Step [2], so Steps [2] and [3] can occur repeatedly without an additional initiation reaction (Step [1]).
- In each propagation step, one radical is consumed and one radical is formed. The two products— $\text{CH}_3\text{CH}_2\text{Cl}$ and HCl—are formed during propagation.

Termination

Step [4] Two radicals react to form a σ bond.



- To terminate the chain, two radicals react with each other in one of three ways (Steps [4a, b, and c]). Because these reactions remove reactive radicals and form stable bonds, they prevent further propagation via Steps [2] and [3].

Problem Solving

Sample Problems

Sample Problems show students how to solve organic chemistry problems in a logical, stepwise manner. More than 800 follow-up problems are located throughout the chapters to test whether students understand concepts covered in the Sample Problems.

"Smith's experience in teaching has allowed her to design problems that seem to address students' most common misconceptions."

Clair J. Cheer
San Jose State University

How To's

How To's provide students with detailed instructions on how to work through key processes.

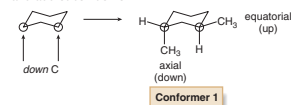
"Each type of problem is presented with a stepwise approach, which provides students with an expert's approach on how to solve the problem. This is invaluable and something that is missing from most organic texts."

Harriet Lindsay
Eastern Michigan University

SAMPLE PROBLEM 4.4 Draw both chair conformers for *trans*-1,3-dimethylcyclohexane.

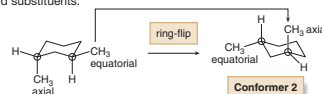
SOLUTION

Step [1] Draw one chair form and add substituents.



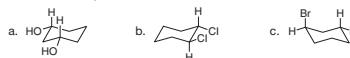
- Pick 2 C's 1,3- to each other.
- The *trans* isomer has two groups on **opposite sides**. In Conformer 1, this means that one CH₃ is equatorial (on an *up* bond), and one group is axial (on a *down* bond).

Steps [2-3] Ring-flip and add substituents.



- The 2 *down* C's flip up.
- The axial CH₃ flips equatorial (still a *down* bond) and the equatorial CH₃ flips axial (still an *up* bond). Conformer 2 is *trans* because the two CH₃'s are still on opposite sides.
- **Conformers 1 and 2 are equally stable** because each has one CH₃ equatorial and one axial.

PROBLEM 4.29 Label each compound as *cis* or *trans*. Then draw the second chair conformer.

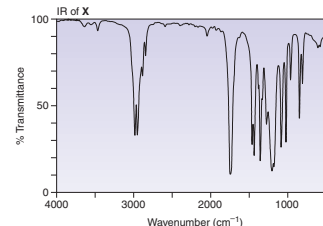
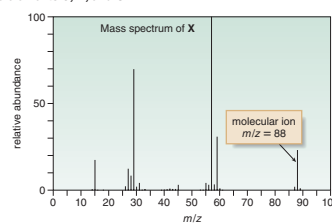


PROBLEM 4.30 Draw the two possible chair conformers for *cis*-1,3-dimethylcyclohexane. Which conformer, if either, is more stable?

PROBLEM 4.31 Consider 1,2-dimethylcyclohexane.
a. Draw structures for the *cis* and *trans* isomers using a hexagon for the six-membered ring.
b. Draw the two possible chair conformers for the *cis* isomer. Which conformer, if either, is more stable?

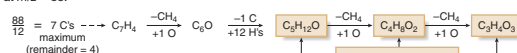
How To Use MS and IR for Structure Determination

Example What information is obtained from the mass spectrum and IR spectrum of an unknown compound X? Assume X contains the elements C, H, and O.



Step [1] Use the molecular ion to determine possible molecular formulas. Use an exact mass (when available) to determine a molecular formula.

- Use the procedure outlined in Sample Problem 14.2 to calculate possible molecular formulas. For a molecular ion at $m/z = 88$:



- Discounting C₇H₄ (a hydrocarbon) and C₆O (because it contains no H's) gives three possible formulas for X.
- If high-resolution mass spectral data are available, the molecular formula can be determined directly. If the molecular ion had an exact mass of 88.0580, the molecular formula of X is C₄H₈O₂ (exact mass = 88.0524) rather than C₅H₁₂O (exact mass = 88.0888) or C₃H₄O₃ (exact mass = 88.0160).

Step [2] Calculate the number of degrees of unsaturation (Section 10.2).

- For a compound of molecular formula C₄H₈O₂, the maximum number of H's = $2n + 2 = 2(4) + 2 = 10$.
- Because the compound contains only 8 H's, it has $10 - 8 = 2$ H's fewer than the maximum number.
- Because each degree of unsaturation removes 2 H's, X has one degree of unsaturation. X has one ring or one π bond.

Applications and Summaries

Key Concept Summaries

Succinct summary tables reinforcing important principles and concepts are provided at the end of each chapter.

18.16 Key Concepts—Electrophilic Aromatic Substitution

Five Examples of Electrophilic Aromatic Substitution

[1] Halogenation—Replacement of H by Cl or Br (18.3)

c1ccccc1 $\xrightarrow[\text{FeX}_3]{\text{X}_2}$ c1ccc(Cl)cc1 or c1ccc(Br)cc1
[X = Cl, Br] • Polyhalogenated substituted (st)ituents (t)

[2] Nitration—Replacement of H by NO₂ (18.4)

c1ccccc1 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$ c1ccc([N+](=O)[O-])cc1
nitro compound

[3] Sulfonation—Replacement of H by SO₃H (18.4)

c1ccccc1 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{SO}_3}$ c1ccc(S(=O)(=O)O)cc1
benzenesulfonic acid

[4] Friedel-Crafts alkylation—Replacement of H by R (18.5)

c1ccccc1 $\xrightarrow[\text{AlCl}_3]{\text{RCl}}$ c1ccc(R)cc1
alkyl benzene (arene)

Variations:

[1] with alcohols c1ccccc1 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{ROH}}$ c1ccc(R)cc1

[2] with alkenes c1ccccc1 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{CH}_2=\text{CHR}}$ c1ccc(R)cc1

[5] Friedel-Crafts acylation—Replacement of H by RCO (18.5)

c1ccccc1 $\xrightarrow[\text{AlCl}_3]{\text{RCOCl}}$ c1ccc(RC(=O))cc1
ketone • The reactio substituted groups (18.

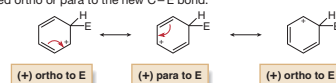
Margin Notes

Margin notes are placed carefully throughout the chapters, providing interesting information relating to topics covered in the text. Some margin notes are illustrated with photos to make the chemistry more relevant.

18.16 Key Concepts—Electrophilic Aromatic Substitution

Mechanism of Electrophilic Aromatic Substitution (18.2)

- Electrophilic aromatic substitution follows a two-step mechanism. Reaction of the aromatic ring with an electrophile forms a carbocation, and loss of a proton regenerates the aromatic ring.
- The first step is rate-determining.
- The intermediate carbocation is stabilized by resonance; a minimum of three resonance structures can be drawn. The positive charge is always located ortho or para to the new C–E bond.



Three Rules Describing the Reactivity and Directing Effects of Common Substituents (18.7–18.9)

- All ortho, para directors except the halogens activate the benzene ring.
- All meta directors deactivate the benzene ring.
- The halogens deactivate the benzene ring and direct ortho, para.

Summary of Substituent Effects in Electrophilic Aromatic Substitution (18.6–18.9)

Substituent	Inductive effect	Resonance effect	Reactivity	Directing effect
[1] <chem>c1ccc(R)cc1</chem> R = alkyl	donating	none	activating	ortho, para
[2] <chem>c1ccc(Z)cc1</chem> Z = N or O	withdrawing	donating	activating	ortho, para

“The summaries are very effective. I think this is the strongest aspect of this text. The summaries will allow students a great way to review for exams (both during the course and when studying for MCATs, GREs, etc.)”

Susan M. Schelble
University of Colorado-Denver

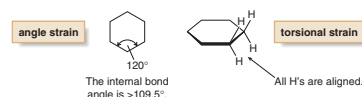
4.12 Cyclohexane

Let's now examine in detail the conformation of cyclohexane, the most common ring size in naturally occurring compounds.

4.12A The Chair Conformation

A planar cyclohexane ring would experience angle strain, because the internal bond angle between the carbon atoms would be 120°, and torsional strain, because all of the hydrogens on adjacent carbon atoms would be eclipsed.

If a cyclohexane ring were flat...



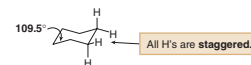
The internal bond angle is >109.5°.

In reality, cyclohexane adopts a puckered conformation, called the **chair** form, which is more stable than any other possible conformation.

The carbon skeleton of chair cyclohexane



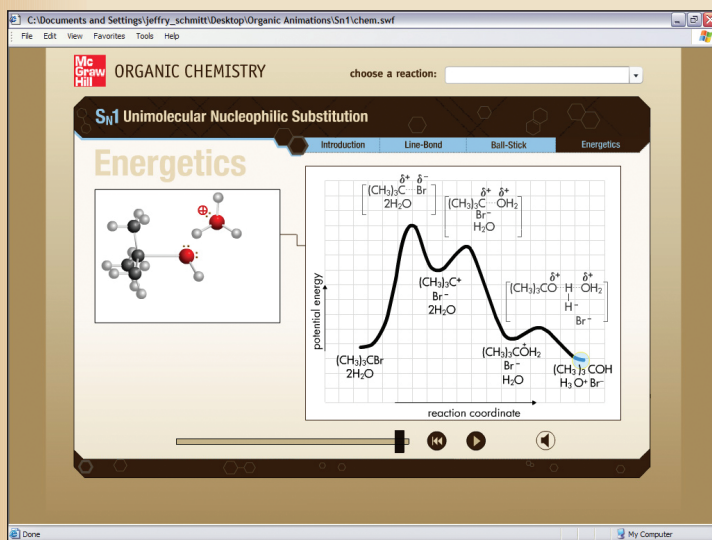
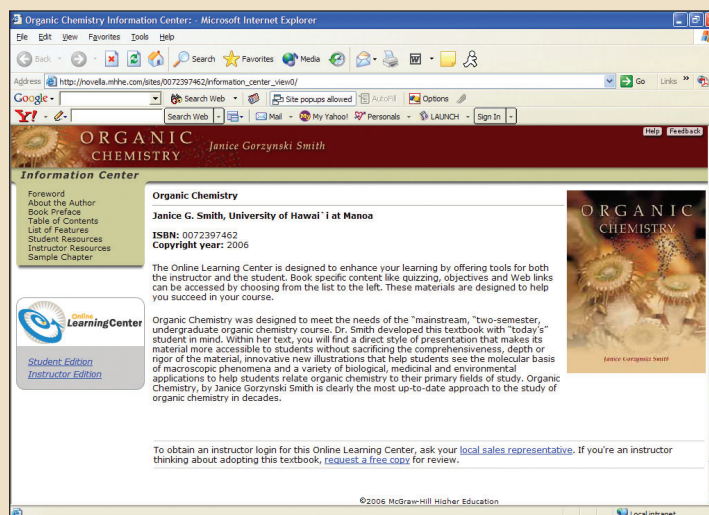
The chair conformation is so stable because it eliminates angle strain (all C–C–C bond angles are 109.5°) and torsional strain (all hydrogens on adjacent carbon atoms are staggered, not eclipsed).



Supplements

Online Learning Center

The Online Learning Center is a comprehensive, exclusive website that provides numerous electronic resources for both instructors and students. Access to this learning tool is FREE with the purchase of a new textbook. Log on at www.smithorganic.com



Digital Content Manager

This cross-platform CD-ROM is a collection of visual resources that allows instructors to create customized PowerPoint presentations from illustrations, figures, tables, and worked examples from the text. The CD also contains full-color animations, Active Art, and PowerPoint lecture outlines.

Student Study Guide/Solutions Manual

Written by Janice Gorzynski Smith and Erin R. Smith, the Student Study Guide/Solutions Manual provides step-by-step solutions to all in-chapter and end-of-chapter problems. Each chapter begins with an overview of key concepts and includes key rules and summary tables.

Transparency Acetates

This boxed set of over 200 full-color transparencies features key color images from the text for use in small and large classroom settings.