APPENDIX

A Nomenclature of Polyfunctional Organic Compounds

With more than 30 million organic compounds now known and thousands more being created daily, naming them all is a real problem. Part of the problem is due to the sheer complexity of organic structures, but part is also due to the fact that chemical names have more than one purpose. For Chemical Abstracts Service (CAS), which catalogs and indexes the worldwide chemical literature, each compound must have only one correct name. It would be chaos if half the entries for CH_3Br were indexed under "M" for methyl bromide and half under "B" for bromomethane. Furthermore, a CAS name must be strictly systematic so that it can be assigned and interpreted by computers; common names are not allowed.

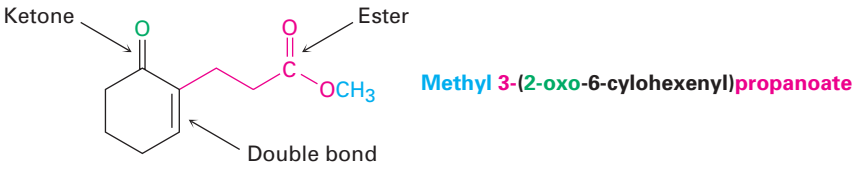
People, however, have different requirements than computers. For people—which is to say chemists in their spoken and written communications—it's best that a chemical name be pronounceable and that it be as easy as possible to assign and interpret. Furthermore, it's convenient if names follow historical precedents, even if that means a particularly well-known compound might have more than one name. People can readily understand that bromomethane and methyl bromide both refer to CH_3Br.

As noted in the text, chemists overwhelmingly use the nomenclature system devised and maintained by the International Union of Pure and Applied Chemistry, or IUPAC. Rules for naming monofunctional compounds were given throughout the text as each new functional group was introduced, and a list of where these rules can be found is given in Table A.1.

Table A.1 Nomenclature Rules for Functional Groups

Functional group	Text section	Functional group	Text section
Acid anhydrides	21.1	Aromatic compounds	15.1
Acid halides	21.1	Carboxylic acids	20.1
Acyl phosphates	21.1	Cycloalkanes	4.1
Alcohols	17.1	Esters	21.1
Aldehydes	19.1	Ethers	18.1
Alkanes	3.4	Ketones	19.1
Alkenes	6.3	Nitriles	20.1
Alkyl halides	10.1	Phenols	17.1
Alkynes	8.1	Sulfides	18.8
Amides	21.1	Thioesters	21.1
Amines	24.1	Thiols	18.8

Naming a monofunctional compound is reasonably straightforward, but even experienced chemists often encounter problems when faced with naming a complex polyfunctional compound. Take the following compound, for instance. It has three functional groups, ester, ketone, and C=C, but how should it be named? As an ester with an *-oate* ending, a ketone with an *-one* ending, or an alkene with an *-ene* ending? It's actually named methyl 3-(2-oxo-6-cyclohexenyl)propanoate.



The name of a polyfunctional organic molecule has four parts—suffix, parent, prefixes, and locants—which must be identified and expressed in the proper order and format. Let's look at each of the four.

Name Part 1. The Suffix: Functional-Group Precedence

Although a polyfunctional organic molecule might contain several different functional groups, we must choose just one suffix for nomenclature purposes. It's not correct to use two suffixes. Thus, keto ester **1** must be named either as a ketone with an *-one* suffix or as an ester with an *-oate* suffix but can't be named as an *-onoate*. Similarly, amino alcohol **2** must be named either as an alcohol (*-ol*) or as an amine (*-amine*) but can't be named as an *-olamine* or *-aminol*.

1. $CH_3CCH_2CH_2COCH_3$ (O, O)

2. $CH_3CHCH_2CH_2CH_2NH_2$ (OH)

The only exception to the rule requiring a single suffix is when naming compounds that have double or triple bonds. Thus, the unsaturated acid $H_2C{=}CHCH_2CO_2H$ is 3-butenoic acid, and the acetylenic alcohol $HC{\equiv}CCH_2CH_2CH_2OH$ is 5-pentyn-1-ol.

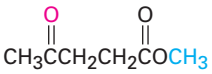
How do we choose which suffix to use? Functional groups are divided into two classes, **principal groups** and **subordinate groups**, as shown in Table A.2. Principal groups can be cited either as prefixes or as suffixes, while subordinate groups are cited only as prefixes. Within the principal groups, an order of priority has been established, with the proper suffix for a given compound determined by choosing the principal group of highest priority. For example, Table A.2 indicates that keto ester **1** should be named as an ester rather than as a ketone because an ester functional group is higher in priority than a ketone. Similarly, amino alcohol **2** should be named as an alcohol rather than as an amine.

Table A.2 Classification of Functional Groups[a]

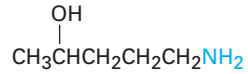
Functional group	Name as suffix	Name as prefix
Principal groups		
Carboxylic acids	-oic acid -carboxylic acid	carboxy
Acid anhydrides	-oic anhydride -carboxylic anhydride	—
Esters	-oate -carboxylate	alkoxycarbonyl
Thioesters	-thioate -carbothioate	alkylthiocarbonyl
Acid halides	-oyl halide -carbonyl halide	halocarbonyl
Amides	-amide -carboxamide	carbamoyl
Nitriles	-nitrile -carbonitrile	cyano
Aldehydes	-al -carbaldehyde	oxo
Ketones	-one	oxo
Alcohols	-ol	hydroxy
Phenols	-ol	hydroxy
Thiols	-thiol	mercapto
Amines	-amine	amino
Imines	-imine	imino
Ethers	ether	alkoxy
Sulfides	sulfide	alkylthio
Disulfides	disulfide	—
Alkenes	-ene	—
Alkynes	-yne	—
Alkanes	-ane	—
Subordinate groups		
Azides	—	azido
Halides	—	halo
Nitro compounds	—	nitro

[a]Principal groups are listed in order of decreasing priority; subordinate groups have no priority order.

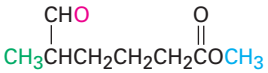
Thus, the name of **1** is methyl 4-oxopentanoate, and the name of **2** is 5-amino-2-pentanol. Further examples are shown:



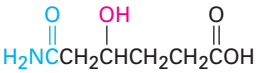
1. Methyl 4-oxopentanoate
(an ester with a ketone group)



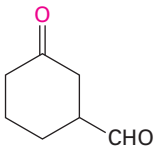
2. 5-Amino-2-pentanol
(an alcohol with an amine group)



3. Methyl 5-methyl-6-oxohexanoate
(an ester with an aldehyde group)



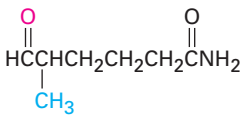
4. 5-Carbamoyl-4-hydroxypentanoic acid
(a carboxylic acid with amide and alcohol groups)



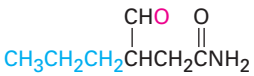
5. 3-Oxocyclohexanecarbaldehyde
(an aldehyde with a ketone group)

Name Part 2. The Parent: Selecting the Main Chain or Ring

The parent, or base, name of a polyfunctional organic compound is usually easy to identify. If the principal group of highest priority is part of an open chain, the parent name is that of the longest chain containing the largest number of principal groups. For example, compounds **6** and **7** are isomeric aldehydo amides, which must be named as amides rather than as aldehydes according to Table A.2. The longest chain in compound **6** has six carbons, and the substance is therefore named 5-methyl-6-oxohexanamide. Compound **7** also has a chain of six carbons, but the longest chain that contains both principal functional groups has only four carbons. The correct name of **7** is 4-oxo-3-propylbutanamide.



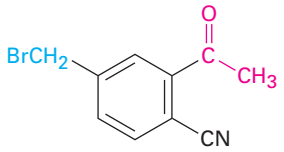
6. 5-Methyl-6-oxohexanamide



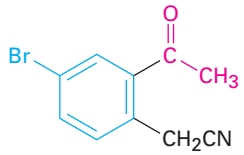
7. 4-Oxo-3-propylbutanamide

If the highest-priority principal group is attached to a ring, the parent name is that of the ring system. Compounds **8** and **9**, for instance, are isomeric keto nitriles and must both be named as nitriles according to Table A.2. Substance **8** is named as a benzonitrile because the −CN functional group is a substituent on the aromatic ring, but substance **9** is named as an acetonitrile because the −CN functional group is on an open chain. The correct names are 2-acetyl-(4-bromomethyl)benzonitrile (**8**) and (2-acetyl-4-bromophenyl)acetonitrile (**9**).

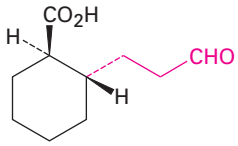
As further examples, compounds **10** and **11** are both keto acids and must be named as acids, but the parent name in **10** is that of a ring system (cyclohexanecarboxylic acid) and the parent name in **11** is that of an open chain (propanoic acid). The full names are *trans*-2-(3-oxopropyl)cyclohexanecarboxylic acid (**10**) and 3-(2-oxocyclohexyl)propanoic acid (**11**).



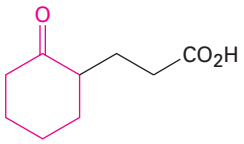
8. 2-Acetyl-(4-bromomethyl)benzonitrile



9. (2-Acetyl-4-bromophenyl)acetonitrile



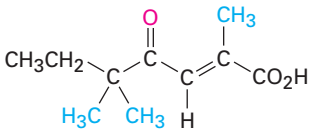
10. *trans*-2-(3-oxopropyl)cyclohexanecarboxylic acid



11. 3-(2-Oxocyclohexyl)propanoic acid

Name Parts 3 and 4. The Prefixes and Locants

With parent name and suffix established, the next step is to identify and give numbers, or *locants,* to all substituents on the parent chain or ring. These substituents include all alkyl groups and all functional groups other than the one cited in the suffix. For example, compound **12** contains three different functional groups (carboxyl, keto, and double bond). Because the carboxyl group is highest in priority and because the longest chain containing the functional groups has seven carbons, compound **12** is a heptenoic acid. In addition, the main chain has a keto (oxo) substituent and three methyl groups. Numbering from the end nearer the highest-priority functional group, compound **12** is named (*E*)-2,5,5-trimethyl-4-oxo-2-heptenoic acid. Look back at some of the other compounds we've named to see other examples of how prefixes and locants are assigned.



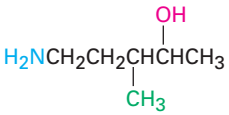
12. (*E*)-2,5,5-Trimethyl-4-oxo-2-heptenoic acid

Writing the Name

With the name parts established, the entire name is then written out. Several additional rules apply:

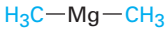
1. **Order of prefixes.** When the substituents have been identified, the main chain has been numbered, and the proper multipliers such as *di-* and *tri-* have been assigned, the name is written with the substituents listed in alphabetical,

rather than numerical, order. Multipliers such as *di-* and *tri-* are not used for alphabetization purposes, but the prefix *iso-* is used.

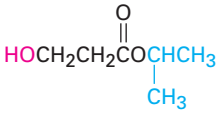


13. 5-Amino-3-methyl-2-pentanol

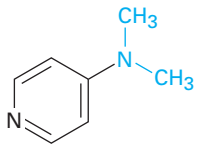
2. **Use of hyphens; single- and multiple-word names.** The general rule is to determine whether the parent is itself an element or compound. If so, then the name is written as a single word; if not, then the name is written as multiple words. Methylbenzene is written as one word, for instance, because the parent—benzene—is itself a compound. Diethyl ether, however, is written as two words because the parent—ether—is a class name rather than a compound name. Some further examples follow:



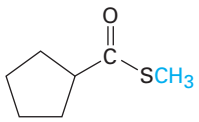
14. Dimethylmagnesium
(one word, because magnesium is an element)



15. Isopropyl 3-hydroxypropanoate
(two words, because "propanoate" is not a compound)

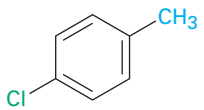


16. 4-(Dimethylamino)pyridine
(one word, because pyridine is a compound)

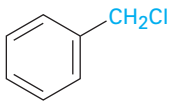


17. Methyl cyclopentanecarbothioate
(two words, because "cyclopentanecarbothioate" is not a compound)

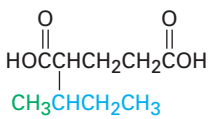
3. **Parentheses.** Parentheses are used to denote complex substituents when ambiguity would otherwise arise. For example, chloromethylbenzene has two substituents on a benzene ring, but (chloromethyl)benzene has only one complex substituent. Note that the expression in parentheses is not set off by hyphens from the rest of the name.



18. *p*-Chloromethylbenzene



19. (Chloromethyl)benzene



20. 2-(1-Methylpropyl)pentanedioic acid

Additional Reading

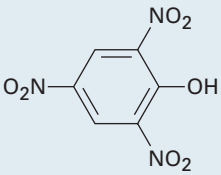
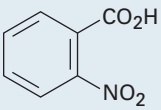
Further explanations of the rules of organic nomenclature can be found online at http://www.acdlabs.com/iupac/nomenclature/ and in the following references:

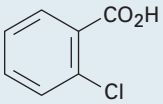
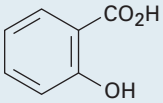
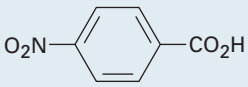
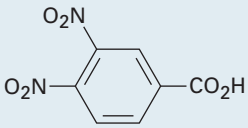
1. "A Guide to IUPAC Nomenclature of Organic Compounds," CRC Press, Boca Raton, FL, 1993.
2. "Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, and H," International Union of Pure and Applied Chemistry, Pergamon Press, Oxford, 1979.

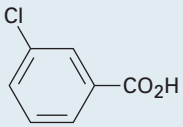
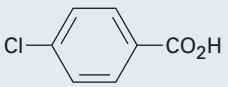
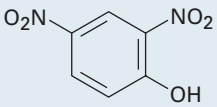
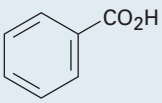
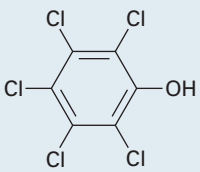
APPENDIX

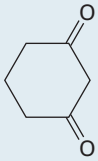
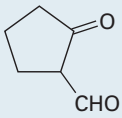
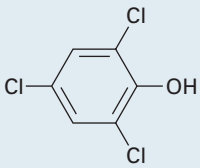
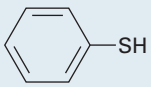
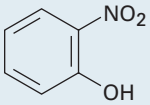
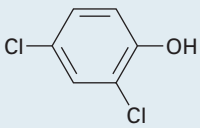
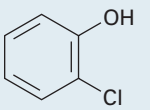
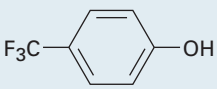
B

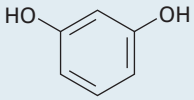
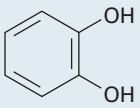
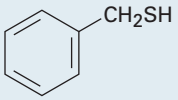
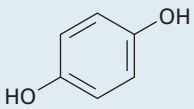
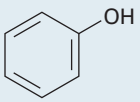
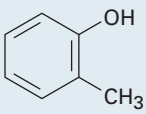
Acidity Constants for Some Organic Compounds

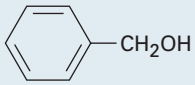
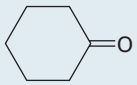
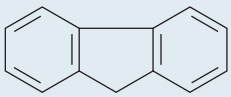
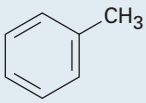
Compound	pK_a
CH_3SO_3H	−1.8
$CH(NO_2)_3$	0.1
	0.3
CCl_3CO_2H	0.5
CF_3CO_2H	0.5
CBr_3CO_2H	0.7
$HO_2CC{\equiv}CCO_2H$	1.2; 2.5
HO_2CCO_2H	1.2; 3.7
$CHCl_2CO_2H$	1.3
$CH_2(NO_2)CO_2H$	1.3
$HC{\equiv}CCO_2H$	1.9
Z $HO_2CCH{=}CHCO_2H$	1.9; 6.3
	2.4
CH_3COCO_2H	2.4
$NCCH_2CO_2H$	2.5
$CH_3C{\equiv}CCO_2H$	2.6
CH_2FCO_2H	2.7

Compound	pK_a
CH_2ClCO_2H	2.8
$HO_2CCH_2CO_2H$	2.8; 5.6
CH_2BrCO_2H	2.9
	3.0
	3.0
CH_2ICO_2H	3.2
$CHOCO_2H$	3.2
	3.4
	3.5
$HSCH_2CO_2H$	3.5; 10.2
$CH_2(NO_2)_2$	3.6
$CH_3OCH_2CO_2H$	3.6
$CH_3COCH_2CO_2H$	3.6
$HOCH_2CO_2H$	3.7
HCO_2H	3.7

Compound	pK_a
	3.8
	4.0
$CH_2BrCH_2CO_2H$	4.0
	4.1
	4.2
$H_2C{=}CHCO_2H$	4.2
$HO_2CCH_2CH_2CO_2H$	4.2; 5.7
$HO_2CCH_2CH_2CH_2CO_2H$	4.3; 5.4
	4.5
$H_2C{=}C(CH_3)CO_2H$	4.7
CH_3CO_2H	4.8

Compound	pK_a
$CH_3CH_2CO_2H$	4.8
$(CH_3)_3CCO_2H$	5.0
$CH_3COCH_2NO_2$	5.1
	5.3
$O_2NCH_2CO_2CH_3$	5.8
	5.8
	6.2
	6.6
HCO_3H	7.1
	7.2
$(CH_3)_2CHNO_2$	7.7
	7.8
CH_3CO_3H	8.2
	8.5
$CH_3CH_2NO_2$	8.5
	8.7

Compound	pK_a
$CH_3COCH_2COCH_3$	9.0
	9.3; 11.1
	9.3; 12.6
	9.4
	9.9; 11.5
	9.9
$CH_3COCH_2SOCH_3$	10.0
	10.3
CH_3NO_2	10.3
CH_3SH	10.3
$CH_3COCH_2CO_2CH_3$	10.6
CH_3COCHO	11.0
$CH_2(CN)_2$	11.2
CCl_3CH_2OH	12.2
Glucose	12.3
$(CH_3)_2C{=}NOH$	12.4
$CH_2(CO_2CH_3)_2$	12.9
$CHCl_2CH_2OH$	12.9
$CH_2(OH)_2$	13.3
$HOCH_2CH(OH)CH_2OH$	14.1
CH_2ClCH_2OH	14.3
	15.0

Compound	pK_a
	15.4
CH_3OH	15.5
$H_2C{=}CHCH_2OH$	15.5
CH_3CH_2OH	16.0
$CH_3CH_2CH_2OH$	16.1
CH_3COCH_2Br	16.1
	16.7
CH_3CHO	17
$(CH_3)_2CHCHO$	17
$(CH_3)_2CHOH$	17.1
$(CH_3)_3COH$	18.0
CH_3COCH_3	19.3
	23
$CH_3CO_2CH_2CH_3$	25
$HC{\equiv}CH$	25
CH_3CN	25
$CH_3SO_2CH_3$	28
$(C_6H_5)_3CH$	32
$(C_6H_5)_2CH_2$	34
CH_3SOCH_3	35
NH_3	36
$CH_3CH_2NH_2$	36
$(CH_3CH_2)_2NH$	40
	41
	43
$H_2C{=}CH_2$	44
CH_4	~60

An acidity list covering more than 5000 organic compounds has been published: E.P. Serjeant and B. Dempsey (eds.), "Ionization Constants of Organic Acids in Aqueous Solution," IUPAC Chemical Data Series No. 23, Pergamon Press, Oxford, 1979.

APPENDIX

C Glossary

Absolute configuration (Section 9.5): The exact three-dimensional structure of a chiral molecule. Absolute configurations are specified verbally by the Cahn–Ingold–Prelog *R*,*S* convention and are represented on paper by Fischer projections.

Absorbance (Section 14.7): In optical spectroscopy, the logarithm of the intensity of the incident light divided by the intensity of the light transmitted through a sample; $A = \log I_0/I$.

Absorption spectrum (Section 12.5): A plot of wavelength of incident light versus amount of light absorbed. Organic molecules show absorption spectra in both the infrared and the ultraviolet regions of the electromagnetic spectrum.

Acetal (Section 19.10): A functional group consisting of two −OR groups bonded to the same carbon, $R_2C(OR')_2$. Acetals are often used as protecting groups for ketones and aldehydes.

Acetoacetic ester synthesis (Section 22.7): The synthesis of a methyl ketone by alkylation of an alkyl halide, followed by hydrolysis and decarboxylation.

Acetyl group (Section 19.1): The CH_3CO- group.

Acetylide anion (Section 8.7): The anion formed by removal of a proton from a terminal alkyne.

Achiral (Section 9.2): Having a lack of handedness. A molecule is achiral if it has a plane of symmetry and is thus superimposable on its mirror image.

Acid anhydride (Section 21.1): A functional group with two acyl groups bonded to a common oxygen atom, RCO_2COR'.

Acid halide (Section 21.1): A functional group with an acyl group bonded to a halogen atom, RCOX.

Acidity constant, K_a (Section 2.8): A measure of acid strength. For any acid HA, the acidity constant is given by the expression $K_a = K_{eq}[H_2O] = \dfrac{[H_3O^+][A^-]}{[HA]}$.

Activating group (Section 16.4): An electron-donating group such as hydroxyl (−OH) or amino ($-NH_2$) that increases the reactivity of an aromatic ring toward electrophilic aromatic substitution.

Activation energy (Section 5.9): The difference in energy between ground state and transition state in a reaction. The amount of activation energy determines the rate at which the reaction proceeds. Most organic reactions have activation energies of 40–100 kJ/mol.

Acyl group (Sections 16.3, 19.1): A −COR group.

Acyl phosphate (Section 21.8): A functional group with an acyl group bonded to a phosphate, $RCO_2PO_3^{2-}$ or $RCO_2PO_3R'^-$.

Acylation (Sections 16.3, 21.4): The introduction of an acyl group, −COR, onto a molecule. For example, acylation of an alcohol yields an ester, acylation of an amine yields an amide, and acylation of an aromatic ring yields an alkyl aryl ketone.

Acylium ion (Section 16.3): A resonance-stabilized carbocation in which the positive charge is located at a carbonyl-group carbon, $R-\overset{+}{C}=O \leftrightarrow R-C\equiv O^+$. Acylium ions are strongly electrophilic and are involved as intermediates in Friedel–Crafts acylation reactions.

Adams catalyst (Section 7.7): The PtO_2 catalyst used for hydrogenations.

1,2-Addition (Sections 14.2, 19.13): The addition of a reactant to the two ends of a double bond.

1,4-Addition (Sections 14.2, 19.13): Addition of a reactant to the ends of a conjugated π system. Conjugated dienes yield 1,4 adducts when treated with electrophiles such as HCl. Conjugated enones yield 1,4 adducts when treated with nucleophiles such as cyanide ion.

Addition reaction (Section 5.1): The reaction that occurs when two reactants add together to form a single new product with no atoms "left over."

Adrenocortical hormone (Section 27.6): A steroid hormone secreted by the adrenal glands. There are two types of adrenocortical hormones: mineralocorticoids and glucocorticoids.

Alcohol (Chapter 17 introduction): A compound with an −OH group bonded to a saturated, alkane-like carbon, ROH.

Aldaric acid (Section 25.6): The dicarboxylic acid resulting from oxidation of an aldose.

Aldehyde (Chapter 19 introduction): A compound containing the −CHO functional group.

Alditol (Section 25.6): The polyalcohol resulting from reduction of the carbonyl group of a sugar.

Aldol reaction (Section 23.1): The carbonyl condensation reaction of an aldehyde or ketone to give a β-hydroxy carbonyl compound.

Aldonic acid (Section 25.6): The monocarboxylic acid resulting from mild oxidation of the −CHO group of an aldose.

Aldose (Section 25.1): A carbohydrate with an aldehyde functional group.

Alicyclic (Section 4.1): An aliphatic cyclic hydrocarbon such as a cycloalkane or cycloalkene.

Aliphatic (Section 3.2): A nonaromatic hydrocarbon such as a simple alkane, alkene, or alkyne.

Alkaloid (Chapter 2 *Focus On*): A naturally occurring organic base, such as morphine.

Alkane (Section 3.2): A compound of carbon and hydrogen that contains only single bonds.

Alkene (Chapter 6 introduction): A hydrocarbon that contains a carbon–carbon double bond, $R_2C{=}CR_2$.

Alkoxide ion (Section 17.2): The anion RO^- formed by deprotonation of an alcohol.

Alkoxymercuration reaction (Section 18.2): A method for synthesizing ethers by mercuric-ion catalyzed addition of an alcohol to an alkene.

Alkyl group (Section 3.3): The partial structure that remains when a hydrogen atom is removed from an alkane.

Alkylamine (Section 24.1): An amino-substituted alkane.

Alkylation (Sections 8.8, 16.3, 18.2, 22.7): Introduction of an alkyl group onto a molecule. For example, aromatic rings can be alkylated to yield arenes, and enolate anions can be alkylated to yield α-substituted carbonyl compounds.

Alkyne (Chapter 8 introduction): A hydrocarbon that contains a carbon–carbon triple bond, $RC{\equiv}CR$.

Allyl group (Section 6.3): A $H_2C{=}CHCH_2-$ substituent.

Allylic (Section 10.5): The position next to a double bond. For example, $H_2C{=}CHCH_2Br$ is an allylic bromide.

***α*-Amino acid** (Section 26.1): A difunctional compound with an amino group on the carbon atom next to a carboxyl group, $RCH(NH_2)CO_2H$.

***α* Anomer** (Section 25.5): The cyclic hemiacetal form of a sugar that has the hemiacetal −OH group on the side of the ring opposite the terminal $-CH_2OH$.

***α* Helix** (Section 26.9): The coiled secondary structure of a protein.

***α* Position** (Chapter 22 introduction): The position next to a carbonyl group.

***α*-Substitution reaction** (Section 22.2): The substitution of the α hydrogen atom of a carbonyl compound by reaction with an electrophile.

Amide (Chapter 21 introduction): A compound containing the $-CONR_2$ functional group.

Amidomalonate synthesis (Section 26.3): A method for preparing α-amino acids by alkylation of diethyl amidomalonate with an alkyl halide.

Amine (Chapter 24 introduction): A compound containing one or more organic substituents bonded to a nitrogen atom, RNH_2, R_2NH, or R_3N.

Amino acid (*See* α-Amino acid; Section 26.1)

Amino sugar (Section 25.7): A sugar with one of its −OH groups replaced by $-NH_2$.

Amphiprotic (Section 26.1): Capable of acting either as an acid or as a base. Amino acids are amphiprotic.

Amplitude (Section 12.5): The height of a wave measured from the midpoint to the maximum. The intensity of radiant energy is proportional to the square of the wave's amplitude.

Anabolism (Section 29.1): The group of metabolic pathways that build up larger molecules from smaller ones.

Androgen (Section 27.6): A male steroid sex hormone.

Angle strain (Section 4.3): The strain introduced into a molecule when a bond angle is deformed from its ideal value. Angle strain is particularly important in small-ring cycloalkanes, where it results from compression of bond angles to less than their ideal tetrahedral values.

Annulation (Section 23.12): The building of a new ring onto an existing molecule.

Anomers (Section 25.5): Cyclic stereoisomers of sugars that differ only in their configuration at the hemiacetal (anomeric) carbon.

Antarafacial (Section 30.6): A pericyclic reaction that takes place on opposite faces of the two ends of a π electron system.

Anti conformation (Section 3.7): The geometric arrangement around a carbon–carbon single bond in which the two largest substituents are 180° apart as viewed in a Newman projection.

Anti periplanar (Section 11.8): Describing a stereochemical relationship whereby two bonds on adjacent carbons lie in the same plane at an angle of 180°.

Anti stereochemistry (Section 7.2): The opposite of syn. An anti addition reaction is one in which the two ends of the double bond are attacked from different sides. An anti elimination reaction is one in which the two groups leave from opposite sides of the molecule.

Antiaromatic (Section 15.3): Referring to a planar, conjugated molecule with $4n$ π electrons. Delocalization of the π electrons leads to an increase in energy.

Antibonding MO (Section 1.11): A molecular orbital that is higher in energy than the atomic orbitals from which it is formed.

Anticodon (Section 28.5): A sequence of three bases on tRNA that reads the codons on mRNA and brings the correct amino acids into position for protein synthesis.

Arene (Section 15.1): An alkyl-substituted benzene.

Arenediazonium salt (Section 24.7): An aromatic compound $Ar—\overset{+}{N}\equiv N\ X^-$; used in the Sandmeyer reaction.

Aromaticity (Chapter 15 introduction): The special characteristics of cyclic conjugated molecules. These characteristics include unusual stability, the presence of a ring current in the ^1H NMR spectrum, and a tendency to undergo substitution reactions rather than addition reactions on treatment with electrophiles. Aromatic molecules are planar, cyclic, conjugated species that have $4n + 2$ π electrons.

Arylamine (Section 24.1): An amino-substituted aromatic compound, $Ar—NH_2$.

Atactic (Section 31.2): A chain-growth polymer in which the substituents are randomly oriented along the backbone.

Atomic mass (Section 1.1): The weighted average mass of an element's naturally occurring isotopes.

Atomic number, *Z* (Section 1.1): The number of protons in the nucleus of an atom.

ATZ Derivative (Section 26.6): An anilinothiazolinone, formed from an amino acid during Edman degradation of a peptide.

Aufbau principle (Section 1.3): The rules for determining the electron configuration of an atom.

Axial bond (Section 4.6): A bond to chair cyclohexane that lies along the ring axis perpendicular to the rough plane of the ring.

Azide synthesis (Section 24.6): A method for preparing amines by S_N2 reaction of an alkyl halide with azide ion, followed by reduction.

Azo compound (Section 24.8): A compound with the general structure $R—N{=}N—R'$.

Backbone (Section 26.4): The continuous chain of atoms running the length of a polymer.

Base peak (Section 12.1): The most intense peak in a mass spectrum.

Basicity constant, K_b (Section 24.3): A measure of base strength. For any base B, the basicity constant is given by the expression

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+]\ [OH^-]}{[B]}$$

Bent bonds (Section 4.4): The bonds in small rings such as cyclopropane that bend away from the internuclear line and overlap at a slight angle, rather than head-on. Bent bonds are highly strained and highly reactive.

Benzoyl group (Section 19.1): The C_6H_5CO- group.

Benzyl group (Section 15.1): The $C_6H_5CH_2-$ group.

Benzylic (Section 11.5): The position next to an aromatic ring.

Benzyne (Section 16.8): An unstable compound having a triple bond in a benzene ring.

***β* Anomer** (Section 25.5): The cyclic hemiacetal form of a sugar that has the hemiacetal $-OH$ group on the same side of the ring as the terminal $-CH_2OH$.

***β*-Diketone** (Section 22.5): A 1,3-diketone.

***β*-Keto ester** (Section 22.5): A 3-oxoester.

***β*-Oxidation pathway** (Section 29.3): The metabolic pathway for degrading fatty acids.

***β*-Pleated sheet** (Section 26.9): A type of secondary structure of a protein.

Betaine (Section 19.11): A neutral dipolar molecule with nonadjacent positive and negative charges. For example, the adduct of a Wittig reagent with a carbonyl compound is a betaine.

Bicycloalkane (Section 4.9): A cycloalkane that contains two rings.

Bimolecular reaction (Section 11.2): A reaction whose rate-limiting step occurs between two reactants.

Block copolymer (Section 31.3): A polymer in which different blocks of identical monomer units alternate with one another.

Boat cyclohexane (Section 4.5): A conformation of cyclohexane that bears a slight resemblance to a boat. Boat cyclohexane has no angle strain but has a large number of

eclipsing interactions that make it less stable than chair cyclohexane.

Boc derivative (Section 26.7): A butyloxycarbonyl amide protected amino acid.

Bond angle (Section 1.6): The angle formed between two adjacent bonds.

Bond dissociation energy, *D* (Section 5.8): The amount of energy needed to break a bond homolytically and produce two radical fragments.

Bond length (Section 1.5): The equilibrium distance between the nuclei of two atoms that are bonded to each other.

Bond strength (Section 1.5): An alternative name for bond dissociation energy.

Bonding MO (Section 1.11): A molecular orbital that is lower in energy than the atomic orbitals from which it is formed.

Branched-chain alkane (Section 3.2): An alkane that contains a branching connection of carbons as opposed to a straight-chain alkane.

Bridgehead atom (Section 4.9): An atom that is shared by more than one ring in a polycyclic molecule.

Bromohydrin (Section 7.3): A 1,2-disubstituted bromoalcohol; obtained by addition of HOBr to an alkene.

Bromonium ion (Section 7.2): A species with a divalent, positively charged bromine, R_2Br^+.

Brønsted–Lowry acid (Section 2.7): A substance that donates a hydrogen ion (proton; H^+) to a base.

Brønsted–Lowry base (Section 2.7): A substance that accepts H^+ from an acid.

C-terminal amino acid (Section 26.4): The amino acid with a free $-CO_2H$ group at the end of a protein chain.

Cahn–Ingold–Prelog sequence rules (Sections 6.5, 9.5): A series of rules for assigning relative priorities to substituent groups on a double-bond carbon atom or on a chirality center.

Cannizzaro reaction (Section 19.12): The disproportionation reaction of an aldehyde to yield an alcohol and a carboxylic acid on treatment with base.

Carbanion (Section 19.7): A carbon anion, or substance that contains a trivalent, negatively charged carbon atom ($R_3C:^-$). Carbanions are sp^3-hybridized and have eight electrons in the outer shell of the negatively charged carbon.

Carbene (Section 7.6): A neutral substance that contains a divalent carbon atom having only six electrons in its outer shell ($R_2C:$).

Carbinolamine (Section 19.8): A molecule that contains the $R_2C(OH)NH_2$ functional group. Carbinolamines are produced as intermediates during the nucleophilic addition of amines to carbonyl compounds.

Carbocation (Sections 5.5, 6.9): A carbon cation, or substance that contains a trivalent, positively charged carbon atom having six electrons in its outer shell (R_3C^+).

Carbohydrate (Section 25.1): A polyhydroxy aldehyde or ketone. Carbohydrates can be either simple sugars, such as glucose, or complex sugars, such as cellulose.

Carbonyl condensation reaction (Section 23.1): A reaction that joins two carbonyl compounds together by a combination of α-substitution and nucleophilic addition reactions.

Carbonyl group (Section 2.1): The C=O functional group.

Carboxyl group (Section 20.1): The $-CO_2H$ functional group.

Carboxylation (Section 20.5): The addition of CO_2 to a molecule.

Carboxylic acid (Chapter 20 introduction): A compound containing the $-CO_2H$ functional group.

Carboxylic acid derivative (Chapter 21 introduction): A compound in which an acyl group is bonded to an electronegative atom or substituent Y that can act as a leaving group in a substitution reaction, RCOY.

Catabolism (Section 29.1): The group of metabolic pathways that break down larger molecules into smaller ones.

Cation radical (Section 12.1): A reactive species formed by loss of an electron from a neutral molecule.

Chain-growth polymer (Section 31.1): A polymer whose bonds are produced by chain reactions. Polyethylene and other alkene polymers are examples.

Chain reaction (Section 5.3): A reaction that, once initiated, sustains itself in an endlessly repeating cycle of propagation steps. The radical chlorination of alkanes is an example of a chain reaction that is initiated by irradiation with light and then continues in a series of propagation steps.

Chair cyclohexane (Section 4.5): A three-dimensional conformation of cyclohexane that resembles the rough shape of a chair. The chair form of cyclohexane is the lowest-energy conformation of the molecule.

Chemical shift (Section 13.3): The position on the NMR chart where a nucleus absorbs. By convention, the chemical shift of tetramethylsilane (TMS) is set at zero, and all other absorptions usually occur downfield (to the left on the chart). Chemical shifts are expressed in delta units, δ, where 1 δ equals 1 ppm of the spectrometer operating frequency.

Chiral (Section 9.2): Having handedness. Chiral molecules are those that do not have a plane of symmetry and are therefore not superimposable on their mirror image. A chiral molecule thus exists in two forms, one right-handed and one left-handed. The most common cause of chirality in a molecule is the presence of a carbon atom that is bonded to four different substituents.

Chiral environment (Section 9.14): Chiral surroundings or conditions in which a molecule resides.

Chirality center (Section 9.2): An atom (usually carbon) that is bonded to four different groups.

Chlorohydrin (Section 7.3): A 1,2-disubstituted chloroalcohol; obtained by addition of HOCl to an alkene.

Chromatography (Chapter 12 *Focus On,* Section 26.7): A technique for separating a mixture of compounds into pure components. Different compounds adsorb to a stationary support phase and are then carried along it at different rates by a mobile phase.

Cis–trans isomers (Sections 4.2, 6.4): Stereoisomers that differ in their stereochemistry about a double bond or ring.

Citric acid cycle (Section 29.7): The metabolic pathway by which acetyl CoA is degraded to CO_2.

Claisen condensation reaction (Section 23.7): The carbonyl condensation reaction of an ester to give a β-keto ester product.

Claisen rearrangement reaction (Sections 18.4, 30.8): The pericyclic conversion of an allyl phenyl ether to an *o*-allylphenol by heating.

Coding strand (Section 28.4): The strand of double-helical DNA that contains the gene.

Codon (Section 28.5): A three-base sequence on a messenger RNA chain that encodes the genetic information necessary to cause a specific amino acid to be incorporated into a protein. Codons on mRNA are read by complementary anticodons on tRNA.

Coenzyme (Section 26.10): A small organic molecule that acts as a cofactor.

Cofactor (Section 26.10): A small nonprotein part of an enzyme that is necessary for biological activity.

Combinatorial chemistry (Chapter 16 *Focus On*): A procedure in which anywhere from a few dozen to several hundred thousand substances are prepared simultaneously.

Complex carbohydrate (Section 25.1): A carbohydrate that is made of two or more simple sugars linked together.

Concerted (Section 30.1): A reaction that takes place in a single step without intermediates. For example, the Diels–Alder cycloaddition reaction is a concerted process.

Condensed structure (Section 1.12): A shorthand way of writing structures in which carbon–hydrogen and carbon–carbon bonds are understood rather than shown explicitly. Propane, for example, has the condensed structure $CH_3CH_2CH_3$.

Configuration (Section 9.5): The three-dimensional arrangement of atoms bonded to a chirality center.

Conformation (Section 3.6): The three-dimensional shape of a molecule at any given instant, assuming that rotation around single bonds is frozen.

Conformational analysis (Section 4.8): A means of assessing the energy of a substituted cycloalkane by totaling the steric interactions present in the molecule.

Conformer (Section 3.6): A conformational isomer.

Conjugate acid (Section 2.7): The product that results from protonation of a Brønsted–Lowry base.

Conjugate addition (Section 19.13): Addition of a nucleophile to the β carbon atom of an α,β-unsaturated carbonyl compound.

Conjugate base (Section 2.7): The product that results from deprotonation of a Brønsted–Lowry acid.

Conjugation (Chapter 14 introduction): A series of overlapping *p* orbitals, usually in alternating single and multiple bonds. For example, 1,3-butadiene is a conjugated diene, 3-buten-2-one is a conjugated enone, and benzene is a cyclic conjugated triene.

Conrotatory (Section 30.2): A term used to indicate that *p* orbitals must rotate in the same direction during electrocyclic ring-opening or ring closure.

Constitutional isomers (Sections 3.2, 9.9): Isomers that have their atoms connected in a different order. For example, butane and 2-methylpropane are constitutional isomers.

Cope rearrangement (Section 30.8): The sigmatropic rearrangement of a 1,5-hexadiene.

Copolymer (Section 31.3): A polymer obtained when two or more different monomers are allowed to polymerize together.

Coupling constant, *J* (Section 13.11): The magnitude (expressed in hertz) of the interaction between nuclei whose spins are coupled.

Covalent bond (Section 1.5): A bond formed by sharing electrons between atoms.

Cracking (Chapter 3 *Focus On*): A process used in petroleum refining in which large alkanes are thermally cracked into smaller fragments.

Crown ether (Section 18.7): A large-ring polyether; used as a phase-transfer catalyst.

Crystallite (Section 31.5): A highly ordered crystal-like region within a long polymer chain.

Curtius rearrangement (Section 24.6): The conversion of an acid chloride into an amine by reaction with azide ion, followed by heating with water.

Cyanohydrin (Section 19.6): A compound with an −OH group and a −CN group bonded to the same carbon atom; formed by addition of HCN to an aldehyde or ketone.

Cycloaddition reaction (Sections 14.4, 30.6): A pericyclic reaction in which two reactants add together in a single step to yield a cyclic product. The Diels–Alder reaction between a diene and a dienophile to give a cyclohexene is an example.

Cycloalkane (Section 4.1): An alkane that contains a ring of carbons.

D Sugar (Section 25.3): A sugar whose hydroxyl group at the chirality center farthest from the carbonyl group points to the right when drawn in Fischer projection.

***d,l* form** (Section 9.8): The racemic modification of a compound.

Deactivating group (Section 16.4): An electron-withdrawing substituent that decreases the reactivity of an aromatic ring toward electrophilic aromatic substitution.

Debye, D (Section 2.2): A unit for measuring dipole moments; 1 D = 3.336×10^{-30} coulomb meter (C · m).

Decarboxylation (Section 22.7): The loss of carbon dioxide from a molecule. β-Keto acids decarboxylate readily on heating.

Degenerate orbitals (Section 15.2): Two or more orbitals that have the same energy level.

Degree of unsaturation (Section 6.2): The number of rings and/or multiple bonds in a molecule.

Dehydration (Sections 7.1, 11.10, 17.6): The loss of water from an alcohol. Alcohols can be dehydrated to yield alkenes.

Dehydrohalogenation (Sections 7.1, 11.8): The loss of HX from an alkyl halide. Alkyl halides undergo dehydrohalogenation to yield alkenes on treatment with strong base.

Delocalization (Section 10.5): A spreading out of electron density over a conjugated π electron system. For example, allylic cations and allylic anions are delocalized because their charges are spread out over the entire π electron system.

Delta scale (Section 13.3): An arbitrary scale used to calibrate NMR charts. One delta unit (δ) is equal to 1 part per million (ppm) of the spectrometer operating frequency.

Denaturation (Section 26.9): The physical changes that occur in a protein when secondary and tertiary structures are disrupted.

Deoxy sugar (Section 25.7): A sugar with one of its −OH groups replaced by an −H.

Deoxyribonucleic acid (DNA) (Section 28.1): The biopolymer consisting of deoxyribonucleotide units linked together through phosphate–sugar bonds. Found in the nucleus of cells, DNA contains an organism's genetic information.

DEPT-NMR (Section 13.6): An NMR method for distinguishing among signals due to CH_3, CH_2, CH, and quaternary carbons. That is, the number of hydrogens attached to each carbon can be determined.

Deshielding (Section 13.2): An effect observed in NMR that causes a nucleus to absorb downfield (to the left) of tetramethylsilane (TMS) standard. Deshielding is caused by a withdrawal of electron density from the nucleus.

Deuterium isotope effect (Section 11.8): A tool used in mechanistic investigations to establish whether a C−H bond is broken in the rate-limiting step of a reaction.

Dextrorotatory (Section 9.3): A word used to describe an optically active substance that rotates the plane of polarization of plane-polarized light in a right-handed (clockwise) direction.

Diastereomers (Section 9.6): Non–mirror-image stereoisomers; diastereomers have the same configuration at one or more chirality centers but differ at other chirality centers.

Diastereotopic (Section 13.8): Two hydrogens in a molecule whose replacement by some other group leads to different diastereomers.

1,3-Diaxial interaction (Section 4.8): The strain energy caused by a steric interaction between axial groups three carbon atoms apart in chair cyclohexane.

Diazonium salt (Section 24.8): A compound with the general structure $RN_2^+ X^-$.

Diazotization (Section 24.8): The conversion of a primary amine, RNH_2, into a diazonium ion, RN_2^+, by treatment with nitrous acid.

Dideoxy DNA sequencing (Section 28.6): A biochemical method for sequencing DNA strands.

Dieckmann cyclization reaction (Section 23.9): An intramolecular Claisen condensation reaction to give a cyclic β-keto ester.

Diels–Alder reaction (Sections 14.4, 30.6): The cycloaddition reaction of a diene with a dienophile to yield a cyclohexene.

Dienophile (Section 14.5): A compound containing a double bond that can take part in the Diels–Alder cycloaddition reaction. The most reactive dienophiles are those that have electron-withdrawing groups on the double bond.

Digestion (Section 29.1): The first stage of catabolism, in which food is broken down by hydrolysis of ester, glycoside (acetal), and peptide (amide) bonds to yield fatty acids, simple sugars, and amino acids.

Dipole moment, μ (Section 2.2): A measure of the net polarity of a molecule. A dipole moment arises when the centers of mass of positive and negative charges within a molecule do not coincide.

Dipole–dipole force (Section 2.13): A noncovalent electrostatic interaction between dipolar molecules.

Disaccharide (Section 25.8): A carbohydrate formed by linking two simple sugars through an acetal bond.

Dispersion force (Section 2.13): A noncovalent interaction between molecules that arises because of constantly changing electron distributions within the molecules.

Disrotatory (Section 30.2): A term used to indicate that *p* orbitals rotate in opposite directions during electrocyclic ring-opening or ring closing.

Disulfide (Section 18.8): A compound of the general structure RSSR′.

DNA (*See* Deoxyribonucleic acid; Section 28.1)

Double helix (Section 28.2): The structure of DNA in which two polynucleotide strands coil around each other.

Doublet (Section 13.11): A two-line NMR absorption caused by spin–spin splitting when the spin of the nucleus under observation couples with the spin of a neighboring magnetic nucleus.

Downfield (Section 13.3): Referring to the left-hand portion of the NMR chart.

***E* geometry** (Section 6.5): A term used to describe the stereochemistry of a carbon–carbon double bond. The two groups on each carbon are assigned priorities according to the Cahn–Ingold–Prelog sequence rules, and the two carbons are compared. If the high-priority groups on each carbon are on opposite sides of the double bond, the bond has *E* geometry.

E1 reaction (Section 11.10): A unimolecular elimination reaction in which the substrate spontaneously dissociates to give a carbocation intermediate, which loses a proton in a separate step.

E1cB reaction (Section 11.10): A unimolecular elimination reaction in which a proton is first removed to give a carbanion intermediate, which then expels the leaving group in a separate step.

E2 reaction (Section 11.8): A bimolecular elimination reaction in which both the hydrogen and the leaving group are lost in the same step.

Eclipsed conformation (Section 3.6): The geometric arrangement around a carbon–carbon single bond in which the bonds to substituents on one carbon are parallel to the bonds to substituents on the neighboring carbon as viewed in a Newman projection.

Eclipsing strain (Section 3.6): The strain energy in a molecule caused by electron repulsions between eclipsed bonds. Eclipsing strain is also called torsional strain.

Edman degradation (Section 26.6): A method for N-terminal sequencing of peptide chains by treatment with *N*-phenylisothiocyanate.

Eicosanoid (Section 27.4): A lipid derived biologically from 5,8,11,14-eicosatetraenoic acid, or arachidonic acid. Prostaglandins, thromboxanes and leukotrienes are examples.

Elastomer (Section 31.5): An amorphous polymer that has the ability to stretch out and spring back to its original shape.

Electrocyclic reaction (Section 30.3): A unimolecular pericyclic reaction in which a ring is formed or broken by a concerted reorganization of electrons through a cyclic transition state. For example, the cyclization of 1,3,5-hexatriene to yield 1,3-cyclohexadiene is an electrocyclic reaction.

Electromagnetic spectrum (Section 12.5): The range of electromagnetic energy, including infrared, ultraviolet, and visible radiation.

Electron configuration (Section 1.3): A list of the orbitals occupied by electrons in an atom.

Electron-dot structure (Section 1.4): A representation of a molecule showing valence electrons as dots.

Electron-transport chain (Section 29.1): The final stage of catabolism in which ATP is produced.

Electronegativity (Section 2.1): The ability of an atom to attract electrons in a covalent bond. Electronegativity increases across the periodic table from right to left and from bottom to top.

Electrophile (Section 5.4): An "electron-lover," or substance that accepts an electron pair from a nucleophile in a polar bond-forming reaction.

Electrophilic addition reaction (Section 6.7): The addition of an electrophile to a carbon–carbon double bond to yield a saturated product.

Electrophilic aromatic substitution (Chapter 16 introduction): A reaction in which an electrophile (E^+) reacts with an aromatic ring and substitutes for one of the ring hydrogens.

Electrophoresis (Section 26.2): A technique used for separating charged organic molecules, particularly proteins and amino acids. The mixture to be separated is placed on a buffered gel or paper, and an electric potential is applied across the ends of the apparatus. Negatively charged molecules migrate toward the positive electrode, and positively charged molecules migrate toward the negative electrode.

Electrostatic potential map (Section 2.1): A molecular representation that uses color to indicate the charge distribution in the molecule as derived from quantum-mechanical calculations.

Elimination reaction (Section 5.1): What occurs when a single reactant splits into two products.

Elution (Chapter 12 *Focus On*): The removal of a substance from a chromatography column.

Embden–Meyerhof pathway (Section 29.5): An alternative name for glycolysis.

Enamine (Section 19.8): A compound with the $R_2N-CR=CR_2$ functional group.

Enantiomers (Section 9.1): Stereoisomers of a chiral substance that have a mirror-image relationship. Enantiomers must have opposite configurations at all chirality centers.

Enantioselective synthesis (Chapter 19 *Focus On*): A reaction method that yields only a single enantiomer of a chiral product starting from an achiral substrate.

Enantiotopic (Section 13.8): Two hydrogens in a molecule whose replacement by some other group leads to different enantiomers.

3′ End (Section 28.1): The end of a nucleic acid chain with a free hydroxyl group at C3′.

5′ End (Section 28.1): The end of a nucleic acid chain with a free hydroxyl group at C5′.

Endergonic (Section 5.7): A reaction that has a positive free-energy change and is therefore nonspontaneous. In a reaction energy diagram, the product of an endergonic reaction has a higher energy level than the reactants.

Endo (Section 14.5): A term indicating the stereochemistry of a substituent in a bridged bicycloalkane. An endo substituent is syn to the larger of the two bridges.

Endothermic (Section 5.7): A reaction that absorbs heat and therefore has a positive enthalpy change.

Energy diagram (Section 5.9): A representation of the course of a reaction, in which free energy is plotted as a function of reaction progress. Reactants, transition states, intermediates, and products are represented, and their appropriate energy levels are indicated.

Enol (Sections 8.4, 22.1): A vinylic alcohol that is in equilibrium with a carbonyl compound.

Enolate ion (Section 22.1): The anion of an enol.

Enthalpy change, ΔH (Section 5.7): The heat of reaction. The enthalpy change that occurs during a reaction is a measure of the difference in total bond energy between reactants and products.

Entropy change, ΔS (Section 5.7): The change in amount of molecular randomness. The entropy change that occurs during a reaction is a measure of the difference in randomness between reactants and products.

Enzyme (Section 26.10): A biological catalyst. Enzymes are large proteins that catalyze specific biochemical reactions.

Epoxide (Section 7.8): A three-membered-ring ether functional group.

Equatorial bond (Section 4.6): A bond to cyclohexane that lies along the rough equator of the ring.

ESI (Section 12.4): Electrospray ionization, a mild method for ionizing a molecule so that fragmentation is minimized during mass spectrometry.

Essential oil (Chapter 6 *Focus On*): The volatile oil obtained by steam distillation of a plant extract.

Ester (Chapter 21 introduction): A compound containing the $-CO_2R$ functional group.

Estrogen (Section 27.6): A female steroid sex hormone.

Ether (Chapter 18 introduction): A compound that has two organic substituents bonded to the same oxygen atom, ROR′.

Exergonic (Section 5.7): A reaction that has a negative free-energy change and is therefore spontaneous. On a reaction energy diagram, the product of an exergonic reaction has a lower energy level than that of the reactants.

Exo (Section 14.5): A term indicating the stereochemistry of a substituent in a bridged bicycloalkane. An exo substituent is anti to the larger of the two bridges.

Exon (Section 28.4): A section of DNA that contains genetic information.

Exothermic (Section 5.7): A reaction that releases heat and therefore has a negative enthalpy change.

Fat (Section 27.1): A solid triacylglycerol derived from an animal source.

Fatty acid (Section 27.1): A long, straight-chain carboxylic acid found in fats and oils.

Fiber (Section 31.5): A thin thread produced by extruding a molten polymer through small holes in a die.

Fibrous protein (Section 26.9): A protein that consists of polypeptide chains arranged side by side in long threads. Such proteins are tough, insoluble in water, and used in nature for structural materials such as hair, hooves, and fingernails.

Fingerprint region (Section 12.7): The complex region of the infrared spectrum from 1500 to 400 cm^{-1}.

First-order reaction (Section 11.4): A reaction whose rate-limiting step is unimolecular and whose kinetics therefore depend on the concentration of only one reactant.

Fischer esterification reaction (Section 21.3): The acid-catalyzed nucleophilic acyl substitution reaction of a carboxylic acid with an alcohol to yield an ester.

Fischer projection (Section 25.2): A means of depicting the absolute configuration of a chiral molecule on a flat page. A Fischer projection uses a cross to represent the chirality center. The horizontal arms of the cross represent bonds coming out of the plane of the page, and the vertical arms of the cross represent bonds going back into the plane of the page.

Fmoc derivative (Section 26.7): A fluorenylmethyloxycarbonyl amide-protected amino acid.

Formal charge (Section 2.3): The difference in the number of electrons owned by an atom in a molecule and by the same atom in its elemental state.

Formyl group (Section 19.1): A $-CHO$ group.

Frequency (Section 12.5): The number of electromagnetic wave cycles that travel past a fixed point in a given unit of time. Frequencies are expressed in units of cycles per second, or hertz.

Friedel–Crafts reaction (Section 16.3): An electrophilic aromatic substitution reaction to alkylate or acylate an aromatic ring.

Frontier orbitals (Section 30.1): The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.

FT-NMR (Section 13.4): Fourier-transform NMR; a rapid technique for recording NMR spectra in which all magnetic nuclei absorb at the same time.

Functional group (Section 3.1): An atom or group of atoms that is part of a larger molecule and that has a characteristic chemical reactivity.

Furanose (Section 25.5): The five-membered-ring form of a simple sugar.

Gabriel amine synthesis (Section 24.6): A method for preparing an amine by S_N2 reaction of an alkyl halide with potassium phthalimide, followed by hydrolysis.

Gauche conformation (Section 3.7): The conformation of butane in which the two methyl groups lie 60° apart as viewed in a Newman projection. This conformation has 3.8 kJ/mol steric strain.

Geminal (Section 19.5): Referring to two groups attached to the same carbon atom. For example, 1,1-dibromopropane is a geminal dibromide.

Gibbs free-energy change, ΔG (Section 5.7): The free-energy change that occurs during a reaction, given by the equation $\Delta G = \Delta H - T\Delta S$. A reaction with a negative free-energy change is spontaneous, and a reaction with a positive free-energy change is nonspontaneous.

Gilman reagent (Section 10.8): A diorganocopper reagent, R_2CuLi.

Glass transition temperature, T_g (Section 31.5): The temperature at which a hard, amorphous polymer becomes soft and flexible.

Globular protein (Section 26.9): A protein that is coiled into a compact, nearly spherical shape. These proteins, which are generally water-soluble and mobile within the cell, are the structural class to which enzymes belong.

Gluconeogenesis (Section 29.8): The anabolic pathway by which organisms make glucose from simple precursors.

Glycal assembly method (Section 25.11): A method for linking monosaccharides together to synthesis polysaccharides.

Glycerophospholipid (Section 27.3): A lipid that contains a glycerol backbone linked to two fatty acids and a phosphoric acid.

Glycoconjugate (Section 25.6): A biological molecule in which a carbohydrate is linked through a glycoside bond to a lipid or protein.

Glycol (Section 7.8): A diol, such as ethylene glycol, $HOCH_2CH_2OH$.

Glycolipid (Section 25.6): A biological molecule in which a carbohydrate is linked through a glycoside bond to a lipid.

Glycoprotein (Section 25.6): A biological molecule in which a carbohydrate is linked through a glycoside bond to a protein.

Glycolysis (Section 29.5): A series of ten enzyme-catalyzed reactions that break down glucose into 2 equivalents of pyruvate, $CH_3COCO_2^-$.

Glycoside (Section 25.6): A cyclic acetal formed by reaction of a sugar with another alcohol.

Graft copolymer (Section 31.3): A copolymer in which homopolymer branches of one monomer unit are "grafted" onto a homopolymer chain of another monomer unit.

Green chemistry (Chapter 11 *Focus On*): The design and implementation of chemical products and processes that reduce waste and minimize or eliminate the generation of hazardous substances.

Grignard reagent (Section 10.7): An organomagnesium halide, RMgX.

Ground state (Section 1.3): The most stable, lowest-energy electron configuration of a molecule or atom.

Haloform reaction (Section 22.6): The reaction of a methyl ketone with halogen and base to yield a haloform (CHX_3) and a carboxylic acid.

Halohydrin (Section 7.3): A 1,2-disubstituted haloalcohol, such as that obtained on addition of HOBr to an alkene.

Halonium ion (Section 7.2): A species containing a positively charged, divalent halogen. Three-membered-ring bromonium ions are implicated as intermediates in the electrophilic addition of Br_2 to alkenes.

Hammond postulate (Section 6.10): A postulate stating that we can get a picture of what a given transition state looks like by looking at the structure of the nearest stable species. Exergonic reactions have transition states that resemble reactant; endergonic reactions have transition states that resemble product.

Heat of hydrogenation (Section 6.6): The amount of heat released when a carbon–carbon double bond is hydrogenated.

Heat of reaction (Section 5.7): An alternative name for the enthalpy change in a reaction, ΔH.

Hell–Volhard–Zelinskii (HVZ) reaction (Section 22.4): The reaction of a carboxylic acid with Br_2 and phosphorus to give an α-bromo carboxylic acid.

Hemiacetal (Section 19.10): A functional group consisting of one −OR and one −OH group bonded to the same carbon.

Henderson–Hasselbalch equation (Sections 20.3, 24.5, 26.2): An equation for determining the extent of deprotonation of a weak acid at various pH values.

Heterocycle (Sections 15.5, 24.9): A cyclic molecule whose ring contains more than one kind of atom. For example, pyridine is a heterocycle that contains five carbon atoms and one nitrogen atom in its ring.

Heterolytic bond breakage (Section 5.2): The kind of bond-breaking that occurs in polar reactions when one fragment leaves with both of the bonding electrons: $A{:}B \rightarrow A^+ + B{:}^-$.

Hofmann elimination (Section 24.7): The elimination reaction of an amine to yield an alkene by reaction with iodomethane, followed by heating with Ag_2O.

Hofmann rearrangement (Section 24.6): The conversion of an amide into an amine by reaction with Br_2 and base.

HOMO (Sections 14.7, 30.2): An acronym for highest occupied molecular orbital. The symmetries of the HOMO and LUMO are important in pericyclic reactions.

Homolytic bond breakage (Section 5.2): The kind of bond-breaking that occurs in radical reactions when each fragment leaves with one bonding electron: $A{:}B \rightarrow A\cdot + B\cdot$.

Homopolymer (Section 31.3): A polymer made up of identical repeating units.

Homotopic (Section 13.8): Hydrogens that give the identical structure on replacement by X and thus show identical NMR absorptions.

Hormone (Section 27.6): A chemical messenger that is secreted by an endocrine gland and carried through the bloodstream to a target tissue.

Hückel's rule (Section 15.3): A rule stating that monocyclic conjugated molecules having $4n + 2$ π electrons (n = an integer) are aromatic.

Hund's rule (Section 1.3): If two or more empty orbitals of equal energy are available, one electron occupies each, with their spins parallel, until all are half-full.

Hybrid orbital (Section 1.6): An orbital derived from a combination of atomic orbitals. Hybrid orbitals, such as the sp^3, sp^2, and sp hybrids of carbon, are strongly directed and form stronger bonds than atomic orbitals do.

Hydration (Section 7.4): Addition of water to a molecule, such as occurs when alkenes are treated with aqueous sulfuric acid to give alcohols.

Hydride shift (Section 6.11): The shift of a hydrogen atom and its electron pair to a nearby cationic center.

Hydroboration (Section 7.5): Addition of borane (BH_3) or an alkylborane to an alkene. The resultant trialkylborane products are useful synthetic intermediates that can be oxidized to yield alcohols.

Hydrocarbon (Section 3.2): A compound that contains only carbon and hydrogen.

Hydrogen bond (Section 2.13): A weak attraction between a hydrogen atom bonded to an electronegative atom and an electron lone pair on another electronegative atom.

Hydrogenation (Section 7.7): Addition of hydrogen to a double or triple bond to yield a saturated product.

Hydrogenolysis (Section 26.7): Cleavage of a bond by reaction with hydrogen. Benzylic ethers and esters, for instance, are cleaved by hydrogenolysis.

Hydrophilic (Section 2.13): Water-loving; attracted to water.

Hydrophobic (Section 2.13): Water-fearing; repelled by water.

Hydroquinone (Section 17.10): A 1,4-dihydroxybenzene.

Hydroxylation (Section 7.8): Addition of two −OH groups to a double bond.

Hyperconjugation (Sections 6.6, 6.9): An interaction that results from overlap of a vacant *p* orbital on one atom with a neighboring C−H σ bond. Hyperconjugation is important in stabilizing carbocations and in stabilizing substituted alkenes.

Imide (Section 24.6): A compound with the −CONHCO− functional group.

Imine (Section 19.8): A compound with the $R_2C{=}NR$ functional group.

Inductive effect (Sections 2.1, 6.9, 16.4): The electron-attracting or electron-withdrawing effect transmitted through σ bonds. Electronegative elements have an electron-withdrawing inductive effect.

Infrared (IR) spectroscopy (Section 12.6): A kind of optical spectroscopy that uses infrared energy. IR spectroscopy is particularly useful in organic chemistry for determining the kinds of functional groups present in molecules.

Initiator (Section 5.3): A substance with an easily broken bond that is used to initiate a radical chain reaction. For example, radical chlorination of alkanes is initiated when light energy breaks the weak Cl−Cl bond to form Cl· radicals.

Integration (Section 13.10): A technique for measuring the area under an NMR peak to determine the relative number of each kind of proton in a molecule. Integrated peak areas are superimposed over the spectrum as a "stair-step" line, with the height of each step proportional to the area underneath the peak.

Intermediate (Section 5.10): A species that is formed during the course of a multistep reaction but is not the final product. Intermediates are more stable than transition states but may or may not be stable enough to isolate.

Intramolecular, intermolecular (Section 23.6): A reaction that occurs within the same molecule is intramolecular; a reaction that occurs between two molecules is intermolecular.

Intron (Section 28.4): A section of DNA that does not contain genetic information.

Ion pair (Section 11.5): A loose complex between two ions in solution. Ion pairs are implicated as intermediates in S_N1 reactions to account for the partial retention of stereochemistry that is often observed.

Isoelectric point, p*I* (Section 26.2): The pH at which the number of positive charges and the number of negative charges on a protein or an amino acid are equal.

Isomers (Sections 3.2, 9.9): Compounds that have the same molecular formula but different structures.

Isoprene rule (Chapter 6 *Focus On*): An observation to the effect that terpenoids appear to be made up of isoprene (2-methyl-1,3-butadiene) units connected head-to-tail.

Isotactic (Section 31.2): A chain-growth polymer in which the substituents are regularly oriented on the same side of the backbone.

Isotopes (Section 1.1): Atoms of the same element that have different mass numbers.

IUPAC system of nomenclature (Section 3.4): Rules for naming compounds, devised by the International Union of Pure and Applied Chemistry.

Kekulé structure (Section 1.4): A method of representing molecules in which a line between atoms indicates a bond.

Keto–enol tautomerism (Sections 8.4, 22.1): The rapid equilibration between a carbonyl form and vinylic alcohol form of a molecule.

Ketone (Chapter 19 introduction): A compound with two organic substituents bonded to a carbonyl group, $R_2C{=}O$.

Ketose (Section 25.1): A carbohydrate with a ketone functional group.

Kiliani–Fischer synthesis (Section 25.6): A method for lengthening the chain of an aldose sugar.

Kinetic control (Section 14.3): A reaction that follows the lowest activation energy pathway is said to be kinetically controlled. The product is the most rapidly formed but is not necessarily the most stable.

Kinetics (Section 11.2): Referring to reaction rates. Kinetic measurements are useful for helping to determine reaction mechanisms.

Koenigs–Knorr reaction (Section 25.6): A method for the synthesis of glycosides by reaction of an alcohol with a pyranosyl bromide.

Krebs cycle (Section 29.7): An alternative name for the citric acid cycle, by which acetyl CoA is degraded to CO_2.

L **Sugar** (Section 25.3): A sugar whose hydroxyl group at the chirality center farthest from the carbonyl group points to the left when drawn in Fischer projection.

Lactam (Section 21.7): A cyclic amide.

Lactone (Section 21.6): A cyclic ester.

Leaving group (Section 11.2): The group that is replaced in a substitution reaction.

Levorotatory (Section 9.3): An optically active substance that rotates the plane of polarization of plane-polarized light in a left-handed (counterclockwise) direction.

Lewis acid (Section 2.11): A substance with a vacant low-energy orbital that can accept an electron pair from a base. All electrophiles are Lewis acids.

Lewis base (Section 2.11): A substance that donates an electron lone pair to an acid. All nucleophiles are Lewis bases.

Lewis structure (Section 1.5): A representation of a molecule showing valence electrons as dots.

Lindlar catalyst (Section 8.5): A hydrogenation catalyst used to convert alkynes to cis alkenes.

Line-bond structure (Section 1.5): A representation of a molecule showing covalent bonds as lines between atoms.

1□4 Link (Section 25.8): An acetal link between the C1 −OH group of one sugar and the C4 −OH group of another sugar.

Lipid (Section 27.1): A naturally occurring substance isolated from cells and tissues by extraction with a nonpolar solvent. Lipids belong to many different structural classes, including fats, terpenes, prostaglandins, and steroids.

Lipid bilayer (Section 27.3): The ordered lipid structure that forms a cell membrane.

Lipoprotein (Chapter 27 *Focus On*): A complex molecule with both lipid and protein parts that transports lipids through the body.

Lone-pair electrons (Section 1.4): Nonbonding valence-shell electron pairs. Lone-pair electrons are used by nucleophiles in their reactions with electrophiles.

LUMO (Sections 14.4, 30.2): An acronym for lowest unoccupied molecular orbital. The symmetries of the LUMO and the HOMO are important in determining the stereochemistry of pericyclic reactions.

Magnetic resonance imaging, MRI (Chapter 13 *Focus On*): A medical diagnostic technique based on nuclear magnetic resonance.

MALDI (Section 12.4): Matrix-assisted laser desorption ionization; a mild method for ionizing a molecule so that fragmentation is minimized during mass spectrometry.

Malonic ester synthesis (Section 22.7): The synthesis of a carboxylic acid by alkylation of an alkyl halide, followed by hydrolysis and decarboxylation.

Markovnikov's rule (Section 6.8): A guide for determining the regiochemistry (orientation) of electrophilic addition reactions. In the addition of HX to an alkene, the hydrogen atom bonds to the alkene carbon that has fewer alkyl substituents.

Mass number, *A* (Section 1.1): The total of protons plus neutrons in an atom.

Mass spectrometry (Section 12.1): A technique for measuring the mass, and therefore the molecular weight (MW), of ions.

McLafferty rearrangement (Section 12.3): A mass-spectral fragmentation pathway for carbonyl compounds.

Mechanism (Section 5.2): A complete description of how a reaction occurs. A mechanism must account for all starting materials and all products and must describe the details of each individual step in the overall reaction process.

Meisenheimer complex (Section 16.7): An intermediate formed by addition of a nucleophile to a halo-substituted aromatic ring.

Melt transition temperature, T_m (Section 31.5): The temperature at which crystalline regions of a polymer melt to give an amorphous material.

Mercapto group (Section 18.8): An alternative name for the thiol group, −SH.

Meso compound (Section 9.7): A compound that contains chirality centers but is nevertheless achiral by virtue of a symmetry plane.

Messenger RNA (Section 28.4): A kind of RNA formed by transcription of DNA and used to carry genetic messages from DNA to ribosomes.

Meta- (Section 15.1): A naming prefix used for 1,3-disubstituted benzenes.

Metabolism (Section 29.1): A collective name for the many reactions that go on in the cells of living organisms.

Methylene group (Section 6.3): A $-CH_2-$ or $=CH_2$ group.

Micelle (Section 27.2): A spherical cluster of soaplike molecules that aggregate in aqueous solution. The ionic heads of the molecules lie on the outside, where they are solvated by water, and the organic tails bunch together on the inside of the micelle.

Michael reaction (Section 23.10): The conjugate addition reaction of an enolate ion to an unsaturated carbonyl compound.

Molar absorptivity (Section 14.7): A quantitative measure of the amount of UV light absorbed by a sample.

Molecular ion (Section 12.1): The cation produced in the mass spectrometer by loss of an electron from the parent molecule. The mass of the molecular ion corresponds to the molecular weight of the sample.

Molecular mechanics (Chapter 4 *Focus On*): A computer-based method for calculating the minimum-energy conformation of a molecule.

Molecular orbital (MO) theory (Section 1.11): A description of covalent bond formation as resulting from a mathematical combination of atomic orbitals (wave functions) to form molecular orbitals.

Molecule (Section 1.5): A neutral collection of atoms held together by covalent bonds.

Molozonide (Section 7.9): The initial addition product of ozone with an alkene.

Monomer (Section 7.10, Chapter 31 introduction): The simple starting unit from which a polymer is made.

Monosaccharide (Section 25.1): A simple sugar.

Monoterpenoid (Chapter 6 *Focus On*, Section 27.5): A ten-carbon lipid.

Multiplet (Section 13.11): A pattern of peaks in an NMR spectrum that arises by spin–spin splitting of a single absorption because of coupling between neighboring magnetic nuclei.

Mutarotation (Section 25.5): The change in optical rotation observed when a pure anomer of a sugar is dissolved in water. Mutarotation is caused by the reversible opening and closing of the acetal linkage, which yields an equilibrium mixture of anomers.

***n* + 1 rule** (Section 13.11): A hydrogen with n other hydrogens on neighboring carbons shows $n + 1$ peaks in its ^{1}H NMR spectrum.

N-terminal amino acid (Section 26.4): The amino acid with a free $-NH_2$ group at the end of a protein chain.

Newman projection (Section 3.6): A means of indicating stereochemical relationships between substituent groups on neighboring carbons. The carbon–carbon bond is viewed end-on, and the carbons are indicated by a circle. Bonds radiating from the center of the circle are attached to the front carbon, and bonds radiating from the edge of the circle are attached to the rear carbon.

Nitrile (Section 20.1): A compound containing the C≡N functional group.

Nitrogen rule (Section 24.10): A compound with an odd number of nitrogen atoms has an odd-numbered molecular weight.

Node (Section 1.2): A surface of zero electron density within an orbital. For example, a *p* orbital has a nodal plane passing through the center of the nucleus, perpendicular to the axis of the orbital.

Nonbonding electrons (Section 1.4): Valence electrons that are not used in forming covalent bonds.

Noncovalent interaction (Section 2.13): An interaction between molecules, commonly called intermolecular forces or van der Waals forces. Hydrogen bonds, dipole–dipole forces, and dispersion forces are examples.

Normal alkane (Section 3.2): A straight-chain alkane, as opposed to a branched alkane. Normal alkanes are denoted by the suffix *n*, as in *n*-C_4H_{10} (*n*-butane).

NSAID (Chapter 15 *Focus On*): A nonsteroidal anti-inflammatory drug, such as aspirin or ibuprofen.

Nuclear magnetic resonance, NMR (Chapter 13 introduction): A spectroscopic technique that provides information about the carbon–hydrogen framework of a molecule. NMR works by detecting the energy absorptions accompanying the transitions between nuclear spin states that occur when a molecule is placed in a strong magnetic field and irradiated with radiofrequency waves.

Nucleophile (Section 5.4): A "nucleus-lover," or species that donates an electron pair to an electrophile in a polar bond-forming reaction. Nucleophiles are also Lewis bases.

Nucleophilic acyl substitution reaction (Section 21.2): A reaction in which a nucleophile attacks a carbonyl compound and substitutes for a leaving group bonded to the carbonyl carbon.

Nucleophilic addition reaction (Section 19.4): A reaction in which a nucleophile adds to the electrophilic carbonyl group of a ketone or aldehyde to give an alcohol.

Nucleophilic aromatic substitution reaction (Section 16.7): The substitution reaction of an aryl halide by a nucleophile.

Nucleophilic substitution reaction (Section 11.1): A reaction in which one nucleophile replaces another attached to a saturated carbon atom.

Nucleophilicity (Section 11.3): The ability of a substance to act as a nucleophile in an S_N2 reaction.

Nucleoside (Section 28.1): A nucleic acid constituent, consisting of a sugar residue bonded to a heterocyclic purine or pyrimidine base.

Nucleotide (Section 28.1): A nucleic acid constituent, consisting of a sugar residue bonded both to a heterocyclic purine or pyrimidine base and to a phosphoric acid.

Nucleotides are the monomer units from which DNA and RNA are constructed.

Nylon (Section 21.9): A synthetic polyamide step-growth polymer.

Olefin (Chapter 6 introduction): An alternative name for an alkene.

Optical isomers (Section 9.4): An alternative name for enantiomers. Optical isomers are isomers that have a mirror-image relationship.

Optically active (Section 9.3): A substance that rotates the plane of polarization of plane-polarized light.

Orbital (Section 1.2): A wave function, which describes the volume of space around a nucleus in which an electron is most likely to be found.

Organic chemistry (Chapter 1 introduction): The study of carbon compounds.

Ortho- (Section 15.1): A naming prefix used for 1,2-disubstituted benzenes.

Oxidation (Sections 7.8, 10.9): A reaction that causes a decrease in electron ownership by carbon, either by bond formation between carbon and a more electronegative atom (usually oxygen, nitrogen, or a halogen) or by bond-breaking between carbon and a less electronegative atom (usually hydrogen).

Oxime (Section 19.8): A compound with the $R_2C{=}NOH$ functional group.

Oxirane (Section 7.8): An alternative name for an epoxide.

Oxymercuration (Section 7.4): A method for double-bond hydration using aqueous mercuric acetate as the reagent.

Ozonide (Section 7.9): The product formed by addition of ozone to a carbon–carbon double bond. Ozonides are usually treated with a reducing agent, such as zinc in acetic acid, to produce carbonyl compounds.

Para- (Section 15.1): A naming prefix used for 1,4-disubstituted benzenes.

Paraffin (Section 3.5): A common name for alkanes.

Parent peak (Section 12.1): The peak in a mass spectrum corresponding to the molecular ion. The mass of the parent peak therefore represents the molecular weight of the compound.

Pauli exclusion principle (Section 1.3): No more than two electrons can occupy the same orbital, and those two must have spins of opposite sign.

Peptide (Section 26.4): A short amino acid polymer in which the individual amino acid residues are linked by amide bonds.

Peptide bond (Section 26.4): An amide bond in a peptide chain.

Pericyclic reaction (Chapter 30 introduction): A reaction that occurs by a concerted reorganization of bonding electrons in a cyclic transition state.

Periplanar (Section 11.8): A conformation in which bonds to neighboring atoms have a parallel arrangement. In an eclipsed conformation, the neighboring bonds are syn periplanar; in a staggered conformation, the bonds are anti periplanar.

Peroxide (Section 18.1): A molecule containing an oxygen–oxygen bond functional group, ROOR′ or ROOH.

Peroxyacid (Section 7.8): A compound with the $-CO_3H$ functional group. Peroxyacids react with alkenes to give epoxides.

Phenol (Chapter 17 introduction): A compound with an $-OH$ group directly bonded to an aromatic ring, ArOH.

Phenyl (Section 15.1): The name for the $-C_6H_5$ unit when the benzene ring is considered as a substituent. A phenyl group is abbreviated as $-Ph$.

Phospholipid (Section 27.3): A lipid that contains a phosphate residue. For example, glycerophospholipids contain a glycerol backbone linked to two fatty acids and a phosphoric acid.

Phosphoric acid anhydride (Section 29.1): A substance that contains PO_2PO link, analogous to the CO_2CO link in carboxylic acid anhydrides.

Photochemical reaction (Section 30.3): A reaction carried out by irradiating the reactants with light.

Pi (π) bond (Section 1.8): The covalent bond formed by sideways overlap of atomic orbitals. For example, carbon–carbon double bonds contain a π bond formed by sideways overlap of two p orbitals.

PITC (Section 26.6): Phenylisothiocyanate; used in the Edman degradation.

Plane of symmetry (Section 9.2): A plane that bisects a molecule such that one half of the molecule is the mirror image of the other half. Molecules containing a plane of symmetry are achiral.

Plane-polarized light (Section 9.3): Ordinary light that has its electromagnetic waves oscillating in a single plane rather than in random planes. The plane of polarization is rotated when the light is passed through a solution of a chiral substance.

Plasticizer (Section 31.5): A small organic molecule added to polymers to act as a lubricant between polymer chains.

Polar aprotic solvent (Section 11.3): A polar solvent that can't function as a hydrogen ion donor. Polar aprotic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) are particularly useful in S_N2 reactions because of their ability to solvate cations.

Polar covalent bond (Section 2.1): A covalent bond in which the electron distribution between atoms is unsymmetrical.

Polar reaction (Section 5.2): A reaction in which bonds are made when a nucleophile donates two electrons to an electrophile and in which bonds are broken when one fragment leaves with both electrons from the bond.

Polarity (Section 2.1): The unsymmetrical distribution of electrons in a molecule that results when one atom attracts electrons more strongly than another.

Polarizability (Section 5.4): The measure of the change in a molecule's electron distribution in response to changing electric interactions with solvents or ionic reagents.

Polycarbonate (Section 31.4): A polyester in which the carbonyl groups are linked to two −OR groups, $[O{=}C(OR)_2]$.

Polycyclic (Section 4.9): A compound that contains more than one ring.

Polycyclic aromatic compound (Section 15.7): A compound with two or more benzene-like aromatic rings fused together.

Polymer (Sections 7.10, 21.9, Chapter 31 introduction): A large molecule made up of repeating smaller units. For example, polyethylene is a synthetic polymer made from repeating ethylene units, and DNA is a biopolymer made of repeating deoxyribonucleotide units.

Polymerase chain reaction, PCR (Section 28.8): A method for amplifying small amounts of DNA to produce larger amounts.

Polysaccharide (Section 25.1): A carbohydrate that is made of many simple sugars linked together by acetal bonds.

Polyunsaturated fatty acid (Section 27.1): A fatty acid that contains more than one double bond.

Polyurethane (Section 31.4): A step-growth polymer prepared by reaction between a diol and a diisocyanate.

Primary, secondary, tertiary, quaternary (Section 3.3): Terms used to describe the substitution pattern at a specific site. A primary site has one organic substituent attached to it, a secondary site has two organic substituents, a tertiary site has three, and a quaternary site has four.

	Carbon	Carbocation	Hydrogen	Alcohol	Amine
Primary	RCH_3	RCH_2^+	RCH_3	RCH_2OH	RNH_2
Secondary	R_2CH_2	R_2CH^+	R_2CH_2	R_2CHOH	R_2NH
Tertiary	R_3CH	R_3C^+	R_3CH	R_3COH	R_3N
Quaternary	R_4C				

Primary structure (Section 26.9): The amino acid sequence in a protein.

pro-R (Section 9.13): One of two identical atoms in a compound, whose replacement leads to an *R* chirality center.

pro-S (Section 9.13): One of two identical atoms in a compound whose replacement leads to an *S* chirality center.

Prochiral (Section 9.13): A molecule that can be converted from achiral to chiral in a single chemical step.

Prochirality center (Section 9.13): An atom in a compound that can be converted into a chirality center by changing one of its attached substituents.

Propagation step (Section 5.3): The step or series of steps in a radical chain reaction that carry on the chain. The propagation steps must yield both product and a reactive intermediate.

Prostaglandin (Section 27.4): A lipid derived from arachidonic acid. Prostaglandins are present in nearly all body tissues and fluids, where they serve many important hormonal functions.

Protecting group (Sections 17.8, 19.10, 26.7): A group that is introduced to protect a sensitive functional group toward reaction elsewhere in the molecule. After serving its protective function, the group is removed.

Protein (Section 26.4): A large peptide containing 50 or more amino acid residues. Proteins serve both as structural materials and as enzymes that control an organism's chemistry.

Protic solvent (Section 11.3): A solvent such as water or alcohol that can act as a proton donor.

Pyramidal inversion (Section 24.2): The rapid stereochemical inversion of a trivalent nitrogen compound.

Pyranose (Section 25.5): The six-membered-ring form of a simple sugar.

Quartet (Section 13.11): A set of four peaks in an NMR spectrum, caused by spin–spin splitting of a signal by three adjacent nuclear spins.

Quaternary (*See* Primary)

Quaternary ammonium salt (Section 24.1): An ionic compound containing a positively charged nitrogen atom with four attached groups, $R_4N^+ X^-$.

Quaternary structure (Section 26.9): The highest level of protein structure, involving a specific aggregation of individual proteins into a larger cluster.

Quinone (Section 17.10): A 2,5-cyclohexadiene-1,4-dione.

R group (Section 3.3): A generalized abbreviation for an organic partial structure.

***R*,*S* convention** (Section 9.5): A method for defining the absolute configuration at chirality centers using the Cahn–Ingold–Prelog sequence rules.

Racemic mixture (Section 9.8): A mixture consisting of equal parts (+) and (−) enantiomers of a chiral substance.

Radical (Section 5.2): A species that has an odd number of electrons, such as the chlorine radical, Cl·.

Radical reaction (Section 5.2): A reaction in which bonds are made by donation of one electron from each of two reactants and in which bonds are broken when each fragment leaves with one electron.

Rate constant (Section 11.2): The constant k in a rate equation.

Rate equation (Section 11.2): An equation that expresses the dependence of a reaction's rate on the concentration of reactants.

Rate-limiting step (Section 11.4): The slowest step in a multistep reaction sequence. The rate-limiting step acts as a kind of bottleneck in multistep reactions.

***Re* face** (Section 9.13): One of two faces of a planar, sp^2-hybridized atom.

Rearrangement reaction (Section 5.1): What occurs when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product.

Reducing sugar (Section 25.6): A sugar that reduces silver ion in the Tollens test or cupric ion in the Fehling or Benedict tests.

Reduction (Sections 7.7, 10.9): A reaction that causes an increase of electron ownership by carbon, either by bond-breaking between carbon and a more electronegative atom or by bond formation between carbon and a less electronegative atom.

Reductive amination (Sections 24.6, 26.3): A method for preparing an amine by reaction of an aldehyde or ketone with ammonia and a reducing agent.

Refining (Chapter 3 *Focus On*): The process by which petroleum is converted into gasoline and other useful products.

Regiochemistry (Section 6.8): A term describing the orientation of a reaction that occurs on an unsymmetrical substrate.

Regiospecific (Section 6.8): A term describing a reaction that occurs with a specific regiochemistry to give a single product rather than a mixture of products.

Replication (Section 28.3): The process by which double-stranded DNA uncoils and is replicated to produce two new copies.

Replication fork (Section 28.3): The point of unraveling in a DNA chain where replication occurs.

Residue (Section 26.4): An amino acid in a protein chain.

Resolution (Section 9.8): The process by which a racemic mixture is separated into its two pure enantiomers.

Resonance effect (Section 16.4): The donation or withdrawal of electrons through orbital overlap with neighboring π bonds. For example, an oxygen or nitrogen substituent donates electrons to an aromatic ring by overlap of the O or N orbital with the aromatic ring p orbitals.

Resonance form (Section 2.4): An individual Lewis structure of a resonance hybrid.

Resonance hybrid (Section 2.4): A molecule, such as benzene, that can't be represented adequately by a single Kekulé structure but must instead be considered as an average of two or more resonance structures. The resonance structures themselves differ only in the positions of their electrons, not their nuclei.

Restriction endonuclease (Section 28.6): An enzyme that is able to cleave a DNA molecule at points in the chain where a specific base sequence occurs.

Retrosynthetic (Sections 8.9, 16.11): A strategy for planning organic syntheses by working backward from the final product to the starting material.

Ribonucleic acid (RNA) (Section 28.1): The biopolymer found in cells that serves to transcribe the genetic information found in DNA and uses that information to direct the synthesis of proteins.

Ribosomal RNA (Section 28.4): A kind of RNA used in the physical makeup of ribosomes.

Ring current (Section 15.8): The circulation of π electrons induced in aromatic rings by an external magnetic field. This effect accounts for the downfield shift of aromatic ring protons in the ^{1}H NMR spectrum.

Ring-flip (Section 4.6): A molecular motion that converts one chair conformation of cyclohexane into another chair conformation. The effect of a ring-flip is to convert an axial substituent into an equatorial substituent.

RNA (*See* Ribonucleic acid; Section 28.1)

Robinson annulation reaction (Section 23.12): A synthesis of cyclohexenones by sequential Michael reaction and intramolecular aldol reaction.

***s*-cis conformation** (Section 14.5): The conformation of a conjugated diene that is cis-like around the single bond.

Saccharide (Section 25.1): A sugar.

Salt bridge (Section 26.9): The ionic attraction between two oppositely charged groups in a protein chain.

Sandmeyer reaction (Section 24.8): The nucleophilic substitution reaction of an arenediazonium salt with a cuprous halide to yield an aryl halide.

Sanger dideoxy method (Section 2.6): The most commonly used method of DNA sequencing.

Saponification (Section 21.6): An old term for the base-induced hydrolysis of an ester to yield a carboxylic acid salt.

Saturated (Section 3.2): A molecule that has only single bonds and thus can't undergo addition reactions. Alkanes are saturated, but alkenes are unsaturated.

Sawhorse structure (Section 3.6): A manner of representing stereochemistry that uses a stick drawing and gives a perspective view of the conformation around a single bond.

Schiff base (Sections 19.8, 29.5): An alternative name for an imine, $R_2C{=}NR'$, used primarily in biochemistry.

Second-order reaction (Section 11.2): A reaction whose rate-limiting step is bimolecular and whose kinetics are therefore dependent on the concentration of two reactants.

Secondary (*See* Primary)

Secondary structure (Section 26.9): The level of protein substructure that involves organization of chain sections into ordered arrangements such as β-pleated sheets or α helices.

Semiconservative replication (Section 28.3): The process by which DNA molecules are made containing one strand of old DNA and one strand of new DNA.

Sequence rules (Sections 6.5, 9.5): A series of rules for assigning relative priorities to substituent groups on a double-bond carbon atom or on a chirality center.

Sesquiterpenoid (Section 27.5): A 15-carbon lipid.

Shell (electron) (Section 1.2): A group of an atom's electrons with the same principal quantum number.

Shielding (Section 13.2): An effect observed in NMR that causes a nucleus to absorb toward the right (upfield) side of the chart. Shielding is caused by donation of electron density to the nucleus.

***Si* face** (Section 9.13): One of two faces of a planar, sp^2-hybridized atom.

Sialic acid (Section 25.7): A group of more than 300 carbohydrates based on acetylneuramic acid.

Side chain (Section 26.1): The substituent attached to the α carbon of an amino acid.

Sigma (σ) bond (Section 1.6): A covalent bond formed by head-on overlap of atomic orbitals.

Sigmatropic reaction (Section 30.8): A pericyclic reaction that involves the migration of a group from one end of a π electron system to the other.

Simmons–Smith reaction (Section 7.6): The reaction of an alkene with CH_2I_2 and Zn−Cu to yield a cyclopropane.

Simple sugar (Section 25.1): A carbohydrate that cannot be broken down into smaller sugars by hydrolysis.

Skeletal structure (Section 1.12): A shorthand way of writing structures in which carbon atoms are assumed to be at each intersection of two lines (bonds) and at the end of each line.

S_N1 reaction (Section 11.4): A unimolecular nucleophilic substitution reaction.

S_N2 reaction (Section 11.2): A bimolecular nucleophilic substitution reaction.

Solid-phase synthesis (Section 26.8): A technique of synthesis whereby the starting material is covalently bound to a solid polymer bead and reactions are carried out on the bound substrate. After the desired transformations have been effected, the product is cleaved from the polymer.

Solvation (Sections 11.3): The clustering of solvent molecules around a solute particle to stabilize it.

***sp* Orbital** (Section 1.9): A hybrid orbital derived from the combination of an *s* and a *p* atomic orbital. The two *sp* orbitals that result from hybridization are oriented at an angle of 180° to each other.

***sp*^{2} Orbital** (Section 1.8): A hybrid orbital derived by combination of an *s* atomic orbital with two *p* atomic orbitals. The three sp^2 hybrid orbitals that result lie in a plane at angles of 120° to each other.

sp^3 Orbital (Section 1.6): A hybrid orbital derived by combination of an *s* atomic orbital with three *p* atomic orbitals. The four sp^3 hybrid orbitals that result are directed toward the corners of a regular tetrahedron at angles of 109° to each other.

Specific rotation, $[\alpha]_D$ (Section 9.3): The optical rotation of a chiral compound under standard conditions.

Sphingomyelin (Section 27.3): A phospholipid that has sphingosine as its backbone.

Spin–spin splitting (Section 13.11): The splitting of an NMR signal into a multiplet because of an interaction between nearby magnetic nuclei whose spins are coupled. The magnitude of spin–spin splitting is given by the coupling constant, *J*.

Staggered conformation (Section 3.4): The three-dimensional arrangement of atoms around a carbon–carbon single bond in which the bonds on one carbon bisect the bond angles on the second carbon as viewed end-on.

Step-growth polymer (Sections 21.9, 31.4): A polymer in which each bond is formed independently of the others. Polyesters and polyamides (nylons) are examples.

Stereochemistry (Chapters 3, 4, 9): The branch of chemistry concerned with the three-dimensional arrangement of atoms in molecules.

Stereoisomers (Section 4.2): Isomers that have their atoms connected in the same order but have different three-dimensional arrangements. The term *stereoisomer* includes both enantiomers and diastereomers.

Stereospecific (Section 7.6): A term indicating that only a single stereoisomer is produced in a given reaction rather than a mixture.

Steric strain (Sections 3.7): The strain imposed on a molecule when two groups are too close together and try to occupy the same space. Steric strain is responsible both for the greater stability of trans versus cis alkenes and for the greater stability of equatorially substituted versus axially substituted cyclohexanes.

Steroid (Section 27.6): A lipid whose structure is based on a tetracyclic carbon skeleton with three 6-membered and one 5-membered ring. Steroids occur in both plants and animals and have a variety of important hormonal functions.

Stork reaction (Section 23.11): A carbonyl condensation between an enamine and an α,β-unsaturated acceptor in a Michael-like reaction to yield a 1,5-dicarbonyl product.

Straight-chain alkane (Section 3.2): An alkane whose carbon atoms are connected without branching.

Substitution reaction (Section 5.1): What occurs when two reactants exchange parts to give two new products. S_N1 and S_N2 reactions are examples.

Sulfide (Section 18.8): A compound that has two organic substituents bonded to the same sulfur atom, RSR′.

Sulfone (Section 18.8): A compound of the general structure RSO_2R'.

Sulfonium ion (Section 18.8): A species containing a positively charged, trivalent sulfur atom, R_3S^+.

Sulfoxide (Section 18.8): A compound of the general structure RSOR′.

Suprafacial (Section 30.6): A word used to describe the geometry of pericyclic reactions. Suprafacial reactions take place on the same side of the two ends of a π electron system.

Symmetry-allowed, symmetry-disallowed (Section 30.2): A symmetry-allowed reaction is a pericyclic process that has a favorable orbital symmetry for reaction through a concerted pathway. A symmetry-disallowed reaction is one that does not have favorable orbital symmetry for reaction through a concerted pathway.

Symmetry plane (Section 9.2): A plane that bisects a molecule such that one half of the molecule is the mirror image of the other half. Molecules containing a plane of symmetry are achiral.

Syn periplanar (Section 11.8): Describing a stereochemical relationship in which two bonds on adjacent carbons lie in the same plane and are eclipsed.

Syn stereochemistry (Section 7.5): The opposite of anti. A syn addition reaction is one in which the two ends of the double bond react from the same side. A syn elimination is one in which the two groups leave from the same side of the molecule.

Syndiotactic (Section 31.2): A chain-growth polymer in which the substituents regularly alternate on opposite sides of the backbone.

Tautomers (Sections 8.4, 22.1): Isomers that are rapidly interconverted.

Template strand (Section 28.4): The strand of double-helical DNA that does not contain the gene.

Terpenoid (Chapter 6 *Focus On,* Section 27.5): A lipid that is formally derived by head-to-tail polymerization of isoprene units.

Tertiary (*See* Primary)

Tertiary structure (Section 26.9): The level of protein structure that involves the manner in which the entire protein chain is folded into a specific three-dimensional arrangement.

Thermodynamic control (Section 14.3): An equilibrium reaction that yields the lowest-energy, most stable product is said to be thermodynamically controlled.

Thermoplastic (Section 31.5): A polymer that has a high T_g and is therefore hard at room temperature, but becomes soft and viscous when heated.

Thermosetting resin (Section 31.5): A polymer that becomes highly cross-linked and solidifies into a hard, insoluble mass when heated.

Thioester (Section 21.8): A compound with the RCOSR′ functional group.

Thiol (Section 18.8): A compound containing the −SH functional group.

Thiolate ion (Section 18.8): The anion of a thiol, RS^-.

TMS (Section 13.3): Tetramethylsilane; used as an NMR calibration standard.

TOF (Section 12.4): Time-of flight mass spectrometry; a sensitive method of mass detection accurate to about 3 ppm.

Tollens' reagent (Section 19.3): A solution of Ag_2O in aqueous ammonia; used to oxidize aldehydes to carboxylic acids.

Torsional strain (Section 3.6): The strain in a molecule caused by electron repulsion between eclipsed bonds. Torsional strain is also called eclipsing strain.

Tosylate (Section 11.1): A *p*-toluenesulfonate ester; useful as a leaving group in nucleophilic substitution reactions.

Transamination (Section 29.9): The exchange of an amino group and a keto group between reactants.

Transcription (Section 28.4): The process by which the genetic information encoded in DNA is read and used to synthesize RNA in the nucleus of the cell. A small portion of double-stranded DNA uncoils, and complementary ribonucleotides line up in the correct sequence for RNA synthesis.

Transfer RNA (Section 28.4): A kind of RNA that transports amino acids to the ribosomes, where they are joined together to make proteins.

Transition state (Section 5.9): An activated complex between reactants, representing the highest energy point on a reaction curve. Transition states are unstable complexes that can't be isolated.

Translation (Section 28.5): The process by which the genetic information transcribed from DNA onto mRNA is read by tRNA and used to direct protein synthesis.

Tree diagram (Section 13.12): A diagram used in NMR to sort out the complicated splitting patterns that can arise from multiple couplings.

Triacylglycerol (Section 27.1): A lipid, such as those found in animal fat and vegetable oil, that is, a triester of glycerol with long-chain fatty acids.

Tricarboxylic acid cycle (Section 29.7): An alternative name for the citric acid cycle by which acetyl CoA is degraded to CO_2.

Triplet (Section 13.11): A symmetrical three-line splitting pattern observed in the ^1H NMR spectrum when a proton has two equivalent neighbor protons.

Turnover number (Section 26.10): The number of substrate molecules acted on by an enzyme per unit time.

Twist-boat conformation (Section 4.5): A conformation of cyclohexane that is somewhat more stable than a pure boat conformation.

Ultraviolet (UV) spectroscopy (Section 14.7): An optical spectroscopy employing ultraviolet irradiation. UV spectroscopy provides structural information about the extent of π electron conjugation in organic molecules.

Unimolecular reaction (Section 11.4): A reaction that occurs by spontaneous transformation of the starting material without the intervention of other reactants. For example, the dissociation of a tertiary alkyl halide in the S_N1 reaction is a unimolecular process.

Unsaturated (Section 6.2): A molecule that has one or more multiple bonds.

Upfield (Section 13.3): The right-hand portion of the NMR chart.

Urethane (Section 31.4): A functional group in which a carbonyl group is bonded to both an −OR group and an $-NR_2$ group.

Uronic acid (Section 25.6): The monocarboxylic acid resulting from enzymatic oxidation of the $-CH_2OH$ group of an aldose.

Valence bond theory (Section 1.5): A bonding theory that describes a covalent bond as resulting from the overlap of two atomic orbitals.

Valence shell (Section 1.4): The outermost electron shell of an atom.

Van der Waals forces (Section 2.13): Intermolecular forces that are responsible for holding molecules together in the liquid and solid states.

Vicinal (Section 8.2): A term used to refer to a 1,2-disubstitution pattern. For example, 1,2-dibromoethane is a vicinal dibromide.

Vinyl group (Section 6.3): An $H_2C{=}CH-$ substituent.

Vinyl monomer (Sections 7.10, 31.1): A substituted alkene monomer used to make chain-growth polymers.

Vinylic (Section 8.3): A term that refers to a substituent at a double-bond carbon atom. For example, chloroethylene is a vinylic chloride, and enols are vinylic alcohols.

Vitamin (Section 26.10): A small organic molecule that must be obtained in the diet and is required in trace amounts for proper growth and function.

Vulcanization (Section 14.6): A technique for cross-linking and hardening a diene polymer by heating with a few percent by weight of sulfur.

Walden inversion (Section 11.1): The inversion of configuration at a chirality center that accompanies an S_N2 reaction.

Wave equation (Section 1.2): A mathematical expression that defines the behavior of an electron in an atom.

Wave function (Section 1.2): A solution to the wave equation for defining the behavior of an electron in an atom. The square of the wave function defines the shape of an orbital.

Wavelength, λ (Section 12.5): The length of a wave from peak to peak. The wavelength of electromagnetic radiation is inversely proportional to frequency and inversely proportional to energy.

Wavenumber, $\tilde{\nu}$ (Section 12.6): The reciprocal of the wavelength in centimeters.

Wax (Section 27.1): A mixture of esters of long-chain carboxylic acids with long-chain alcohols.

Williamson ether synthesis (Section 18.2): A method for synthesizing ethers by S_N2 reaction of an alkyl halide with an alkoxide ion.

Wittig reaction (Section 19.11): The reaction of a phosphorus ylide with a ketone or aldehyde to yield an alkene.

Wohl degradation (Section 25.6): A method for shortening the chain of an aldose sugar.

Wolff–Kishner reaction (Section 19.9): The conversion of an aldehyde or ketone into an alkane by reaction with hydrazine and base.

Wood alcohol (Chapter 17 introduction): An old name for methanol.

Ylide (Section 19.11): A neutral dipolar molecule with adjacent positive and negative charges. The phosphoranes used in Wittig reactions are ylides.

***Z* geometry** (Section 6.5): A term used to describe the stereochemistry of a carbon–carbon double bond. The two groups on each carbon are assigned priorities according to the Cahn–Ingold–Prelog sequence rules, and the two carbons are compared. If the high-priority groups on each carbon are on the same side of the double bond, the bond has *Z* geometry.

Zaitsev's rule (Section 11.7): A rule stating that E2 elimination reactions normally yield the more highly substituted alkene as major product.

Ziegler–Natta catalyst (Section 31.2): A catalyst of an alkylaluminum and a titanium compound used for preparing alkene polymers.

Zwitterion (Section 26.1): A neutral dipolar molecule in which the positive and negative charges are not adjacent. For example, amino acids exist as zwitterions, $H_3\overset{+}{N}{-}CHR{-}CO_2^-$.

APPENDIX

D Answers to In-Text Problems

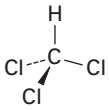
The following answers are meant only as a quick check while you study. Full answers for all problems are provided in the accompanying *Study Guide and Solutions Manual*.

CHAPTER 1

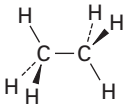
1.1 **(a)** $1s^2\ 2s^2\ 2p^4$ **(b)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

1.2 **(a)** 2 **(b)** 2 **(c)** 6

1.3

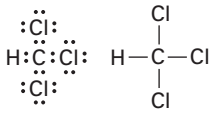


1.4

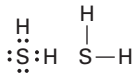


1.5 **(a)** $GeCl_4$ **(b)** AlH_3
(c) CH_2Cl_2 **(d)** SiF_4
(e) CH_3NH_2

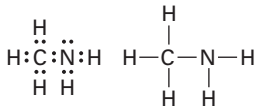
1.6 **(a)**



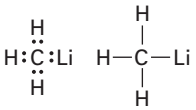
(b)



(c)

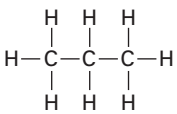


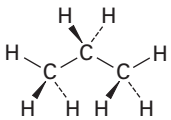
(d)



1.7 C_2H_7 has too many hydrogens for a compound with two carbons.

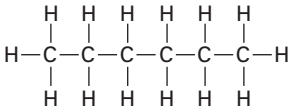
1.8



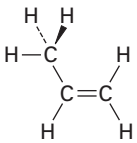


All bond angles are near 109°.

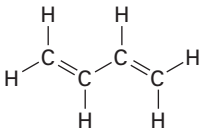
1.9



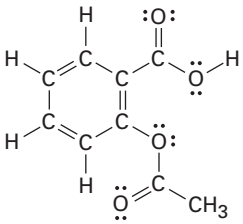
1.10 The CH_3 carbon is sp^3; the double-bond carbons are sp^2; the C=C−C and C=C−H bond angles are approximately 120°; other bond angles are near 109°.



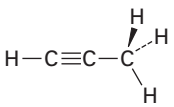
1.11 All carbons are sp^2, and all bond angles are near 120°.



1.12 All carbons except CH_3 are sp^2.

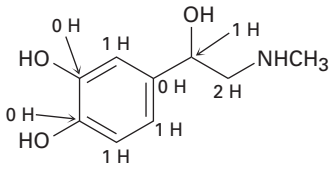


1.13 The CH_3 carbon is sp^3; the triple-bond carbons are sp; the C≡C−C and H−C≡C bond angles are approximately 180°.



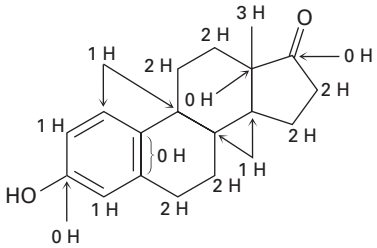
1.14 **(a)** O has 2 lone pairs and is sp^3-hybridized.
(b) N has 1 lone pair and is sp^3-hybridized.
(c) P has 1 lone pair and is sp^3-hybridized.
(d) S has 2 lone pairs and is sp^3-hybridized.

1.15 **(a)**



Adrenaline—$C_9H_{13}NO_3$

(b)



Estrone—$C_{18}H_{22}O_2$

1.16 There are numerous possibilities, such as:

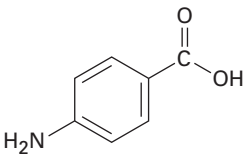
(a) C_5H_{12} $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH(CH_3)_2$ $CH_3C(CH_3)_3$

(b) C_2H_7N $CH_3CH_2NH_2$ CH_3NHCH_3

(c) C_3H_6O CH_3COCH_3 $H_2C{=}CHCH_2OH$ $H_2C{=}CHOCH_3$

(d) C_4H_9Cl $CH_3CH_2CH_2CH_2Cl$ $CH_3CH_2CHClCH_3$ $CH_3CH(CH_3)CH_2Cl$

1.17



CHAPTER 2

2.1 **(a)** H **(b)** Br **(c)** Cl **(d)** C

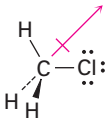
2.2

(a) $H_3C{-}\overset{\delta+}{C}{-}\overset{\delta-}{Cl}$ **(b)** $H_3C{-}\overset{\delta+}{N}H_2$ **(c)** $H_2\overset{\delta-}{N}{-}\overset{\delta+}{H}$

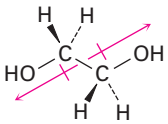
(d) $H_3C{-}SH$ Carbon and sulfur have identical electronegativities. **(e)** $H_3C{-}\overset{\delta-}{M}g\overset{\delta+}{B}r$ **(f)** $H_3C{-}\overset{\delta+}{F}$

2.3 $H_3C{-}OH < H_3C{-}MgBr < H_3C{-}Li = H_3C{-}F < H_3C{-}K$

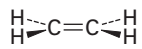
2.4 The chlorine is electron-rich, and the carbon is electron-poor.



2.5 The two C–O dipoles cancel because of the symmetry of the molecule:

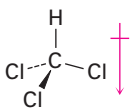


2.6 **(a)**

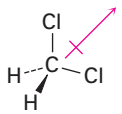


No dipole moment

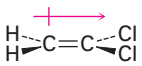
(b)



(c)



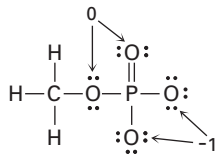
(d)



2.7 For nitrogen: FC = 5 − 8/2 − 0 = +1
For singly bonded oxygen: FC = 6 − 2/2 − 6 = −1

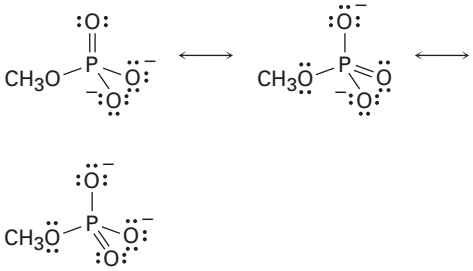
2.8 **(a)** For carbon: FC = 4 − 8/2 − 0 = 0
For the middle nitrogen: FC = 5 − 8/2 − 0 = +1
For the end nitrogen: FC = 5 − 4/2 − 4 = −1
(b) For nitrogen: FC = 5 − 8/2 − 0 = +1
For oxygen: FC = 6 − 2/2 − 6 = −1
(c) For nitrogen: FC = 5 − 8/2 − 0 = +1
For the end carbon: FC = 4 − 6/2 − 2 = −1

2.9

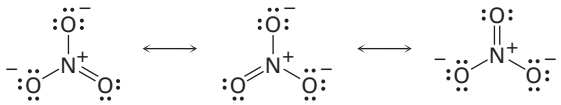


2.10

(a)

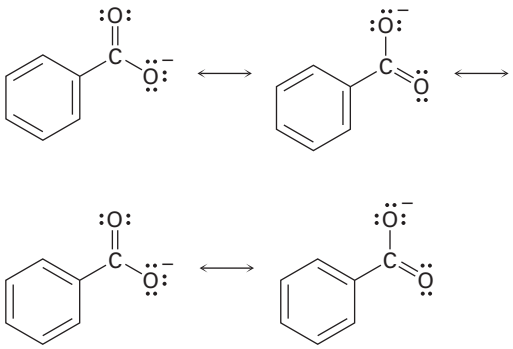


(b)



(c) $H_2C{=}CH{-}CH_2^+ \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2$

(d)



2.11

HNO_3	+	NH_3	⟶	NH_4^+	NO_3^-
Acid		Base		Conjugate acid	Conjugate base

2.12 Phenylalanine is stronger.

2.13 Water is a stronger acid.

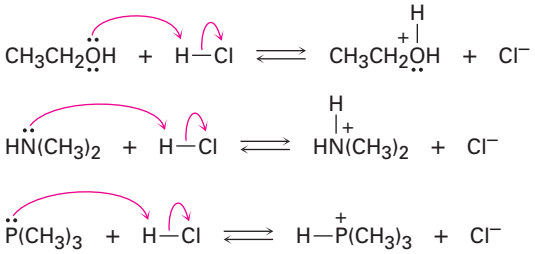
2.14 Neither reaction will take place.

2.15 Reaction will take place.

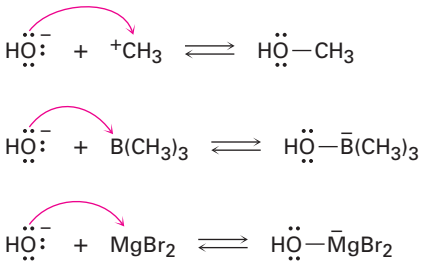
2.16 $K_a = 4.9 \times 10^{-10}$

2.17

(a)

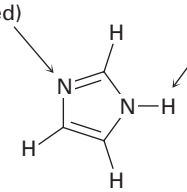


(b)



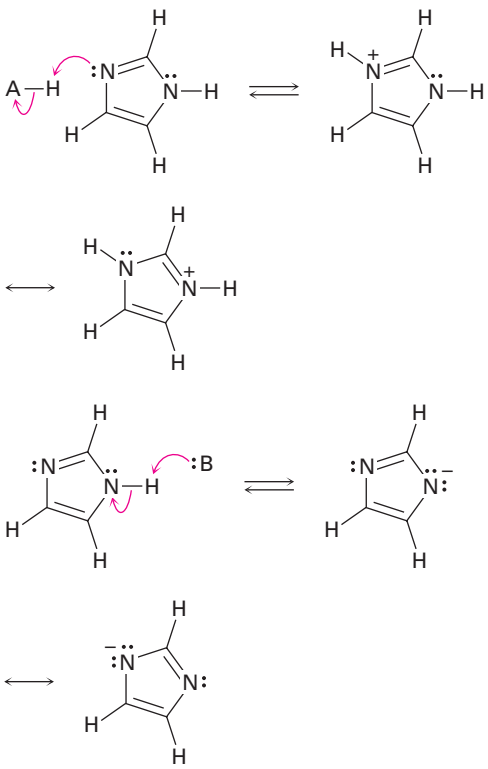
2.18

(a) More basic (red) Most acidic (blue)



Imidazole

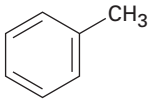
(b)

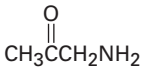
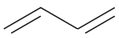


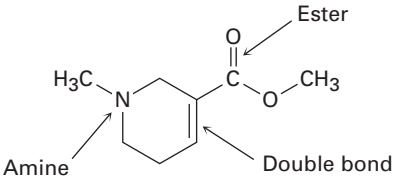
2.19 Vitamin C is water-soluble (hydrophilic); vitamin A is fat-soluble (hydrophilic).

CHAPTER 3

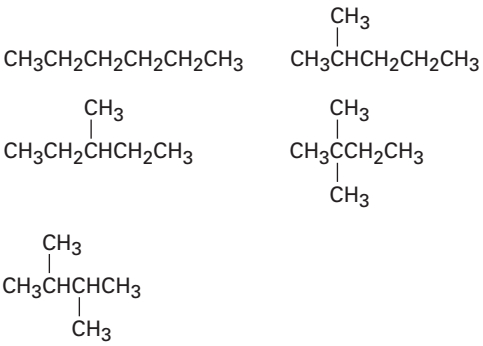
3.1 **(a)** Sulfide, carboxylic acid, amine
(b) Aromatic ring, carboxylic acid
(c) Ether, alcohol, aromatic ring, amide, C=C bond

3.2 **(a)** CH_3OH **(b)**  **(c)** 

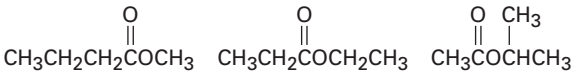
(d) CH_3NH_2 **(e)**  **(f)** 

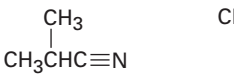
3.3 

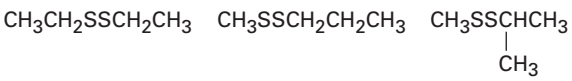
$C_8H_{13}NO_2$

3.4 

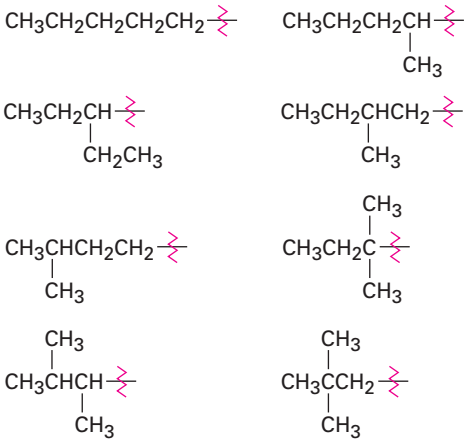
3.5 Part **(a)** has nine possible answers.

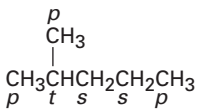
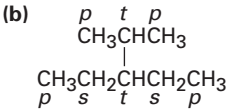
(a) 

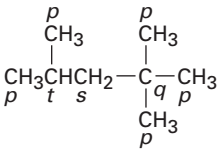
(b) 

(c) 

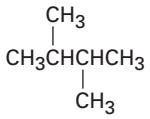
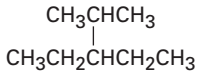
3.6 **(a)** Two **(b)** Four

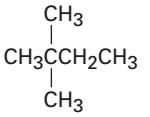
3.7 

3.8 **(a)**  **(b)** 

(c) 

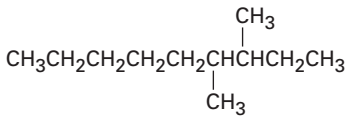
3.9 Primary carbons have primary hydrogens, secondary carbons have secondary hydrogens, and tertiary carbons have tertiary hydrogens.

3.10 **(a)**  **(b)** 

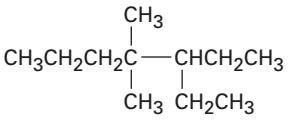
(c) 

3.11 **(a)** Pentane, 2-methylbutane, 2,2-dimethylpropane
(b) 3,4-Dimethylhexane
(c) 2,4-Dimethylpentane
(d) 2,2,5-Trimethylheptane

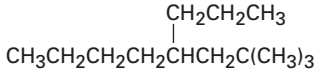
3.12 **(a)**



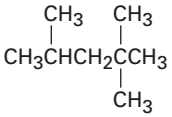
(b)



(c)

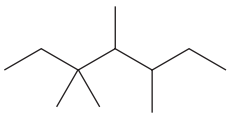


(d)



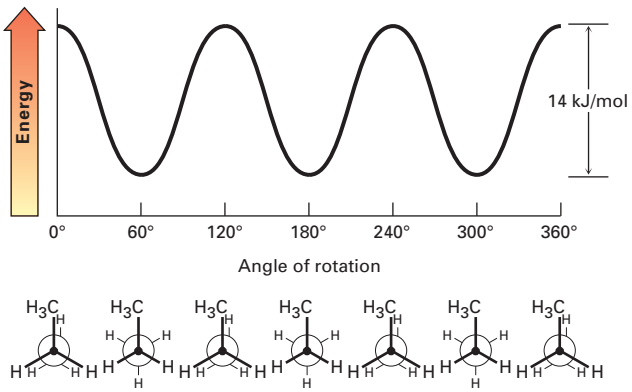
3.13 Pentyl, 1-methylbutyl, 1-ethylpropyl, 3-methylbutyl, 2-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl

3.14



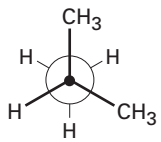
3,3,4,5-Tetramethylheptane

3.15

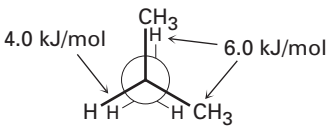


3.16

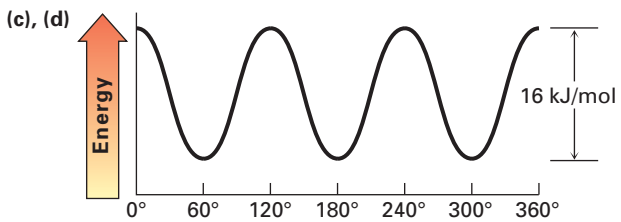
(a)



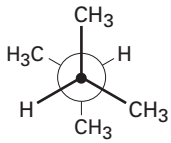
(b)



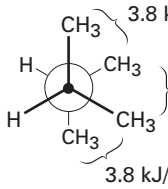
(c), (d)



3.17



3.18

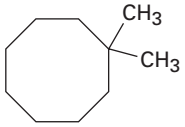


Total: 11.4 kJ/mol

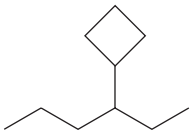
CHAPTER 4

4.1 **(a)** 1,4-Dimethylcyclohexane
(b) 1-Methyl-3-propylcyclopentane
(c) 3-Cyclobutylpentane
(d) 1-Bromo-4-ethylcyclodecane
(e) 1-Isopropyl-2-methylcyclohexane
(f) 4-Bromo-1-*tert*-butyl-2-methylcycloheptane

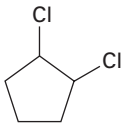
4.2 **(a)**



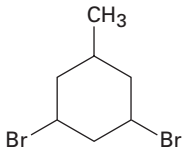
(b)



(c)



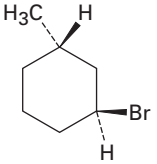
(d)



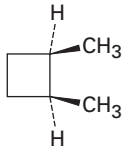
4.3 3-Ethyl-1,1-dimethylcyclopentane

4.4 **(a)** *trans*-1-Chloro-4-methylcyclohexane
(b) *cis*-1-Ethyl-3-methylcycloheptane

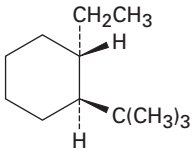
4.5 **(a)**



(b)



(c)



4.6 The two hydroxyl groups are cis. The two side chains are trans.

4.7 **(a)** *cis*-1,2-Dimethylcyclopentane
(b) *cis*-1-Bromo-3-methylcyclobutane

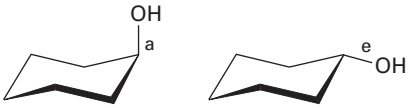
4.8 Six interactions; 21% of strain

4.9 The cis isomer is less stable because the methyl groups eclipse each other.

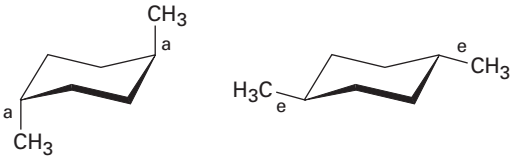
4.10 Ten eclipsing interactions; 40 kJ/mol; 35% is relieved.

4.11 Conformation **(a)** is more stable because the methyl groups are farther apart.

4.12



4.13



4.14 Before ring-flip, red and blue are equatorial and green is axial. After ring-flip, red and blue are axial and green is equatorial.

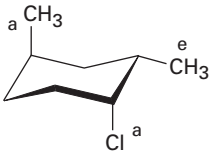
4.15 4.2 kJ/mol

4.16 Cyano group points straight up.

4.17 Equatorial = 70%; axial = 30%

4.18 **(a)** 2.0 kJ/mol **(b)** 11.4 kJ/mol
(c) 2.0 kJ/mol **(d)** 8.0 kJ/mol

4.19



1-Chloro-2,4-dimethylcyclohexane
(less stable chair form)

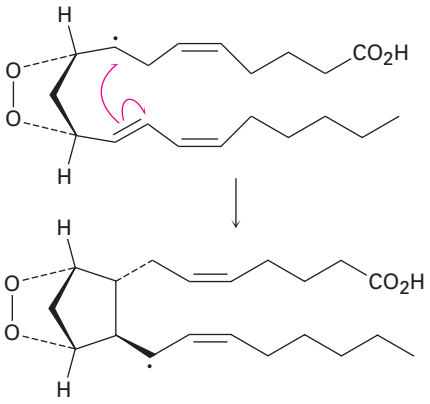
4.20 *trans*-Decalin is more stable because it has no 1,3-diaxial interactions.

CHAPTER 5

5.1 **(a)** Substitution **(b)** Elimination
(c) Addition

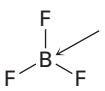
5.2 1-Chloro-2-methylpentane
2-Chloro-2-methylpentane
3-Chloro-2-methylpentane
2-Chloro-4-methylpentane
1-Chloro-4-methylpentane

5.3 A radical addition reaction



5.4 **(a)** Carbon is electrophilic.
(b) Sulfur is nucleophilic.
(c) Nitrogens are nucleophilic.
(d) Oxygen is nucleophilic; carbon is electrophilic.

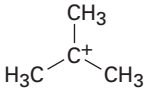
5.5



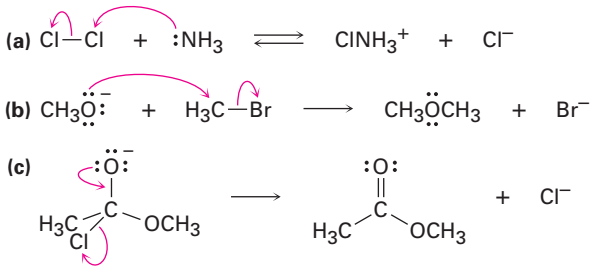
Electrophilic;
vacant *p* orbital

5.6 Bromocyclohexane; chlorocyclohexane

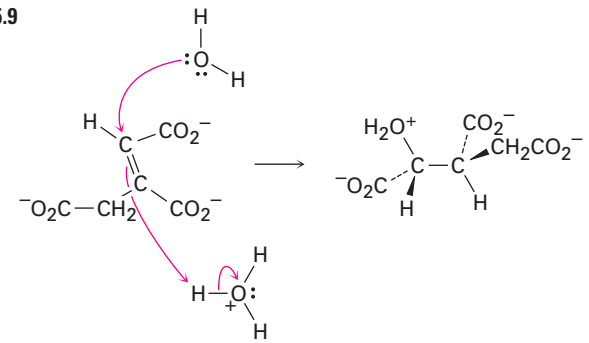
5.7



5.8



5.9

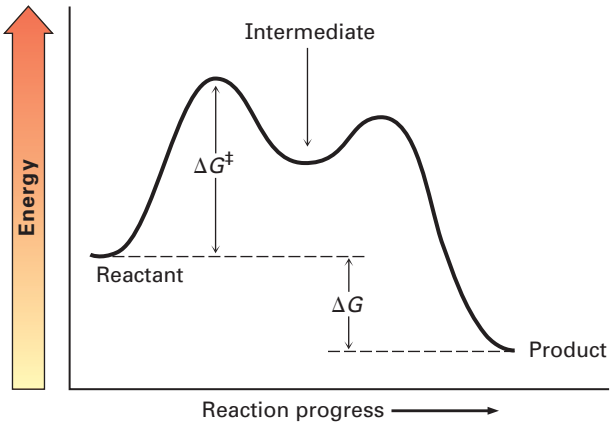


5.10 Negative $\Delta G°$ is more favored.

5.11 Larger K_{eq} is more exergonic.

5.12 Lower $\Delta G^{‡}$ is faster.

5.13



CHAPTER 6

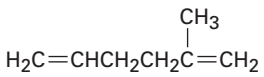
6.1 **(a)** 1 **(b)** 2 **(c)** 2

6.2 **(a)** 5 **(b)** 5 **(c)** 3
(d) 1 **(e)** 6 **(f)** 5

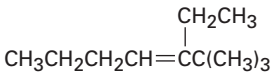
6.3 $C_{16}H_{13}ClN_2O$

6.4 **(a)** 3,4,4-Trimethyl-1-pentene
(b) 3-Methyl-3-hexene
(c) 4,7-Dimethyl-2,5-octadiene
(d) 6-Ethyl-7-methyl-4-nonene

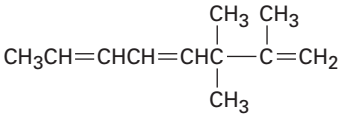
6.5 **(a)**



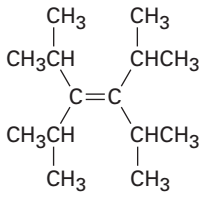
(b)



(c)



(d)



6.6 **(a)** 1,2-Dimethylcyclohexene
(b) 4,4-Dimethylcycloheptene
(c) 3-Isopropylcyclopentene

6.7 Compounds **(c)**, **(e)**, and **(f)** have cis–trans isomers.

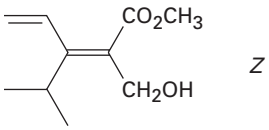
6.8 **(a)** *cis*-4,5-Dimethyl-2-hexene
(b) *trans*-6-Methyl-3-heptene

6.9 **(a)** $-Br$ **(b)** $-Br$ **(c)** $-CH_2CH_3$
(d) $-OH$ **(e)** $-CH_2OH$ **(f)** $-CH{=}O$

6.10 **(a)** $-Cl$, $-OH$, $-CH_3$, $-H$
(b) $-CH_2OH$, $-CH{=}CH_2$, $-CH_2CH_3$, $-CH_3$
(c) $-CO_2H$, $-CH_2OH$, $-C{\equiv}N$, $-CH_2NH_2$
(d) $-CH_2OCH_3$, $-C{\equiv}N$, $-C{\equiv}CH$, $-CH_2CH_3$

6.11 **(a)** *Z* **(b)** *E* **(c)** *Z* **(d)** *E*

6.12



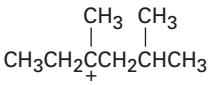
Z

6.13 **(a)** 2-Methylpropene more stable than 1-butene
(b) *trans*-2-Hexene more stable than *cis*-2-hexene
(c) 1-Methylcyclohexene more stable than 3-methylcyclohexene

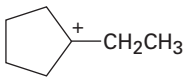
6.14 **(a)** Chlorocyclohexane
(b) 2-Bromo-2-methylpentane
(c) 4-Methyl-2-pentanol
(d) 1-Bromo-1-methylcyclohexane

6.15 **(a)** Cyclopentene
(b) 1-Ethylcyclohexene or ethylidenecyclohexane
(c) 3-Hexene
(d) Vinylcyclohexane (cyclohexylethylene)

6.16 **(a)**



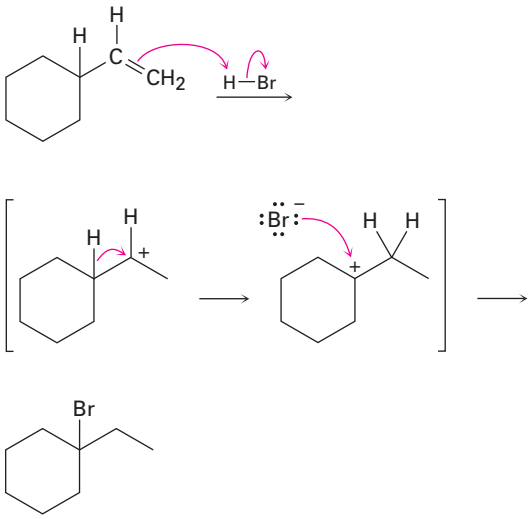
(b)



6.17 In the conformation shown, only the methyl-group C−H that is parallel to the carbocation *p* orbital can show hyperconjugation.

6.18 The second step is exergonic; the transition state resembles the carbocation.

6.19



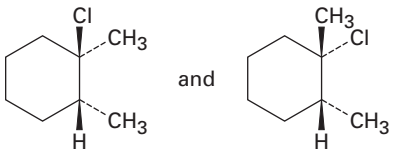
CHAPTER 7

7.1 2-Methyl-2-butene and 2-methyl-1-butene

7.2 Five

7.3 *trans*-1,2-Dichloro-1,2-dimethylcyclohexane

7.4



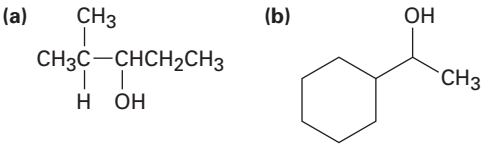
7.5 *trans*-2-Bromocyclopentanol

7.6 Markovnikov

7.7 **(a)** 2-Pentanol **(b)** 2-Methyl-2-pentanol

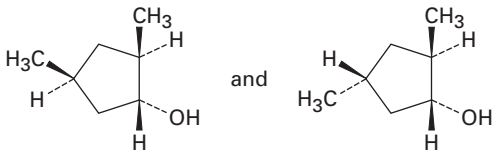
7.8 **(a)** Oxymercuration of 2-methyl-1-hexene or 2-methyl-2-hexene
(b) Oxymercuration of cyclohexylethylene or hydroboration of ethylidenecyclohexane

7.9

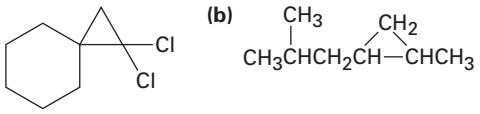


7.10 **(a)** 3-Methyl-1-butene
(b) 2-Methyl-2-butene
(c) Methylenecyclohexane

7.11

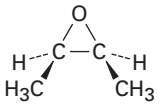


7.12



7.13 **(a)** 2-Methylpentane
(b) 1,1-Dimethylcyclopentane

7.14



cis-2,3-Epoxybutane

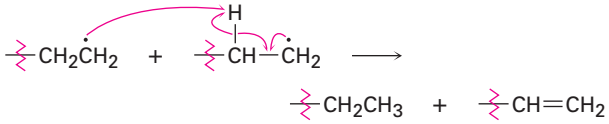
7.15 **(a)** 1-Methylcyclohexene
(b) 2-Methyl-2-pentene
(c) 1,3-Butadiene

7.16 **(a)** $CH_3COCH_2CH_2CH_2CH_2CO_2H$
(b) $CH_3COCH_2CH_2CH_2CH_2CHO$

7.17 **(a)** 2-Methylpropene **(b)** 3-Hexene

7.18 **(a)** $H_2C{=}CHOCH_3$ **(b)** $ClCH{=}CHCl$

7.19



CHAPTER 8

8.1 **(a)** 2,5-Dimethyl-3-hexyne
(b) 3,3-Dimethyl-1-butyne
(c) 3,3-Dimethyl-4-octyne
(d) 2,5,5-Trimethyl-3-heptyne
(e) 6-Isopropylcyclodecyne
(f) 2,4-Octadiene-6-yne

8.2 1-Hexyne, 2-hexyne, 3-hexyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 3,3-dimethyl-1-butyne

8.3 **(a)** 1,1,2,2-Tetrachloropentane
(b) 1-Bromo-1-cyclopentylethylene
(c) 2-Bromo-2-heptene and 3-bromo-2-heptene

8.4 **(a)** 4-Octanone
(b) 2-Methyl-4-octanone and 7-methyl-4-octanone

8.5 **(a)** 1-Pentyne **(b)** 2-Pentyne

8.6 **(a)** $C_6H_5C{\equiv}CH$ **(b)** 2,5-Dimethyl-3-hexyne

8.7 **(a)** Mercuric sulfate–catalyzed hydration of phenylacetylene
(b) Hydroboration/oxidation of cyclopentylacetylene

8.8 **(a)** Reduce 2-octyne with Li/NH_3
(b) Reduce 3-heptyne with H_2/Lindlar catalyst
(c) Reduce 3-methyl-1-pentyne

8.9 No: **(a)**, **(c)**, **(d)**; yes: **(b)**

8.10 **(a)** 1-Pentyne + CH_3I, or propyne + $CH_3CH_2CH_2I$
(b) 3-Methyl-1-butyne + CH_3CH_2I
(c) Cyclohexylacetylene + CH_3I

8.11 $CH_3C{\equiv}CH \xrightarrow[2.\ CH_3I]{1.\ NaNH_2} CH_3C{\equiv}CCH_3$

$\xrightarrow[\text{cat.}]{H_2,\ \text{Lindlar}}$ *cis*-$CH_3CH{=}CHCH_3$

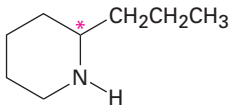
8.12 **(a)** $KMnO_4$, H_3O^+
(b) H_2/Lindlar
(c) 1. H_2/Lindlar; 2. HBr
(d) 1. H_2/Lindlar; 2. BH_3; 3. NaOH, H_2O_2
(e) 1. H_2/Lindlar; 2. Cl_2
(f) O_3

8.13 **(a)** 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3(CH_2)_6CH_2Br$; 3. 2 H_2/Pd
(b) 1. $HC{\equiv}CH + NaNH_2$; 2. $(CH_3)_3CCH_2CH_2I$; 3. 2 H_2/Pd
(c) 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3CH_2CH_2CH_2I$; 3. BH_3; 4. H_2O_2
(d) 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3CH_2CH_2CH_2CH_2I$; 3. $HgSO_4$, H_3O^+

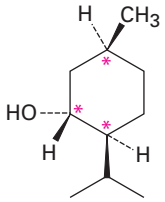
CHAPTER 9

9.1 Chiral: screw, beanstalk, shoe

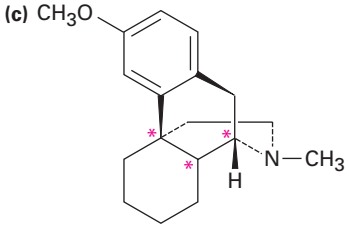
9.2 **(a)**



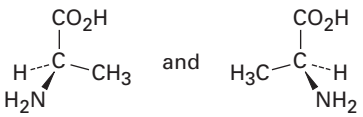
(b)



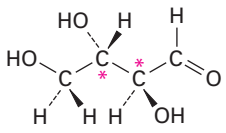
(c)



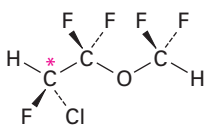
9.3



9.4 **(a)**



(b)



9.5 Levorotatory

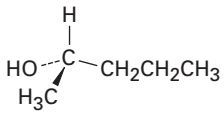
9.6 +16.1°

9.7 **(a)** −OH, $-CH_2CH_2OH$, $-CH_2CH_3$, −H
(b) −OH, $-CO_2CH_3$, $-CO_2H$, $-CH_2OH$
(c) $-NH_2$, −CN, $-CH_2NHCH_3$, $-CH_2NH_2$
(d) $-SSCH_3$, −SH, $-CH_2SCH_3$, $-CH_3$

9.8 **(a)** *S* **(b)** *R* **(c)** *S*

9.9 **(a)** *S* **(b)** *S* **(c)** *R*

9.10



9.11 *S*

9.12 **(a)** *R,R* **(b)** *S,R* **(c)** *R,S* **(d)** *S,S*

Compounds **(a)** and **(d)** are enantiomers and are diastereomeric with **(b)** and **(c)**.

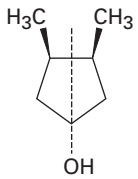
9.13 *R,R*

9.14 *S,S*

9.15 **(a)**, **(d)**

9.16 Compounds **(a)** and **(c)** have meso forms.

9.17



Meso

9.18 The product retains its *S* stereochemistry.

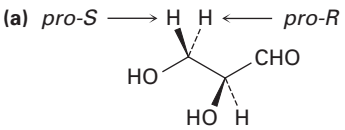
9.19 Two diastereomeric salts: (*R*)-lactic acid plus (*S*)-1-phenylethylamine and (*S*)-lactic acid plus (*S*)-1-phenylethylamine

9.20 **(a)** Constitutional isomers **(b)** Diastereomers

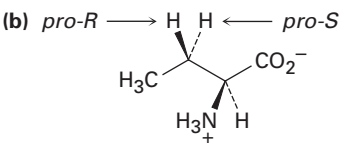
9.21 An optically inactive, non-50:50 mixture of two racemic pairs: (2*R*,4*R*) + (2*S*,4*S*) and (2*R*,4*S*) + (2*S*,4*R*)

9.22 Non-50:50 mixture of two racemic pairs: (1*S*,3*R*) + (1*R*,3*S*) and (1*S*,3*S*) + (1*R*,3*R*)

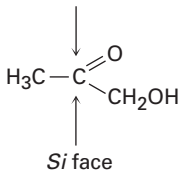
9.23 **(a)**



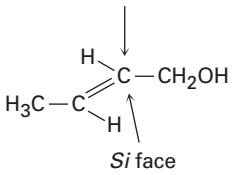
(b)



9.24 **(a)** *Re* face



(b) *Re* face



9.25 (*S*)-Lactate

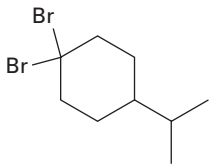
9.26 The −OH adds to the *Re* face of C2, and −H adds to the *Re* face of C3. The overall addition has anti stereochemistry.

CHAPTER 10

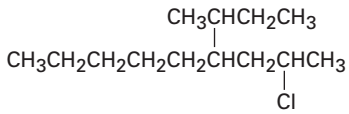
10.1 **(a)** 1-Iodobutane
(b) 1-Chloro-3-methylbutane
(c) 1,5-Dibromo-2,2-dimethylpentane
(d) 1,3-Dichloro-3-methylbutane
(e) 1-Chloro-3-ethyl-4-iodopentane
(f) 2-Bromo-5-chlorohexane

10.2 **(a)** $CH_3CH_2CH_2C(CH_3)_2CH(Cl)CH_3$
(b) $CH_3CH_2CH_2C(Cl)_2CH(CH_3)_2$
(c) $CH_3CH_2C(Br)(CH_2CH_3)_2$

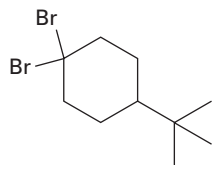
(d)



(e)



(f)

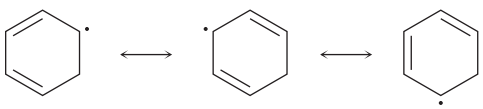


10.3 Chiral: 1-chloro-2-methylpentane, 3-chloro-2-methylpentane, 2-chloro-4-methylpentane

Achiral: 2-chloro-2-methylpentane, 1-chloro-4-methylpentane

10.4 1-Chloro-2-methylbutane (29%), 1-chloro-3-methylbutane (14%), 2-chloro-2-methylbutane (24%), 2-chloro-3-methylbutane (33%)

10.5



10.6 The intermediate allylic radical reacts at the more accessible site and gives the more highly substituted double bond.

10.7 **(a)** 3-Bromo-5-methylcycloheptene and 3-bromo-6-methylcycloheptene
(b) Four products

10.8 **(a)** 2-Methyl-2-propanol + HCl
(b) 4-Methyl-2-pentanol + PBr_3
(c) 5-Methyl-1-pentanol + PBr_3
(d) 2,4-Dimethyl-2-hexanol + HCl

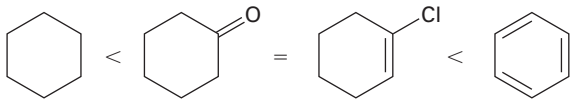
10.9 Both reactions occur.

10.10 React Grignard reagent with D_2O.

10.11 **(a)** 1. NBS; 2. $(CH_3)_2CuLi$
(b) 1. Li; 2. CuI; 3. $CH_3CH_2CH_2CH_2Br$
(c) 1. BH_3; 2. H_2O_2, NaOH; 3. PBr_3; 4. Li, then CuI; 5. $CH_3(CH_2)_4Br$

10.12

(a)



(b) $CH_3CH_2NH_2 < H_2NCH_2CH_2NH_2 < CH_3C{\equiv}N$

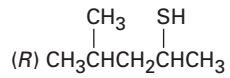
10.13 **(a)** Reduction **(b)** Neither

CHAPTER 11

11.1 (*R*)-1-Methylpentyl acetate, $CH_3CO_2CH(CH_3)CH_2CH_2CH_2CH_3$

11.2 (*S*)-2-Butanol

11.3 (*S*)-2-Bromo-4-methylpentane ⟶



11.4 **(a)** 1-Iodobutane **(b)** 1-Butanol
(c) 1-Hexyne **(d)** Butylammonium bromide

11.5 **(a)** $(CH_3)_2N^-$ **(b)** $(CH_3)_3N$ **(c)** H_2S

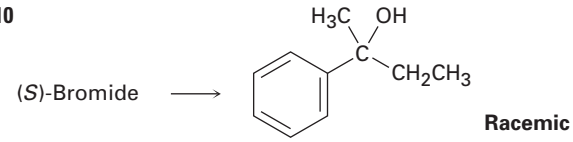
11.6 $CH_3OTos > CH_3Br > (CH_3)_2CHCl > (CH_3)_3CCl$

11.7 Similar to protic solvents

11.8 Racemic 1-ethyl-1-methylhexyl acetate

11.9 90.1% racemization, 9.9% inversion

11.10

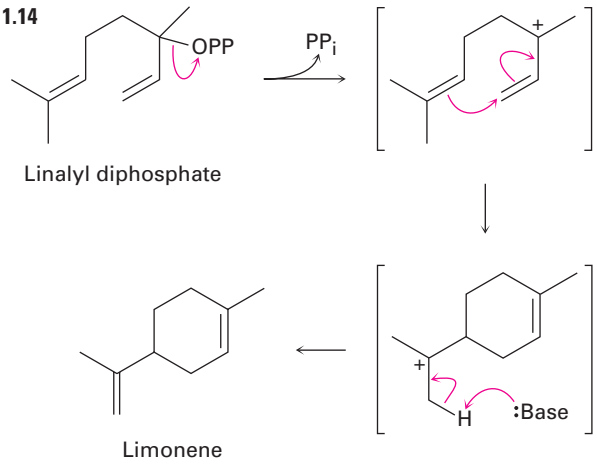


11.11 $H_2C{=}CHCH(Br)CH_3 > CH_3CH(Br)CH_3 > CH_3CH_2Br > H_2C{=}CHBr$

11.12 The same allylic carbocation intermediate is formed.

11.13 **(a)** S_N1 **(b)** S_N2

11.14



Linalyl diphosphate

Limonene

11.15 **(a)** Major: 2-methyl-2-pentene; minor: 4-methyl-2-pentene
(b) Major: 2,3,5-trimethyl-2-hexene; minor: 2,3,5-trimethyl-3-hexene and 2-isopropyl-4-methyl-1-pentene
(c) Major: ethylidenecyclohexane; minor: cyclohexylethylene

11.16 **(a)** 1-Bromo-3,6-dimethylheptane
(b) 4-Bromo-1,2-dimethylcyclopentane

11.17 (*Z*)-1-Bromo-1,2-diphenylethylene

11.18 (*Z*)-3-Methyl-2-pentene

11.19 Cis isomer reacts faster because the bromine is axial.

11.20 **(a)** S_N2 **(b)** E2 **(c)** S_N1 **(d)** E1cB

CHAPTER 12

12.1 $C_{19}H_{28}O_2$

12.2 **(a)** 2-Methyl-2-pentene **(b)** 2-Hexene

12.3 **(a)** 43, 71 **(b)** 82 **(c)** 58 **(d)** 86

12.4 102 (M^+), 84 (dehydration), 87 (alpha cleavage), 59 (alpha cleavage)

12.5 X-ray energy is higher; $\lambda = 9.0 \times 10^{-6}$ m is higher in energy.

12.6 **(a)** 2.4×10^6 kJ/mol **(b)** 4.0×10^4 kJ/mol
(c) 2.4×10^3 kJ/mol **(d)** 2.8×10^2 kJ/mol
(e) 6.0 kJ/mol **(f)** 4.0×10^{-2} kJ/mol

12.7 **(a)** Ketone or aldehyde **(b)** Nitro compound
(c) Carboxylic acid

12.8 **(a)** CH_3CH_2OH has an −OH absorption.
(b) 1-Hexene has a double-bond absorption.
(c) $CH_3CH_2CO_2H$ has a very broad −OH absorption.

12.9 1450–1600 cm^{-1}: aromatic ring; 2100 cm^{-1}: C≡C; 3300 cm^{-1}: C≡C−H

12.10 **(a)** 1715 cm^{-1} **(b)** 1730, 2100, 3300 cm^{-1}
(c) 1720, 2500–3100, 3400–3650 cm^{-1}

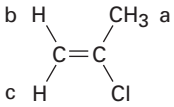
12.11 1690, 1650, 2230 cm^{-1}

CHAPTER 13

13.1 7.5×10^{-5} kJ/mol for ^{19}F; 8.0×10^{-5} kJ/mol for ^1H

13.2 1.2×10^{-4} kJ/mol

13.3 The vinylic C−H protons are nonequivalent.



13.4 **(a)** 7.27 δ **(b)** 3.05 δ
(c) 3.46 δ **(d)** 5.30 δ

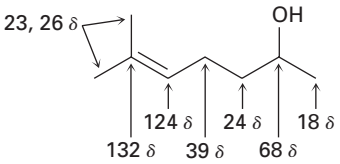
13.5 **(a)** 420 Hz **(b)** 2.1 δ **(c)** 1050 Hz

13.6 **(a)** 4 **(b)** 7 **(c)** 4 **(d)** 5 **(e)** 5 **(f)** 7

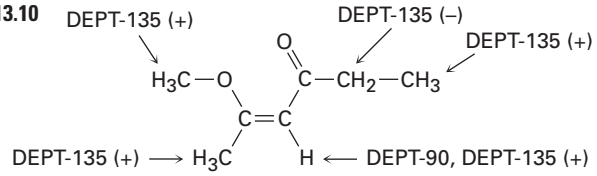
13.7 **(a)** 1,3-Dimethylcyclopentene
(b) 2-Methylpentane
(c) 1-Chloro-2-methylpropane

13.8 $-CH_3$, 9.3 δ; $-CH_2-$, 27.6 δ; C=O, 174.6 δ; $-OCH_3$, 51.4 δ

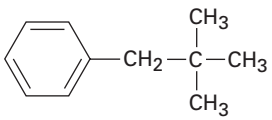
13.9



13.10



13.11



13.12 A DEPT-90 spectrum would show two absorptions for the non-Markovnikov product (RCH═CHBr) but no absorptions for the Markovnikov product ($RBrC{=}CH_2$).

13.13 **(a)** Enantiotopic **(b)** Diastereotopic
(c) Diastereotopic **(d)** Diastereotopic
(e) Diastereotopic **(f)** Homotopic

13.14 **(a)** 2 **(b)** 4 **(c)** 3 **(d)** 4 **(e)** 5 **(f)** 3

13.15 4

13.16 **(a)** 1.43 δ **(b)** 2.17 δ **(c)** 7.37 δ
(d) 5.30 δ **(e)** 9.70 δ **(f)** 2.12 δ

13.17 Seven kinds of protons

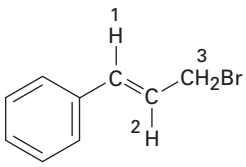
13.18 Two peaks; 3:2 ratio

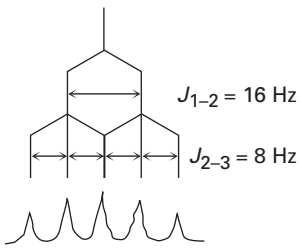
13.19 **(a)** $-CHBr_2$, quartet; $-CH_3$, doublet
(b) CH_3O-, singlet; $-OCH_2-$, triplet; $-CH_2Br$, triplet
(c) $ClCH_2-$, triplet; $-CH_2-$, quintet
(d) CH_3-, triplet; $-CH_2-$, quartet; $-CH-$, septet; $(CH_3)_2$, doublet
(e) CH_3-, triplet; $-CH_2-$, quartet; $-CH-$, septet; $(CH_3)_2$, doublet
(f) =CH, triplet, $-CH_2-$, doublet, aromatic C−H, two multiplets

13.20 **(a)** CH_3OCH_3 **(b)** $CH_3CH(Cl)CH_3$
(c) $ClCH_2CH_2OCH_2CH_2Cl$
(d) $CH_3CH_2CO_2CH_3$ or $CH_3CO_2CH_2CH_3$

13.21 $CH_3CH_2OCH_2CH_3$

13.22 J_{1-2} = 16 Hz; J_{2-3} = 8 Hz





13.23 1-Chloro-1-methylcyclohexane has a singlet methyl absorption.

CHAPTER 14

14.1 Expected $\Delta H°_{hydrog}$ for allene is −252 kJ/mol. Allene is less stable than a nonconjugated diene, which is less stable than a conjugated diene.

14.2 1-Chloro-2-pentene, 3-chloro-1-pentene, 4-chloro-2-pentene

14.3 4-Chloro-2-pentene predominates in both.

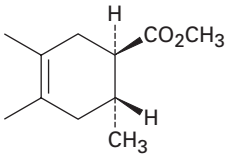
14.4 1,2-Addition: 6-bromo-1,6-dimethylcyclohexene

1,4-Addition: 6-bromo-1,6-dimethylcyclohexene, 3-bromo-1,2-dimethylcyclohexene

14.5 Interconversion occurs by S_N1 dissociation to a common intermediate cation.

14.6 The double bond is more highly substituted.

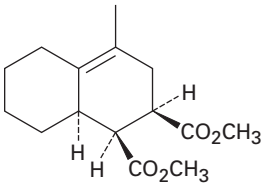
14.7



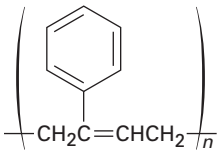
14.8 Good dienophiles: **(a)**, **(d)**

14.9 Compound **(a)** is *s*-cis. Compound **(c)** can rotate to *s*-cis.

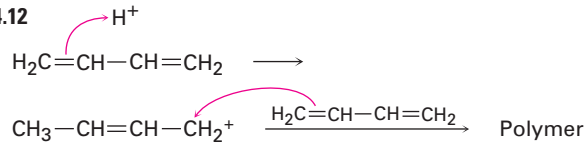
14.10



14.11



14.12



14.13 300–600 kJ/mol; UV energy is greater than IR or NMR energy.

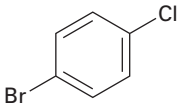
14.14 1.46×10^{-5} M

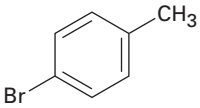
14.15 All except **(a)** have UV absorptions.

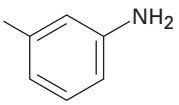
CHAPTER 15

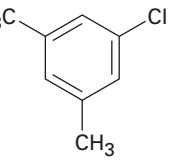
15.1 **(a)** Meta **(b)** Para **(c)** Ortho

15.2 **(a)** *m*-Bromochlorobenzene
(b) (3-Methylbutyl)benzene
(c) *p*-Bromoaniline
(d) 2,5-Dichlorotoluene
(e) 1-Ethyl-2,4-dinitrobenzene
(f) 1,2,3,5-Tetramethylbenzene

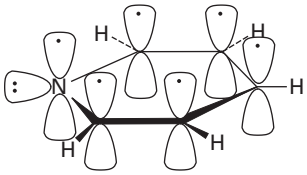
15.3 **(a)** 

(b) 

(c) 

(d) 

15.4 Pyridine has an aromatic sextet of electrons.



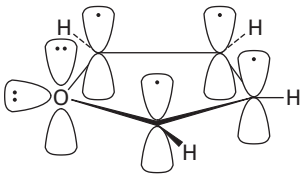
Pyridine

15.5 Cyclodecapentaene is not flat because of steric interactions.

15.6 All C−C bonds are equivalent; one resonance line in both ^1H and ^{13}C NMR spectra.

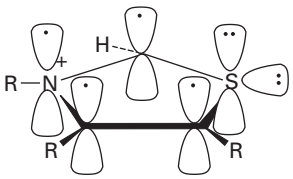
15.7 The cyclooctatetraenyl dianion is aromatic (ten π electrons) and flat.

15.8

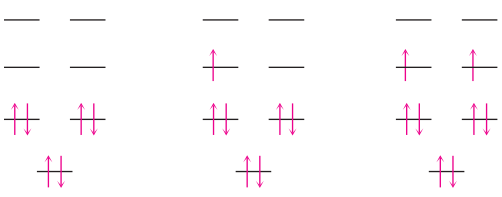


Furan

15.9 The thiazolium ring has six π electrons.

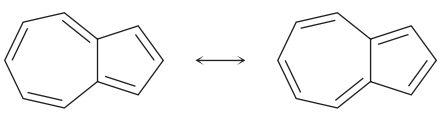


15.10



Cation **Radical** **Anion**

15.11



15.12 The three nitrogens in double bonds each contribute one; the remaining nitrogen contributes two.

CHAPTER 16

16.1 *o*-, *m*-, and *p*-Bromotoluene

16.2 *o*-Xylene: 2; *p*-xylene: 1; *m*-xylene: 3

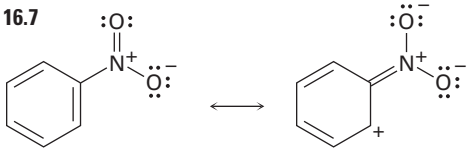
16.3 D^+ does electrophilic substitutions on the ring.

16.4 No rearrangement: **(a)**, **(b)**, **(e)**

16.5 *tert*-Butylbenzene

16.6 **(a)** $(CH_3)_2CHCOCl$ **(b)** PhCOCl

16.7



and others

16.8

and others

16.9
(a) *o*- and *p*-Bromonitrobenzene
(b) *m*-Bromonitrobenzene
(c) *o*- and *p*-Chlorophenol
(d) *o*- and *p*-Bromoaniline

16.10
(a) Phenol > Toluene > Benzene > Nitrobenzene
(b) Phenol > Benzene > Chlorobenzene > Benzoic acid
(c) Aniline > Benzene > Bromobenzene > Benzaldehyde

16.11 Alkylbenzenes are more reactive than benzene itself, but acylbenzenes are less reactive.

16.12 Toluene is more reactive; the trifluoromethyl group is electron-withdrawing.

16.13 The nitrogen electrons are donated to the nearby carbonyl group and are less available to the ring.

16.14 The meta intermediate is most favored.

16.15
(a) Ortho and para to $-OCH_3$
(b) Ortho and para to $-NH_2$
(c) Ortho and para to $-Cl$

16.16
(a) Reaction occurs ortho and para to the $-CH_3$ group.
(b) Reaction occurs ortho and para to the $-OCH_3$ group.

16.17 The phenol is deprotonated by KOH to give an anion that carries out a nucleophilic acyl substitution reaction on the fluoronitrobenzene.

16.18 Only one benzyne intermediate can form from *p*-bromotoluene; two different benzyne intermediates can form from *m*-bromotoluene.

16.19 **(a)** *m*-Nitrobenzoic acid
(b) *p*-*tert*-Butylbenzoic acid

16.20 A benzyl radical is more stable than a primary alkyl radical by 52 kJ/mol and is similar in stability to an allyl radical.

16.21 1. CH_3CH_2Cl, $AlCl_3$; 2. NBS; 3. KOH, ethanol

16.22 1. PhCOCl, $AlCl_3$; 2. H_2/Pd

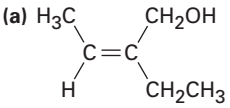
16.23 **(a)** 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$
(b) 1. CH_3COCl, $AlCl_3$; 2. Cl_2, $FeCl_3$; 3. H_2/Pd
(c) 1. CH_3CH_2COCl, $AlCl_3$; 2. Cl_2, $FeCl_3$; 3. H_2/Pd; 4. HNO_3, H_2SO_4
(d) 1. CH_3Cl, $AlCl_3$; 2. Br_2, $FeBr_3$; 3. SO_3, H_2SO_4

16.24 **(a)** Friedel–Crafts acylation does not occur on a deactivated ring.
(b) Rearrangement occurs during Friedel–Crafts alkylation with primary halides; chlorination occurs ortho to the alkyl group.

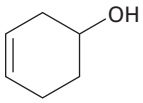
CHAPTER 17

17.1 **(a)** 5-Methyl-2,4-hexanediol
(b) 2-Methyl-4-phenyl-2-butanol
(c) 4,4-Dimethylcyclohexanol
(d) *trans*-2-Bromocyclopentanol
(e) 4-Bromo-3-methylphenol
(f) 2-Cyclopenten-1-ol

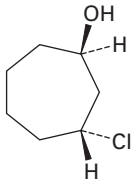
17.2 **(a)**



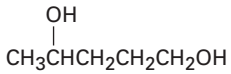
(b)



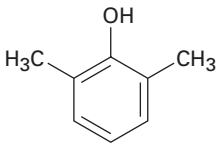
(c)



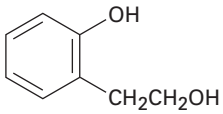
(d)



(e)



(f)



17.3 Hydrogen-bonding is more difficult in hindered alcohols.

17.4 **(a)** $HC{\equiv}CH < (CH_3)_2CHOH < CH_3OH < (CF_3)_2CHOH$
(b) *p*-Methylphenol < Phenol < *p*-(Trifluoromethyl)phenol
(c) Benzyl alcohol < Phenol < *p*-Hydroxybenzoic acid

17.5 The electron-withdrawing nitro group stabilizes an alkoxide ion, but the electron-donating methoxyl group destabilizes the anion.

17.6 **(a)** 2-Methyl-3-pentanol
(b) 2-Methyl-4-phenyl-2-butanol
(c) *meso*-5,6-Decanediol

17.7 **(a)** $NaBH_4$ **(b)** $LiAlH_4$ **(c)** $LiAlH_4$

17.8 **(a)** Benzaldehyde or benzoic acid (or ester)
(b) Acetophenone
(c) Cyclohexanone
(d) 2-Methylpropanal or 2-methylpropanoic acid (or ester)

17.9 **(a)** 1-Methylcyclopentanol
(b) 1,1-Diphenylethanol
(c) 3-Methyl-3-hexanol

17.10 **(a)** Acetone + CH_3MgBr, or ethyl acetate + 2 CH_3MgBr
(b) Cyclohexanone + CH_3MgBr
(c) 3-Pentanone + CH_3MgBr, or 2-butanone + CH_3CH_2MgBr, or ethyl acetate + 2 CH_3CH_2MgBr
(d) 2-Butanone + PhMgBr, or ethyl phenyl ketone + CH_3MgBr, or acetophenone + CH_3CH_2MgBr
(e) Formaldehyde + PhMgBr
(f) Formaldehyde + $(CH_3)_2CHCH_2MgBr$

17.11 Cyclohexanone + CH_3CH_2MgBr

17.12 1. *p*-TosCl, pyridine; 2. NaCN

17.13 **(a)** 2-Methyl-2-pentene
(b) 3-Methylcyclohexene
(c) 1-Methylcyclohexene
(d) 2,3-Dimethyl-2-pentene
(e) 2-Methyl-2-pentene

17.14 **(a)** 1-Phenylethanol **(b)** 2-Methyl-1-propanol
(c) Cyclopentanol

17.15 **(a)** Hexanoic acid, hexanal **(b)** 2-Hexanone
(c) Hexanoic acid, no reaction

17.16 S_N2 reaction of F^- on silicon with displacement of alkoxide ion.

17.17 Protonation of 2-methylpropene gives the *tert*-butyl cation, which carries out an electrophilic aromatic substitution reaction.

17.18 Disappearance of −OH absorption; appearance of C=O

17.19 **(a)** Singlet **(b)** Doublet **(c)** Triplet **(d)** Doublet **(e)** Doublet **(f)** Singlet

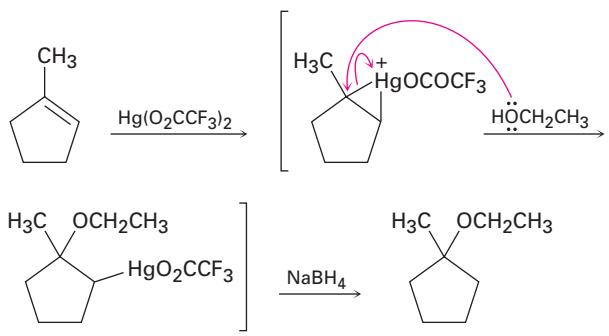
CHAPTER 18

18.1 **(a)** Diisopropyl ether
(b) Cyclopentyl propyl ether
(c) *p*-Bromoanisole or 4-bromo-1-methoxybenzene
(d) 1-Methoxycyclohexene
(e) Ethyl isobutyl ether
(f) Allyl vinyl ether

18.2 A mixture of diethyl ether, dipropyl ether, and ethyl propyl ether is formed in a 1:1:2 ratio.

18.3 **(a)** $CH_3CH_2CH_2O^- + CH_3Br$
(b) $PhO^- + CH_3Br$
(c) $(CH_3)_2CHO^- + PhCH_2Br$
(d) $(CH_3)_3CCH_2O^- + CH_3CH_2Br$

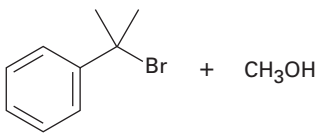
18.4



18.5 **(a)** Either method **(b)** Williamson **(c)** Alkoxymercuration **(d)** Williamson

18.6 **(a)** Bromoethane > 2-Bromopropane > Bromobenzene
(b) Bromoethane > Chloroethane > 1-Iodopropene

18.7 **(a)**



(b)

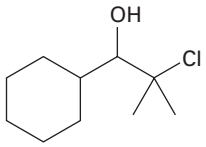
18.8 Protonation of the oxygen atom, followed by E1 reaction

18.9 Br^- and I^- are better nucleophiles than Cl^-.

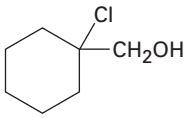
18.10 *o*-(1-Methylallyl)phenol

18.11 Epoxidation of *cis*-2-butene yields *cis*-2,3-epoxybutane, while epoxidation of *trans*-2-butene yields *trans*-2,3-epoxybutane.

18.12 **(a)**

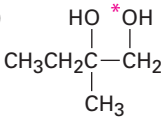


(b)

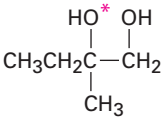


18.13 **(a)** 1-Methylcyclohexene + OsO_4; then $NaHSO_3$
(b) 1-Methylcyclohexene + *m*-chloroperoxybenzoic acid, then H_3O^+

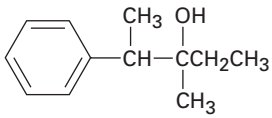
18.14 **(a)**



(b)



(c)



18.16 **(a)** 2-Butanethiol
(b) 2,2,6-Trimethyl-4-heptanethiol
(c) 2-Cyclopentene-1-thiol
(d) Ethyl isopropyl sulfide
(e) *o*-Di(methylthio)benzene
(f) 3-(Ethylthio)cyclohexanone

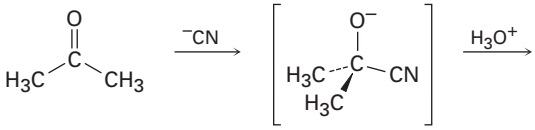
18.17 **(a)** 1. $LiAlH_4$; 2. PBr_3; 3. $(H_2N)_2C{=}S$; 4. H_2O, NaOH
(b) 1. HBr; 2. $(H_2N)_2C{=}S$; 3. H_2O, NaOH

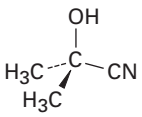
18.18 1,2-Epoxybutane

PREVIEW OF CARBONYL CHEMISTRY

1. Acetyl chloride is more electrophilic than acetone.

2.





3. **(a)** Nucleophilic acyl substitution
(b) Nucleophilic addition
(c) Carbonyl condensation

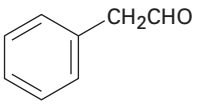
CHAPTER 19

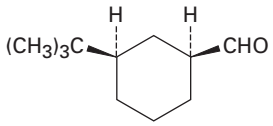
19.1 **(a)** 2-Methyl-3-pentanone
(b) 3-Phenylpropanal
(c) 2,6-Octanedione
(d) *trans*-2-Methylcyclohexanecarbaldehyde
(e) Pentanedial
(f) *cis*-2,5-Dimethylcyclohexanone

19.2

(a) CH_3CHCH_2CHO (CH$_3$ branch)

(b) $CH_3CHCH_2CCH_3$ (Cl branch, O double bond)

(c) 

(d) 

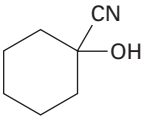
(e) $H_2C{=}CCH_2CHO$ (CH$_3$ branch)

(f) $CH_3CH_2CHCH_2CH_2CHCHO$ (CH$_3$ and CH$_3$CHCl branches)

19.3 **(a)** PCC **(b)** 1. O_3; 2. Zn **(c)** DIBAH

19.4 **(a)** $Hg(OAc)_2$, H_3O^+
(b) 1. CH_3COCl, $AlCl_3$; 2. Br_2, $FeBr_3$
(c) 1. Mg; 2. CH_3CHO; 3. H_3O^+; 4. PCC
(d) 1. BH_3; 2. H_2O_2, NaOH; 3. PCC

19.5



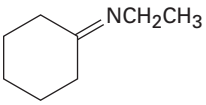
19.6 The electron-withdrawing nitro group in *p*-nitrobenzaldehyde polarizes the carbonyl group.

19.7 $CCl_3CH(OH)_2$

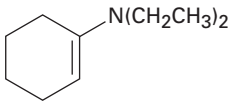
19.8 Labeled water adds reversibly to the carbonyl group.

19.9 The equilibrium is unfavorable for sterically hindered ketones.

19.10

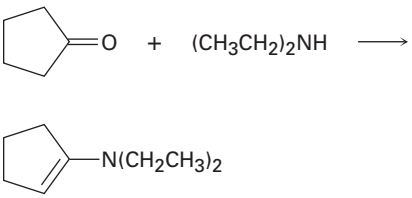


and



19.11 The steps are the exact reverse of the forward reaction.

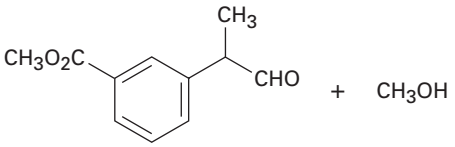
19.12



19.13 **(a)** H_2/Pd **(b)** N_2H_4, KOH
(c) 1. H_2/Pd; 2. N_2H_4, KOH

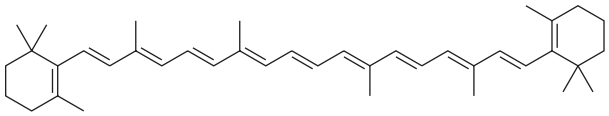
19.14 The mechanism is identical to that between a ketone and 2 equivalents of a monoalcohol (text Figure 19.12).

19.15



19.16 **(a)** Cyclohexanone + $(Ph)_3P{=}CHCH_3$
(b) 2-Cyclohexenone + $(Ph)_3P{=}CH_2$
(c) Acetone + $(Ph)_3P{=}CHCH_2CH_2CH_3$
(d) Acetone + $(Ph)_3P{=}CHPh$
(e) $PhCOCH_3$ + $(Ph)_3P{=}CHPh$
(f) 2-Cyclohexenone + $(Ph)_3P{=}CH_2$

19.17



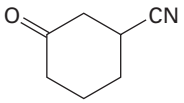
β-Carotene

19.18 Intramolecular Cannizzaro reaction

19.19 Addition of the *pro-R* hydrogen of NADH takes place on the *Re* face of pyruvate.

19.20 The −OH group adds to the *Re* face at C2, and −H adds to the *Re* face at C3, to yield (2*R*,3*S*)-isocitrate.

19.21



19.22 **(a)** 3-Buten-2-one + $(CH_3CH_2CH_2)_2CuLi$
(b) 3-Methyl-2-cyclohexenone + $(CH_3)_2CuLi$
(c) 4-*tert*-Butyl-2-cyclohexenone + $(CH_3CH_2)_2CuLi$
(d) Unsaturated ketone + $(H_2C{=}CH)_2CuLi$

19.23 Look for appearance of either an alcohol or a saturated ketone in the product.

19.24 **(a)** 1715 cm^{-1} **(b)** 1685 cm^{-1}
(c) 1750 cm^{-1} **(d)** 1705 cm^{-1}
(e) 1715 cm^{-1} **(f)** 1705 cm^{-1}

19.25 **(a)** Different peaks due to McLafferty rearrangement
(b) Different peaks due to α cleavage and McLafferty rearrangement
(c) Different peaks due to McLafferty rearrangement

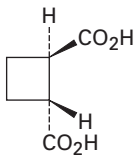
19.26 IR: 1750 cm^{-1}; MS: 140, 84

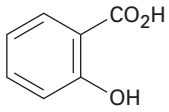
CHAPTER 20

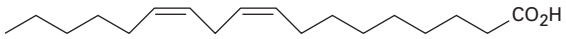
20.1 **(a)** 3-Methylbutanoic acid
(b) 4-Bromopentanoic acid
(c) 2-Ethylpentanoic acid
(d) *cis*-4-Hexenoic acid
(e) 2,4-Dimethylpentanenitrile
(f) *cis*-1,3-Cyclopentanedicarboxylic acid

20.2

(a) $CH_3CH_2CH_2CH(CH_3)CHCO_2H$ **(b)** $CH_3CH(CH_3)CH_2CH_2CO_2H$

(c) 

(d) 

(e) 

(f) $CH_3CH_2CH{=}CHCN$

20.3 Dissolve the mixture in ether, extract with aqueous NaOH, separate and acidify the aqueous layer, and extract with ether.

20.4 43%

20.5 **(a)** 82% dissociation **(b)** 73% dissociation

20.6 Lactic acid is stronger because of the inductive effect of the −OH group.

20.7 The dianion is destabilized by repulsion between charges.

20.8 More reactive

20.9 **(a)** *p*-Methylbenzoic acid < Benzoic acid < *p*-Chlorobenzoic acid
(b) Acetic acid < Benzoic acid < *p*-Nitrobenzoic acid

20.10 **(a)** 1. Mg; 2. CO_2; 3. H_3O^+
(b) 1. Mg; 2. CO_2; 3. H_3O^+ or 1. NaCN; 2. H_3O^+

20.11 1. NaCN; 2. H_3O^+; 3. $LiAlH_4$

20.12 1. PBr_3; 2. NaCN; 3. H_3O^+; 4. $LiAlH_4$

20.13 **(a)** Propanenitrile + CH_3CH_2MgBr, then H_3O^+
(b) *p*-Nitrobenzonitrile + CH_3MgBr, then H_3O^+

20.14 1. NaCN; 2. CH_3CH_2MgBr, then H_3O^+

20.15 A carboxylic acid has a very broad −OH absorption at 2500–3300 cm^{-1}.

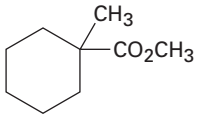
20.16 4-Hydroxycyclohexanone: **H**−C−O absorption near 4 δ in ^1H spectrum and **C**=O absorption near 210 δ in ^{13}C spectrum. Cyclopentanecarboxylic acid: $-CO_2\mathbf{H}$ absorption near 12 δ in ^1H spectrum and $-CO_2H$ absorption near 170 δ in ^{13}C spectrum.

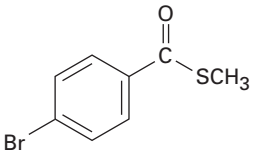
CHAPTER 21

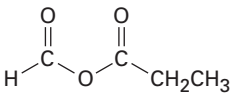
21.1 **(a)** 4-Methylpentanoyl chloride
(b) Cyclohexylacetamide
(c) Isopropyl 2-methylpropanoate
(d) Benzoic anhydride
(e) Isopropyl cyclopentanecarboxylate
(f) Cyclopentyl 2-methylpropanoate
(g) *N*-Methyl-4-pentenamide
(h) (*R*)-2-Hydroxypropanoyl phosphate
(i) Ethyl 2,3-Dimethyl-2-butenethioate

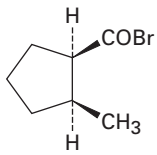
21.2

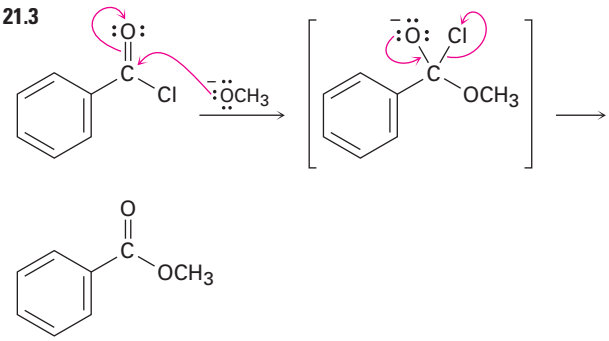
(a) $C_6H_5CO_2C_6H_5$ **(b)** $CH_3CH_2CH_2CON(CH_3)CH_2CH_3$

(c) $(CH_3)_2CHCH_2CH(CH_3)COCl$ **(d)** 

(e) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$ **(f)** 

(g) 

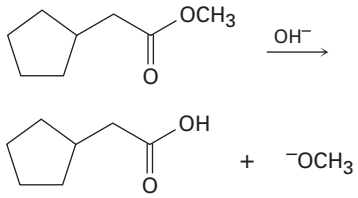
(h) 

21.3 

21.4 **(a)** Acetyl chloride > Methyl acetate > Acetamide
(b) Hexafluoroisopropyl acetate > 2,2,2-Trichloroethyl acetate > Methyl acetate

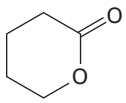
21.5 **(a)** $CH_3CO_2^-\ Na^+$ **(b)** CH_3CONH_2
(c) $CH_3CO_2CH_3 + CH_3CO_2^-\ Na^+$
(d) $CH_3CONHCH_3$

21.6



21.7 **(a)** Acetic acid + 1-butanol
(b) Butanoic acid + methanol
(c) Cyclopentanecarboxylic acid + isopropyl alcohol

21.8



21.9 **(a)** Propanoyl chloride + methanol
(b) Acetyl chloride + ethanol
(c) Benzoyl chloride + ethanol

21.10 Benzoyl chloride + cyclohexanol

21.11 This is a typical nucleophilic acyl substitution reaction, with morpholine as the nucleophile and chloride as the leaving group.

21.12 **(a)** Propanoyl chloride + methylamine
(b) Benzoyl chloride + diethylamine
(c) Propanoyl chloride + ammonia

21.13 **(a)** Benzoyl chloride + $[(CH_3)_2CH]_2CuLi$, or 2-methylpropanoyl chloride + Ph_2CuLi
(b) 2-Propenoyl chloride + $(CH_3CH_2CH_2)_2CuLi$, or butanoyl chloride + $(H_2C{=}CH)_2CuLi$

21.14 This is a typical nucleophilic acyl substitution reaction, with *p*-hydroxyaniline as the nucleophile and acetate ion as the leaving group.

21.15 Monomethyl ester of benzene-1,2-dicarboxylic acid

21.16 Reaction of a carboxylic acid with an alkoxide ion gives the carboxylate ion.

21.17 $HOCH_2CH_2CH_2CHO$

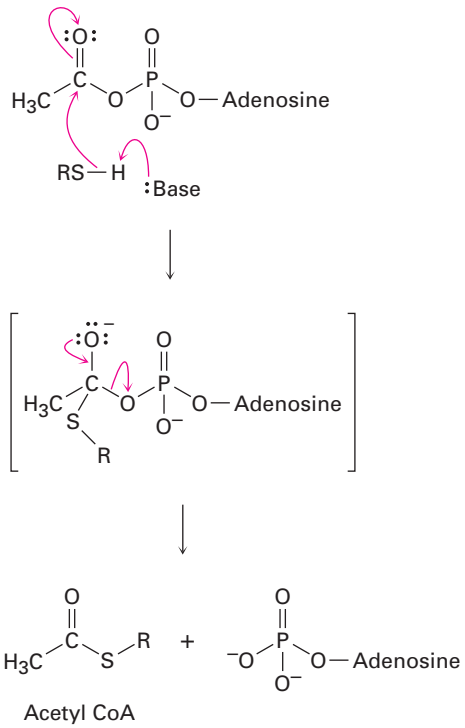
21.18 **(a)** $CH_3CH_2CH_2CH(CH_3)CH_2OH$
(b) $PhOH + PhCH_2OH$

21.19 **(a)** Ethyl benzoate + 2 CH_3MgBr
(b) Ethyl acetate + 2 $PhMgBr$
(c) Ethyl pentanoate + 2 CH_3CH_2MgBr

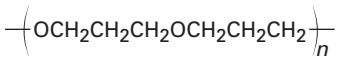
21.20 **(a)** H_2O, NaOH
(b) Benzoic acid + BH_3
(c) $LiAlH_4$

21.21 1. Mg; 2. CO_2, then H_3O^+; 3. $SOCl_2$; 4. $(CH_3)_2NH$; 5. $LiAlH_4$

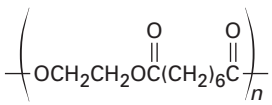
21.22



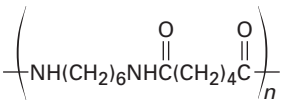
21.23 **(a)**



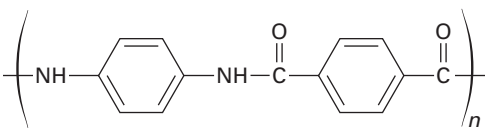
(b)



(c)



21.24

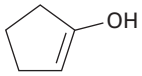
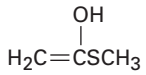
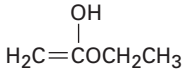
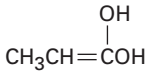
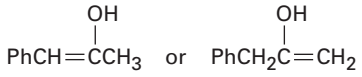


21.25 The product has a large amount of cross-linking.

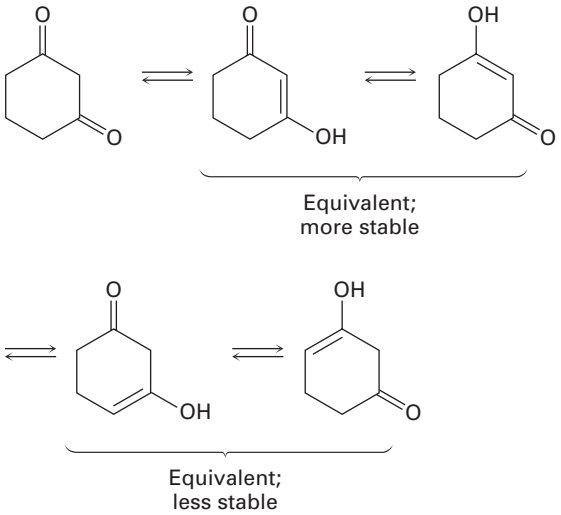
21.26 **(a)** Ester **(b)** Acid chloride
(c) Carboxylic acid
(d) Aliphatic ketone or cyclohexanone

21.27 **(a)** $CH_3CH_2CH_2CO_2CH_2CH_3$ and other possibilities
(b) $CH_3CON(CH_3)_2$
(c) $CH_3CH{=}CHCOCl$ or $H_2C{=}C(CH_3)COCl$

CHAPTER 22

22.1 **(a)** 
(b) 
(c) 
(d) $CH_3CH{=}CHOH$
(e) 
(f) 

22.2 **(a)** 4 **(b)** 3 **(c)** 3 **(d)** 2 **(e)** 4 **(f)** 5

22.3 

22.4 Acid-catalyzed formation of an enol is followed by deuteronation of the enol double bond and dedeuteronation of oxygen.

22.5 1. Br_2; 2. Pyridine, heat

22.6 The intermediate α-bromo acid bromide undergoes a nucleophilic acyl substitution reaction with methanol to give an α-bromo ester.

22.7 **(a)** $CH_3C\underline{H}_2CHO$ **(b)** $(CH_3)_3CCOC\underline{H}_3$
(c) $CH_3CO_2\underline{H}$ **(d)** $PhCON\underline{H}_2$
(e) $CH_3CH_2C\underline{H}_2CN$ **(f)** $C\underline{H}_3CON(CH_3)_2$

22.8 $^{-}{:}CH_2C{\equiv}N{:} \longleftrightarrow H_2C{=}C{=}\ddot{N}{:}^{-}$

22.9 Acid is regenerated, but base is used stoichiometrically.

22.10 **(a)** 1. $Na^+\ {}^-OEt$; 2. $PhCH_2Br$; 3. H_3O^+
(b) 1. $Na^+\ {}^-OEt$; 2. $CH_3CH_2CH_2Br$; 3. $Na^+\ {}^-OEt$; 4. CH_3Br; 5. H_3O^+
(c) 1. $Na^+\ {}^-OEt$; 2. $(CH_3)_2CHCH_2Br$; 3. H_3O^+

22.11 Malonic ester has only two acidic hydrogens to be replaced.

22.12 1. $Na^+\ {}^-OEt$; 2. $(CH_3)_2CHCH_2Br$; 3. $Na^+\ {}^-OEt$; 4. CH_3Br; 5. H_3O^+

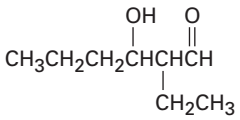
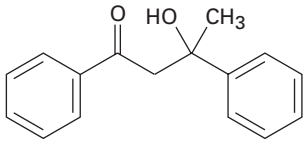
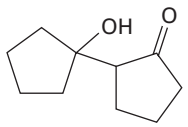
22.13 **(a)** $(CH_3)_2CHCH_2Br$ **(b)** $PhCH_2CH_2Br$

22.14 None can be prepared.

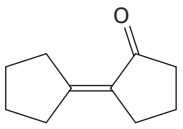
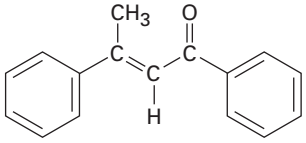
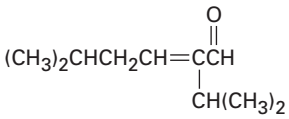
22.15 1. 2 $Na^+\ {}^-OEt$; 2. $BrCH_2CH_2CH_2CH_2Br$; 3. H_3O^+

22.16 **(a)** Alkylate phenylacetone with CH_3I
(b) Alkylate pentanenitrile with CH_3CH_2I
(c) Alkylate cyclohexanone with $H_2C{=}CHCH_2Br$
(d) Alkylate cyclohexanone with excess CH_3I
(e) Alkylate $C_6H_5COCH_2CH_3$ with CH_3I
(f) Alkylate methyl 3-methylbutanoate with CH_3CH_2I

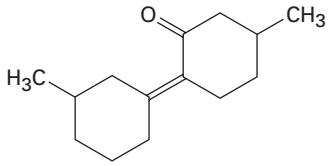
CHAPTER 23

23.1 **(a)** 
(b) 
(c) 

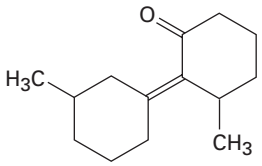
23.2 The reverse reaction is the exact opposite of the forward reaction.

23.3
(a) 
(b) 
(c) 

23.4



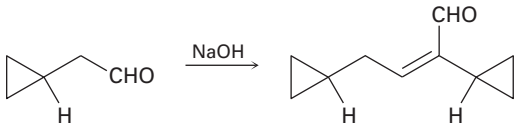
and



23.5 **(a)** Not an aldol product **(b)** 3-Pentanone

23.6 1. NaOH; 2. $LiAlH_4$; 3. H_2/Pd

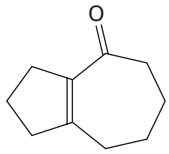
23.7



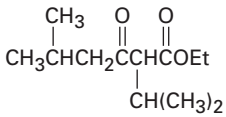
23.8 **(a)** $C_6H_5CHO + CH_3COCH_3$
(b), **(c)** Not easily prepared

23.9 The CH_2 position between the two carbonyl groups is so acidic that it is completely deprotonated to give a stable enolate ion.

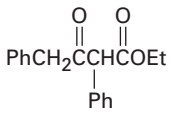
23.10



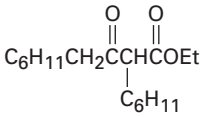
23.11 **(a)**



(b)

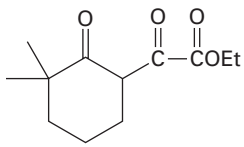


(c)

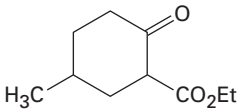


23.12 The cleavage reaction is the exact reverse of the forward reaction.

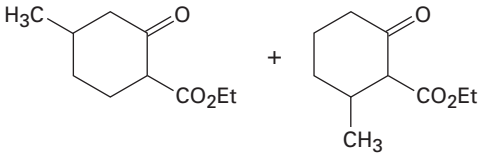
23.13



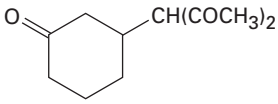
23.14



23.15

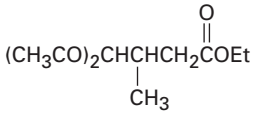


23.16 **(a)**



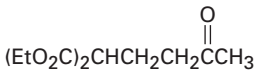
(b) $(CH_3CO)_2CHCH_2CH_2CN$

(c)

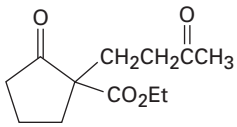


23.17

(a)



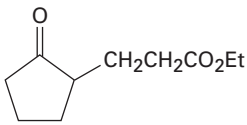
(b)



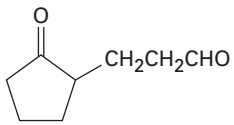
23.18 $CH_3CH_2COCH{=}CH_2 + CH_3CH_2NO_2$

23.19

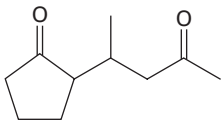
(a)



(b)

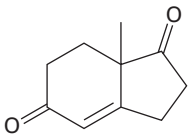


(c)



23.20 **(a)** Cyclopentanone enamine + propenenitrile
(b) Cyclohexanone enamine + methyl propenoate

23.21



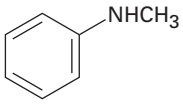
23.22 2,5,5-Trimethyl-1,3-cyclohexanedione + 1-penten-3-one

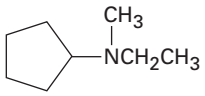
CHAPTER 24

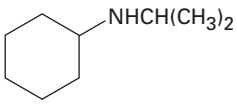
24.1 **(a)** *N*-Methylethylamine
(b) Tricyclohexylamine
(c) *N*-Methyl-*N*-propylcyclohexylamine
(d) *N*-Methylpyrrolidine
(e) Diisopropylamine
(f) 1,3-Butanediamine

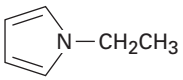
24.2

(a) $[(CH_3)_2CH]_3N$ **(b)** $(H_2C{=}CHCH_2)_2NH$

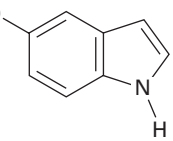
(c) 

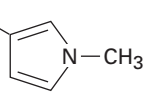
(d) 

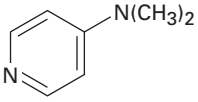
(e) 

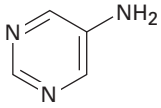
(f) 

24.3

(a) 

(b) 

(c) 

(d) 

24.4 **(a)** $CH_3CH_2NH_2$ **(b)** NaOH
(c) CH_3NHCH_3

24.5 Propylamine is stronger; benzylamine $pK_b = 4.67$; propylamine $pK_b = 3.29$

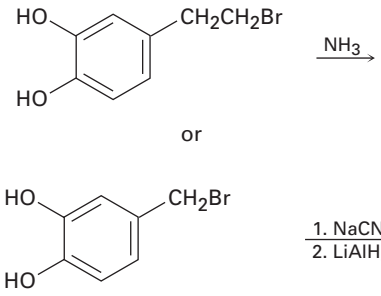
24.6 **(a)** *p*-Nitroaniline < *p*-Aminobenzaldehyde < *p*-Bromoaniline
(b) *p*-Aminoacetophenone < *p*-Chloroaniline < *p*-Methylaniline
(c) *p*-(Trifluoromethyl)aniline < *p*-(Fluoromethyl)aniline < *p*-Methylaniline

24.7 Pyrimidine is essentially 100% neutral (unprotonated).

24.8 **(a)** Propanenitrile or propanamide
(b) *N*-Propylpropanamide
(c) Benzonitrile or benzamide
(d) *N*-Phenylacetamide

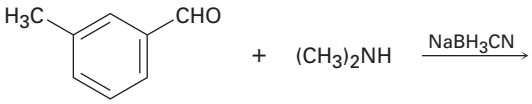
24.9 The reaction takes place by two nucleophilic acyl substitution reactions.

24.10



24.11 **(a)** Ethylamine + acetone, or isopropylamine + acetaldehyde
(b) Aniline + acetaldehyde
(c) Cyclopentylamine + formaldehyde, or methylamine + cyclopentanone

24.12



24.13 **(a)** 4,4-Dimethylpentanamide or 4,4-dimethylpentanoyl azide
(b) *p*-Methylbenzamide or *p*-methylbenzoyl azide

24.14 **(a)** 3-Octene and 4-octene
(b) Cyclohexene
(c) 3-Heptene
(d) Ethylene and cyclohexene

24.15 $H_2C{=}CHCH_2CH_2CH_2N(CH_3)_2$

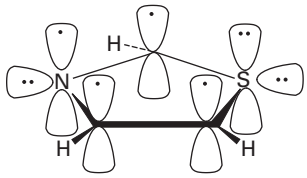
24.16 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. $HOSO_2Cl$; 5. aminothiazole; 6. H_2O, NaOH

24.17 **(a)** 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. 2 CH_3Br
(b) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. Cl_2; 5. H_2O, NaOH
(c) 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$; 3. $SnCl_2$
(d) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. 2 CH_3Cl, $AlCl_3$; 5. H_2O, NaOH

24.18 **(a)** 1. CH_3Cl, $AlCl_3$; 2. HNO_3, H_2SO_4; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuBr; 6. $KMnO_4$, H_2O
(b) 1. HNO_3, H_2SO_4; 2. Br_2, $FeBr_3$; 3. $SnCl_2$, H_3O^+; 4. $NaNO_2$, H_2SO_4; 5. CuCN; 6. H_3O^+
(c) 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuBr
(d) 1. CH_3Cl, $AlCl_3$; 2. HNO_3, H_2SO_4; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuCN; 6. H_3O^+
(e) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. 2 Br_2; 5. H_2O, NaOH; 6. $NaNO_2$, H_2SO_4; 7. CuBr

24.19 1. HNO_3, H_2SO_4; 2. $SnCl_2$; 3a. 2 equiv. CH_3I; 3b. $NaNO_2$, H_2SO_4; 4. product of 3a + product of 3b

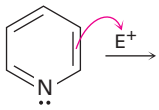
24.20

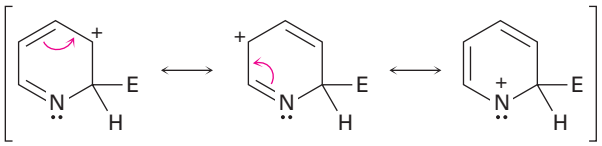


24.21 4.1% protonated

24.22

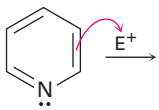
Attack at C2:

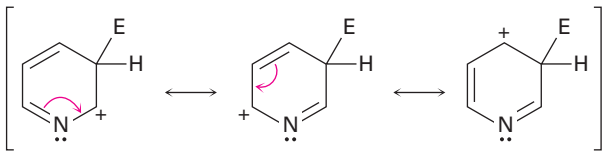




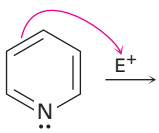
Unfavorable

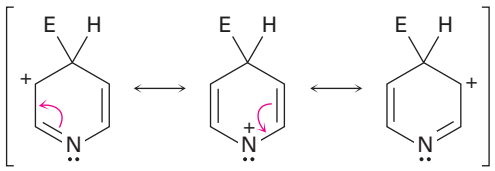
Attack at C3:





Attack at C4:

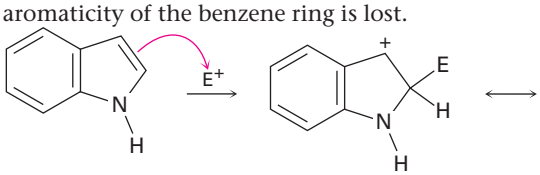


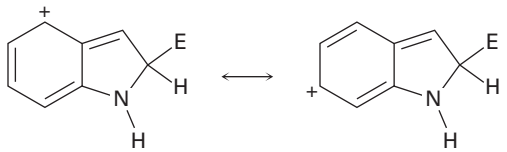


Unfavorable

24.23 The side-chain nitrogen is more basic than the ring nitrogen.

24.24 Reaction at C2 is disfavored because the aromaticity of the benzene ring is lost.





24.25 $(CH_3)_3CCOCH_3 \longrightarrow (CH_3)_3CCH(NH_2)CH_3$

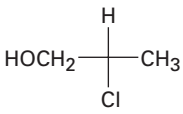
CHAPTER 25

25.1 **(a)** Aldotetrose
(b) Ketopentose
(c) Ketohexose
(d) Aldopentose

25.2 **(a)** *S* **(b)** *R* **(c)** *S*

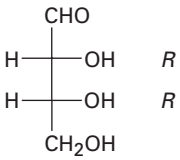
25.3 A, B, and C are the same.

25.4



R

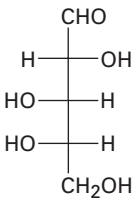
25.5



R
R

25.6 **(a)** L-Erythrose; 2*S*,3*S*
(b) D-Xylose; 2*R*,3*S*,4*R*
(c) D-Xylulose; 3*S*,4*R*

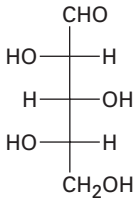
25.7



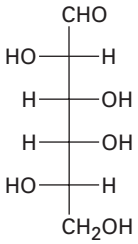
L-(+)-Arabinose

25.8

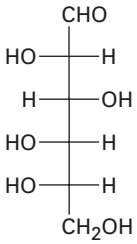
(a)



(b)

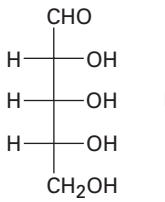


(c)



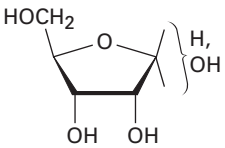
25.9 16 D and 16 L aldoheptoses

25.10

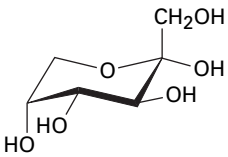


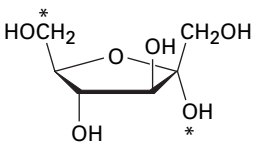
D-Ribose

25.11

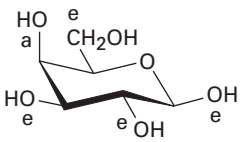


25.12

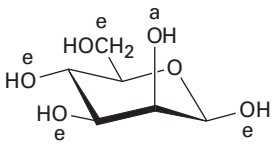




25.13

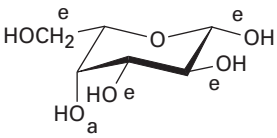


β-D-Galactopyranose



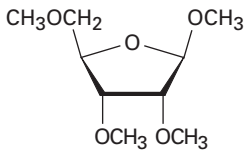
β-D-Mannopyranose

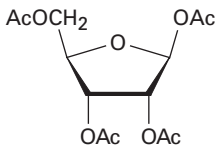
25.14



25.15 α-D-Allopyranose

25.16





25.17 D-Galactitol has a plane of symmetry and is a meso compound, whereas D-glucitol is chiral.

25.18 The −CHO end of L-gulose corresponds to the $-CH_2OH$ end of D-glucose after reduction.

25.19 D-Allaric acid has a symmetry plane and is a meso compound, but D-glucaric acid is chiral.

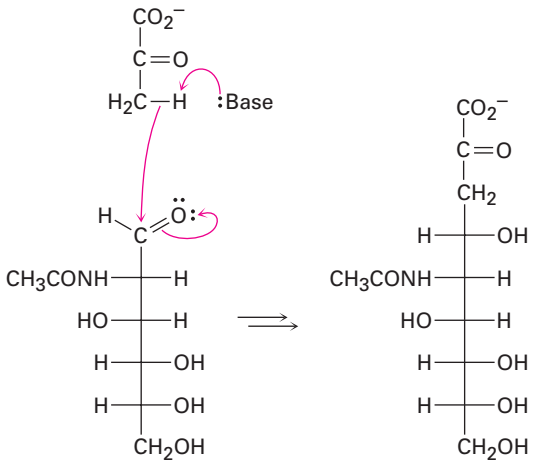
25.20 D-Allose and D-galactose yield meso aldaric acids; the other six D-hexoses yield optically active aldaric acids.

25.21 D-Allose + D-altrose

25.22 L-Xylose

25.23 D-Xylose and D-lyxose

25.24



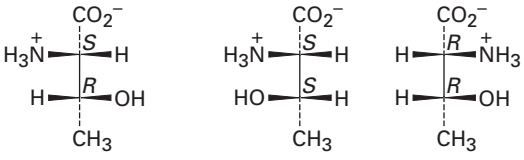
25.25 **(a)** The hemiacetal ring is reduced.
(b) The hemiacetal ring is oxidized.
(c) All hydroxyl groups are acetylated.

CHAPTER 26

26.1 Aromatic: Phe, Tyr, Trp, His; sulfur-containing: Cys, Met; alcohols: Ser, Thr; hydrocarbon side chains: Ala, Ile, Leu, Val, Phe

26.2 The sulfur atom in the $-CH_2SH$ group of cysteine makes the side chain higher in priority than the $-CO_2H$ group.

26.3

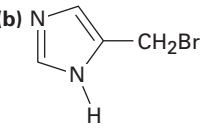


L-Threonine Diastereomers of L-threonine

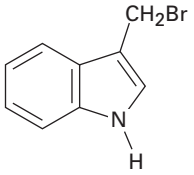
26.4 Net positive at pH = 5.3; net negative at pH = 7.3

26.5 **(a)** Start with 3-phenylpropanoic acid:
1. Br_2, PBr_3; 2. NH_3
(b) Start with 3-methylbutanoic acid:
1. Br_2, PBr_3; 2. NH_3

26.6 **(a)** $(CH_3)_2CHCH_2Br$ **(b)**

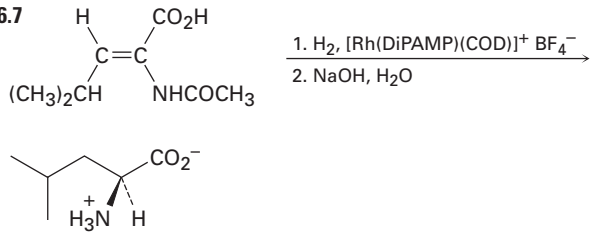


(c)



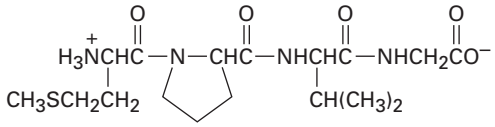
(d) $CH_3SCH_2CH_2Br$

26.7

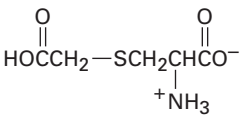


26.8 Val-Tyr-Gly (VYG), Tyr-Gly-Val (YGV), Gly-Val-Tyr (GVY), Val-Gly-Tyr (VGY), Tyr-Val-Gly (YVG), Gly-Tyr-Val (GYV)

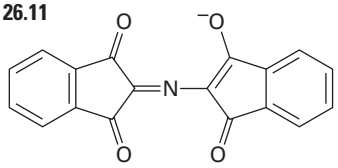
26.9



26.10



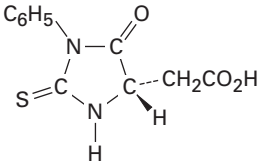
26.11



26.12 Trypsin: Asp-Arg + Val-Tyr-Ile-His-Pro-Phe
Chymotrypsin: Asp-Arg-Val-Tyr + Ile-His-Pro-Phe

26.13 Methionine

26.14



26.15 **(a)** Arg-Pro-Leu-Gly-Ile-Val
(b) Val-Met-Trp-Asp-Val-Leu (VMWNVL)

26.16 This is a typical nucleophilic acyl substitution reaction, with the amine of the amino acid as the nucleophile and *tert*-butyl carbonate as the leaving group. The *tert*-butyl carbonate then loses CO_2 and gives *tert*-butoxide, which is protonated.

26.17 (1) Protect the amino group of leucine.
(2) Protect the carboxylic acid group of alanine.
(3) Couple the protected amino acids with DCC.
(4) Remove the leucine protecting group.
(5) Remove the alanine protecting group.

26.18 **(a)** Lyase **(b)** Hydrolase **(c)** Oxidoreductase

CHAPTER 27

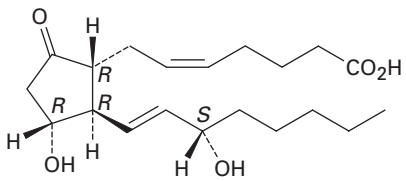
27.1 $CH_3(CH_2)_{18}CO_2CH_2(CH_2)_{30}CH_3$

27.2 Glyceryl tripalmitate is higher melting.

27.3 $[CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2^-]_2\ Mg^{2+}$

27.4 Glyceryl dioleate monopalmitate → glycerol + 2 sodium oleate + sodium palmitate

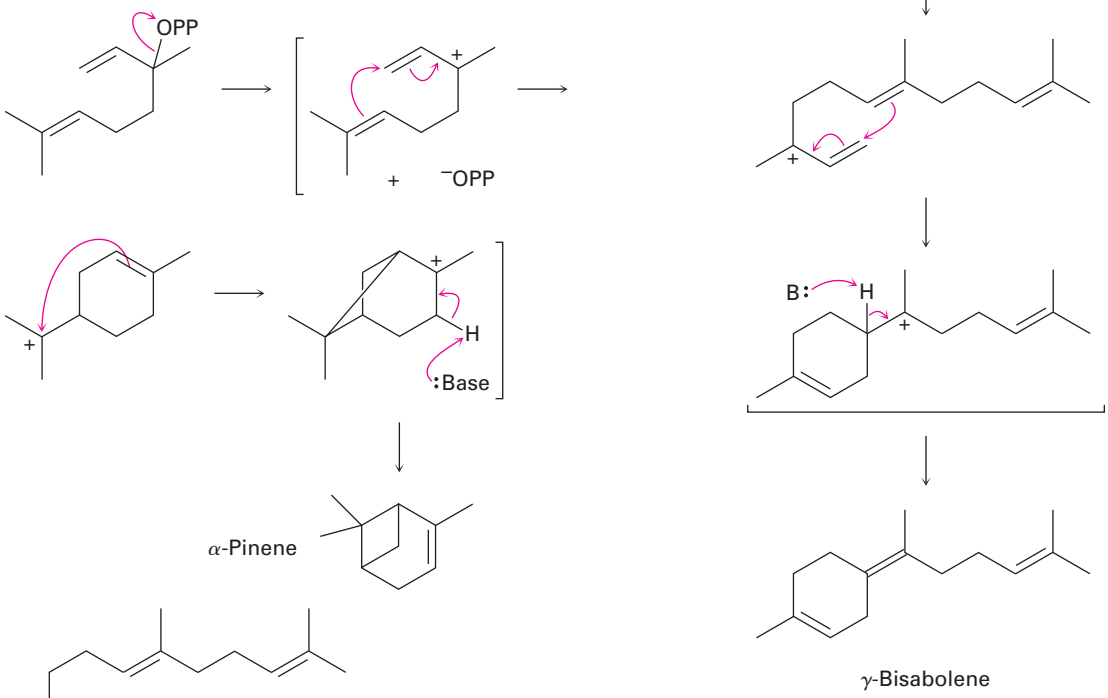
27.5



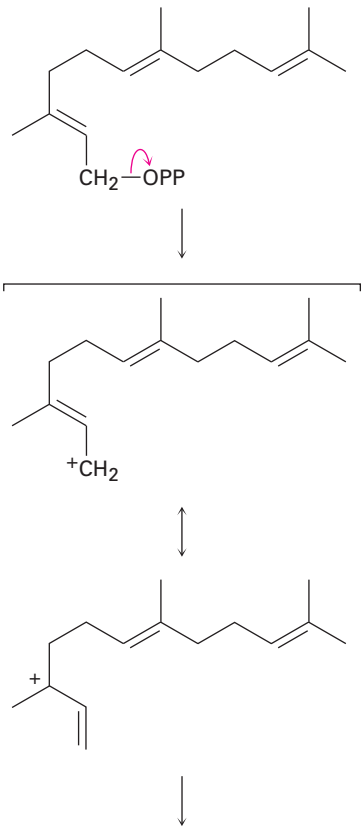
27.6 The *pro-S* hydrogen is cis to the $-CH_3$ group; the *pro-R* hydrogen is trans.

27.7

(a)

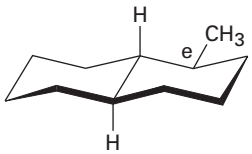


(b)

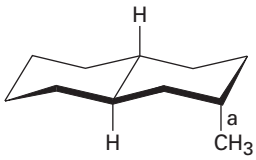


27.8

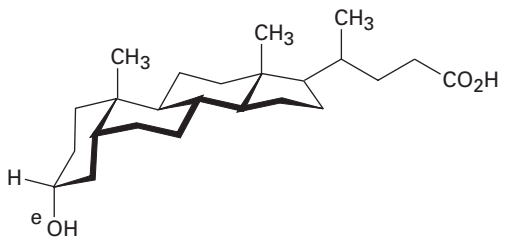
(a)



(b)



27.9

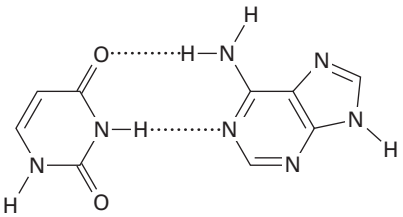


27.10 Three methyl groups are removed, the side-chain double bond is reduced, and the double bond in the B ring is migrated.

CHAPTER 28

28.3 (5′) ACGGATTAGCC (3′)

28.4



28.5 (3′) CUAAUGGCAU (5′)

28.6 (5′) ACTCTGCGAA (3′)

28.7 **(a)** GCU, GCC, GCA, GCG
(b) UUU, UUC
(c) UUA, UUG, CUU, CUC, CUA, CUG
(d) UAU, UAC

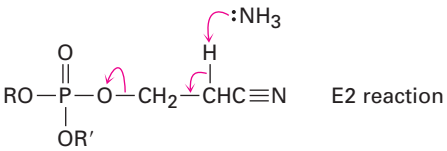
28.8 **(a)** AGC, GGC, UGC, CGC
(b) AAA, GAA
(c) UAA, CAA, GAA, GAG, UAG, CAG
(d) AUA, GUA

28.9 Leu-Met-Ala-Trp-Pro-Stop

28.10 (5′) TTA-GGG-CCA-AGC-CAT-AAG (3′)

28.11 The cleavage is an S_N1 reaction that occurs by protonation of the oxygen atom followed by loss of the stable triarylmethyl carbocation.

28.12



CHAPTER 29

29.1 $HOCH_2CH(OH)CH_2OH + ATP \longrightarrow HOCH_2CH(OH)CH_2OPO_3^{2-} + ADP$

29.2 Caprylyl CoA ⟶ Hexanoyl CoA ⟶ Butyryl CoA ⟶ 2 Acetyl CoA

29.3 **(a)** 8 acetyl CoA; 7 passages
(b) 10 acetyl CoA; 9 passages

29.4 The dehydration is an E1cB reaction.

29.5 At C2, C4, C6, C8, and so forth

29.6 The *Si* face

29.7 Steps 7 and 10

29.8 Steps 1, 3: Phosphate transfers; steps 2, 5, 8: isomerizations; step 4: retro-aldol reaction; step 5: oxidation and nucleophilic acyl substitution; steps 7, 10: phosphate transfers; step 9: E2 dehydration

29.9 C1 and C6 of glucose become $-CH_3$ groups; C3 and C4 become CO_2.

29.10 Citrate and isocitrate

29.11 E2 elimination of water, followed by conjugate addition

29.12 *pro-R*; anti geometry

29.13 The reaction occurs by two sequential nucleophilic acyl substitutions, the first by a cysteine residue in the enzyme, with phosphate as leaving group, and the second by hydride donation from NADH, with the cysteine residue as leaving group.

29.14 Initial imine formation between PMP and α-ketoglutarate is followed by double-bond rearrangement to an isomeric imine and hydrolysis.

29.15 $(CH_3)_2CHCH_2COCO_2^-$

29.16 Asparagine

CHAPTER 30

30.1 Ethylene: ψ_1 is the HOMO and ψ_2^* is the LUMO in the ground state; ψ_2^* is the HOMO and there is no LUMO in the excited state. 1,3-Butadiene: ψ_2 is the HOMO and ψ_3^* is the LUMO in the ground state; ψ_3^* is the HOMO and ψ_4^* is the LUMO in the excited state.

30.2 Disrotatory: *cis*-5,6-dimethyl-1,3-cyclohexadiene; conrotatory: *trans*-5,6-dimethyl-1,3-cyclohexadiene. Disrotatory closure occurs.

30.3 The more stable of two allowed products is formed.

30.4 *trans*-5,6-Dimethyl-1,3-cyclohexadiene; *cis*-5,6-dimethyl-1,3-cyclohexadiene

30.5 *cis*-3,6-Dimethylcyclohexene; *trans*-3,6-dimethylcyclohexene

30.6 A [6 + 4] suprafacial cycloaddition

30.7 An antarafacial [1,7] sigmatropic rearrangement

30.8 A series of [1,5] hydrogen shifts occur.

30.9 Claisen rearrangement is followed by a Cope rearrangement.

30.10 **(a)** Conrotatory **(b)** Disrotatory
(c) Suprafacial **(d)** Antarafacial
(e) Suprafacial

CHAPTER 31

31.1 $H_2C{=}CHCO_2CH_3 < H_2C{=}CHCl < H_2C{=}CHCH_3 < H_2C{=}CH{-}C_6H_5$

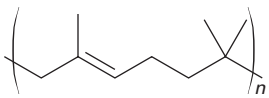
31.2 $H_2C{=}CHCH_3 < H_2C{=}CHC_6H_5 < H_2C{=}CHC{\equiv}N$

31.3 The intermediate is a resonance-stabilized benzylic carbanion, $Ph{-}\ddot{C}HR$.

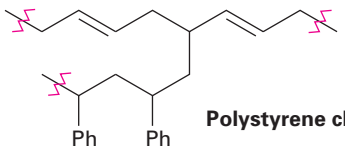
31.4 The polymer has no chirality centers.

31.5 No, the polymers are racemic.

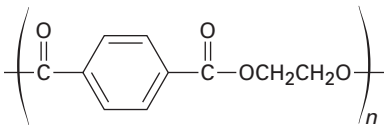
31.6



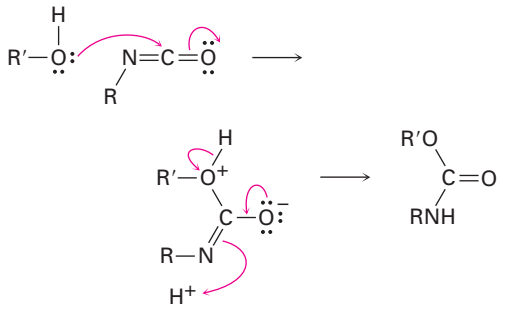
31.7



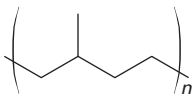
31.8



31.9



31.10



Atactic

31.11