## GLOSSARY

**Absolute configuration** (Section 7.5): The three-dimensional arrangement of atoms or groups at a stereogenic center.

**Acetal** (Section 17.8): Product of the reaction of an aldehyde or a ketone with two moles of an alcohol according to the equation

$$\begin{array}{c} O \\ \parallel \\ RCR' \ + \ 2R''OH \xrightarrow{H^+} \begin{array}{c} OR'' \\ \mid \\ RCR' \ + \ H_2O \end{array}$$

Acetoacetic ester synthesis (Section 21.6): A synthetic method for the preparation of ketones in which alkylation of the enolate of ethyl acetoacetate

$$\begin{matrix} O & O \\ \parallel & \parallel \\ CH_3CCH_2COCH_2CH_3 \end{matrix}$$

is the key carbon—earbon bond-forming step.

**Acetyl coenzyme A** (Section 26.1): A thiol ester abbreviated as

that acts as the source of acetyl groups in biosynthetic processes involving acetate.

**Acetylene** (Sections 1.18 and 9.1): The simplest alkyne, HC≡CH.

**Achiral** (Section 7.1): Opposite of *chiral*. An achiral object is superimposable on its mirror image.

Acid (Section 4.6): According to the Arrhenius definition, a substance that ionizes in water to produce protons. According to the Brønsted—Lowry definition, a substance that donates a proton to some other substance. According to the Lewis definition, an electron-pair acceptor.

Acid anhydride (Sections 2.3 and 20.1): Compound of the type

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ RCOCR \end{array}$$

Both R groups are usually the same, although they need not always be.

**Acid dissociation constant**  $K_a$  (Section 4.6): Equilibrium constant for dissociation of an acid:

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm A}^-]}{[{\rm HA}]}$$

Activating substituent (Sections 12.10 and 12.12): A group that when present in place of a hydrogen causes a particular reaction to occur faster. Term is most often applied to substituents that increase the rate of electrophilic aromatic substitution.

**Active site** (Section 27.20): The region of an enzyme at which the substrate is bound.

**Acylation** (Section 12.7 and Chapter 20): Reaction in which an acyl group becomes attached to some structural unit in a molecule. Examples include the Friedel—Crafts acylation and the conversion of amines to amides.

Acyl chloride (Sections 2.3 and 20.1): Compound of the type



R may be alkyl or aryl.

**Acyl group** (Sections 12.7 and 20.1): The group

R may be alkyl or aryl.

**Acylium ion** (Section 12.7): The cation  $R-C \equiv 0$ :

Acyl transfer (Section 20.3): A nucleophilic acyl substitution. A reaction in which one type of carboxylic acid derivative is converted to another.

**Addition** (Section 6.1): Reaction in which a reagent X—Y adds to a multiple bond so that X becomes attached to one of the carbons of the multiple bond and Y to the other.

**1,2 Addition** (Section 10.10): Addition of reagents of the type X—Y to conjugated dienes in which X and Y add to adjacent doubly bonded carbons:

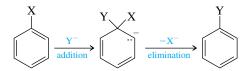
$$\begin{array}{c} R_2C = CH - CH = CR_2 \xrightarrow{X-Y} R_2C - CH - CH = CR_2 \\ \downarrow & \downarrow \\ X & Y \end{array}$$

1,4 Addition (Section 10.10): Addition of reagents of the type X—Y to conjugated dienes in which X and Y add to the termini of the diene system:

$$\begin{array}{c} R_2C = CH - CH = CR_2 \xrightarrow{X-Y} R_2C - CH = CH - CR_2 \\ \downarrow X & Y \end{array}$$

Addition—elimination mechanism (Section 23.6): Two-stage mechanism for nucleophilic aromatic substitution. In the

addition stage, the nucleophile adds to the carbon that bears the leaving group. In the elimination stage, the leaving group is expelled.



**Alcohol** (Section 4.2): Compound of the type ROH.

**Alcohol dehydrogenase** (Section 15.11): Enzyme in the liver that catalyzes the oxidation of alcohols to aldehydes and ketones.

Aldaric acid (Section 25.19): Carbohydrate in which carboxylic acid functions are present at both ends of the chain. Aldaric acids are typically prepared by oxidation of aldoses with nitric acid.

**Aldehyde** (Sections 2.3 and 17.1): Compound of the type

**Alditol** (Section 25.18): The polyol obtained on reduction of the carbonyl group of a carbohydrate.

**Aldol addition** (Section 18.9): Nucleophilic addition of an aldehyde or ketone enolate to the carbonyl group of an aldehyde or a ketone. The most typical case involves two molecules of an aldehyde, and is usually catalyzed by bases.

$$\begin{array}{c} O & OH \\ \parallel & \parallel \\ 2RCH_2CH \xrightarrow{HO^-} RCH_2CHCHR \\ & \parallel \\ CH = O \end{array}$$

Aldol condensation (Sections 18.9—48.10): When an aldol addition is carried out so that the β-hydroxy aldehyde or ketone dehydrates under the conditions of its formation, the product is described as arising by an aldol condensation.

$$\begin{array}{ccc}
O \\
1 & HO^{-} \\
2RCH_{2}CH \xrightarrow{HO^{-}} & RCH_{2}CH = CR & + H_{2}O \\
CH = O
\end{array}$$

**Aldonic acid** (Section 25.19): Carboxylic acid obtained by oxidation of the aldehyde function of an aldose.

**Aldose** (Section 25.1): Carbohydrate that contains an aldehyde carbonyl group in its open-chain form.

**Alicyclic** (Section 2.12): Term describing an *aliphatic cyclic* structural unit.

Aliphatic (Section 2.1): Term applied to compounds that do not contain benzene or benzene-like rings as structural units. (Historically, *aliphatic* was used to describe compounds derived from fats and oils.)

**Alkadiene** (Section 10.5): Hydrocarbon that contains two carbon—earbon double bonds; commonly referred to as a *diene*.

**Alkaloid** (Section 22.5): Amine that occurs naturally in plants. The name derives from the fact that such compounds are weak bases.

**Alkane** (Section 2.1): Hydrocarbon in which all the bonds are single bonds. Alkanes have the general formula  $C_nH_{2n+2}$ .

Alkene (Section 2.1): Hydrocarbon that contains a carbon—earbon double bond (C=C); also known by the older name *olefin*.

**Alkoxide ion** (Section 5.14): Conjugate base of an alcohol; a species of the type  $R - \ddot{O}$ :

**Alkylamine** (Section 22.1): Amine in which the organic groups attached to nitrogen are alkyl groups.

**Alkylation** (Section 9.6): Reaction in which an alkyl group is attached to some structural unit in a molecule.

**Alkyl group** (Section 2.10): Structural unit related to an alkane by replacing one of the hydrogens by a potential point of attachment to some other atom or group. The general symbol for an alkyl group is R—.

**Alkyl halide** (Section 4.1): Compound of the type RX, in which X is a halogen substituent (F, Cl, Br, I).

**Alkyloxonium ion** (Section 4.6): Positive ion of the type  $ROH_2^+$ .

**Alkyne** (Section 2.1): Hydrocarbon that contains a carbon—earbon triple bond.

Allene (Section 10.5): The compound  $CH_2 = C = CH_2$ . Allyl cation (Section 10.2): The carbocation

The carbocation is stabilized by delocalization of the  $\pi$  electrons of the double bond, and the positive charge is shared by the two CH<sub>2</sub> groups. Substituted analogs of allyl cation are called *allylic carbocations*.

Allyl group (Sections 5.1, 10.1): The group

$$CH_2 = CHCH_2 -$$

**Allylic rearrangement** (Section 10.2): Functional group transformation in which double-bond migration has converted one allylic structural unit to another, as in:

$$\begin{array}{c} R_2C = CHCH_2X \longrightarrow R_2CCH = CH_2 \\ \downarrow \\ Y \end{array}$$

O

Amide (Sections 2.3 and 20.1): Compound of the type  $RCNR_2'$  Amine (Chapter 22): Molecule in which a nitrogen-containing group of the type  $-NH_2$ , -NHR, or  $-NR_2$  is attached to an alkyl or aryl group.

**α-Amino acid** (Section 27.1): A carboxylic acid that contains an amino group at the  $\alpha$ -carbon atom.  $\alpha$ -Amino acids are the building blocks of peptides and proteins. An  $\alpha$ -amino acid normally exists as a *zwitterion*.

$${\rm RCHCO_2}^-\\ {\mid}^+{\rm NH_3}$$

G-3 GLOSSARY

**L-Amino acid** (Section 27.2): A description of the stereochemistry at the  $\alpha$ -carbon atom of a chiral amino acid. The Fischer projection of an  $\alpha$ -amino acid has the amino group on the left when the carbon chain is vertical with the carboxyl group at the top.

$$H_3N \xrightarrow{CO_2} H$$

Amino acid racemization (Section 27.2) A method for dating archeological samples based on the rate at which the stereochemistry at the  $\alpha$  carbon of amino acid components is randomized. It is useful for samples too old to be reliably dated by  $^{14}C$  decay.

**Amino acid residues** (Section 27.7): Individual amino acid components of a peptide or protein.

**Amino sugar** (Section 25.11): Carbohydrate in which one of the hydroxyl groups has been replaced by an amino group.

**Amylopectin** (Section 25.15): A polysaccharide present in starch. Amylopectin is a polymer of  $\alpha(1,4)$ -linked glucose units, as is amylose (see *amylose*). Unlike amylose, amylopectin contains branches of 24–30 glucose units connected to the main chain by an  $\alpha(1,6)$  linkage.

**Amylose** (Section 25.15): The water-dispersible component of starch. It is a polymer of  $\alpha(1,4)$ -linked glucose units.

**Anabolic steroid** (Section 26.15): A steroid that promotes muscle growth.

Androgen (Section 26.15): A male sex hormone.

Angle strain (Section 3.4): The strain a molecule possesses because its bond angles are distorted from their normal values.

Anion (Section 1.2): Negatively charged ion.

**Annulene** (Section 11.19): Monocyclic hydrocarbon characterized by a completely conjugated system of double bonds. Annulenes may or may not be aromatic.

**Anomeric carbon** (Section 25.6): The carbon atom in a furanose or pyranose form that is derived from the carbonyl carbon of the open-chain form. It is the ring carbon that is bonded to two oxygens.

**Anomeric effect** (Section 25.8): The preference for an electronegative substituent, especially a hydroxyl group, to occupy an axial orientation when bonded to the anomeric carbon in the pyranose form of a carbohydrate.

**Anti** (Section 3.1): Term describing relative position of two substituents on adjacent atoms when the angle between their bonds is on the order of 180°. Atoms X and Y in the structure shown are anti to each other.

**Anti addition** (Section 6.3): Addition reaction in which the two portions of the attacking reagent X—Y add to opposite faces of the double bond.

Antibonding orbital (Section 1.14): An orbital in a molecule in which an electron is less stable than when localized on an isolated atom.

Anticodon (Section 27.28): Sequence of three bases in a molecule of tRNA that is complementary to the codon of mRNA for a particular amino acid.

**Anti-Markovnikov addition** (Sections 6.8, 6.11): Addition reaction for which the regioselectivity is opposite to that predicted on the basis of Markovnikov's rule.

**Aprotic solvent** (Section 8.12): A solvent that does not have easily exchangeable protons such as those bonded to oxygen of hydroxyl groups.

**Ar**— (Section 2.2): Symbol for an aryl group.

Arene (Section 2.1): Aromatic hydrocarbon. Often abbreviated ArH.

Arenium ion (Section 12.2): The carbocation intermediate formed by attack of an electrophile on an aromatic substrate in electrophilic aromatic substitution. See cyclohexadienyl cation.

**Aromatic compound** (Section 11.3): An electron-delocalized species that is much more stable than any structure written for it in which all the electrons are localized either in covalent bonds or as unshared electron pairs.

**Aromaticity** (Section 11.4): Special stability associated with aromatic compounds.

**Arylamine** (Section 22.1): An amine that has an aryl group attached to the amine nitrogen.

**Aryne** (Section 23.8): A species that contains a triple bond within an aromatic ring (see *benzyne*).

**Asymmetric** (Section 7.1): Lacking all significant symmetry elements; an asymmetric object does not have a plane, axis, or center of symmetry.

**Asymmetric center** (Section 7.2): Obsolete name for a *ste-reogenic center*.

**Atactic polymer** (Section 7.15): Polymer characterized by random stereochemistry at its stereogenic centers. An atactic polymer, unlike an isotactic or a syndiotactic polymer, is not a stereoregular polymer.

**Atomic number** (Section 1.1): The number of protons in the nucleus of a particular atom. The symbol for atomic number is *Z*, and each element has a unique atomic number.

**Axial bond** (Section 3.6): A bond to a carbon in the chair conformation of cyclohexane oriented like the six "up-and-down" bonds in the following:

Azo coupling (Section 22.19): Formation of a compound of the type ArN=NAr' by reaction of an aryl diazonium salt with an arene. The arene must be strongly activated toward electrophilic aromatic substitution; that is, it must bear a powerful electron-releasing substituent such as —OH or —NR<sub>2</sub>.

Baeyer strain theory (Section 3.4): Incorrect nineteenth-century theory that considered the rings of cycloalkanes to be planar and assessed their stabilities according to how much the angles of a corresponding regular polygon deviated from the tetrahedral value of 109.5°.

Baeyer—Villiger oxidation (Section 17.16): Oxidation of an aldehyde or, more commonly, a ketone with a peroxy acid. The product of Baeyer—Villiger oxidation of a ketone is an ester.

$$\begin{array}{ccc}
O & O & O \\
\parallel & \parallel & \parallel \\
RCR' & \xrightarrow{R'COOH} & RCOR'
\end{array}$$

**Ball-and-stick model** (Section 1.10): Type of molecular model in which balls representing atoms are connected by sticks representing bonds. Similar to ball-and-spoke models of *Learning By Modeling*.

Base (Section 4.6): According to the Arrhenius definition, a substance that ionizes in water to produce hydroxide ions. According to the Brønsted—Lowry definition, a substance that accepts a proton from some suitable donor. According to the Lewis definition, an electron-pair donor.

**Base pair** (Section 27.27): Term given to the purine of a nucleotide and its complementary pyrimidine. Adenine (A) is complementary to thymine (T), and guanine (G) is complementary to cytosine (C).

Base peak (Section 13.21): The most intense peak in a mass spectrum. The base peak is assigned a relative intensity of 100, and the intensities of all other peaks are cited as a percentage of the base peak.

**Basicity constant**  $K_b$  (Section 22.4): A measure of base strength, especially of amines.

$$K_{\rm b} = \frac{[{\rm R_3NH^+}][{\rm HO^-}]}{[{\rm R_3N}]}$$

**Bending vibration** (Section 13.19): The regular, repetitive motion of an atom or a group along an arc the radius of which is the bond connecting the atom or group to the rest of the molecule. Bending vibrations are one type of molecular motion that gives rise to a peak in the infrared spectrum.

**Benedict's reagent** (Section 25.19): A solution containing the citrate complex of CuSO<sub>4</sub>. It is used to test for the presence of reducing sugars.

**Benzene** (Section 11.1): The most typical aromatic hydrocarbon:

$$H \longrightarrow H$$

**Benzyl group** (Section 11.7): The group  $C_6H_5CH_2$ —.

**Benzylic carbon** (Section 11.10): A carbon directly attached to a benzene ring. A hydrogen attached to a benzylic carbon is a benzylic hydrogen. A carbocation in which the benzylic carbon is positively charged is a benzylic carbocation. A free radical in which the benzylic carbon bears the unpaired electron is a benzylic radical.

Benzyne (Section 23.8): The compound

Benzyne is formed as a reactive intermediate in the reaction of aryl halides with very strong bases such as potassium amide.

**Bile acids** (Section 26.13): Steroid derivatives biosynthesized in the liver that aid digestion by emulsifying fats.

**Bimolecular** (Section 4.7): A process in which two particles react in the same elementary step.

**Biological isoprene unit** (Section 26.8): Isopentenyl pyrophosphate, the biological precursor to terpenes and steroids:

**Birch reduction** (Section 11.11): Reduction of an aromatic ring to a 1,4-cyclohexadiene on treatment with a group I metal (Li, Na, K) and an alcohol in liquid ammonia.

**Boat conformation** (Section 3.5): An unstable conformation of cyclohexane, depicted as

 $\pi$  bond (Section 1.17): In alkenes, a bond formed by overlap of p orbitals in a side-by-side manner. A  $\pi$  bond is weaker than a  $\sigma$  bond. The carbon—earbon double bond in alkenes consists of two  $sp^2$ -hybridized carbons joined by a  $\sigma$  bond and a  $\pi$  bond.

**σ bond** (Section 1.14): A connection between two atoms in which the electron probability distribution has rotational symmetry along the internuclear axis. A cross section perpendicular to the internuclear axis is a circle.

**Bond dissociation energy** (Section 1.3): For a substance A:B, the energy required to break the bond between A and B so that each retains one of the electrons in the bond. Table 4.3 (Section 4.17) gives bond dissociation energies for some representative compounds.

**Bonding orbital** (Section 1.14): An orbital in a molecule in which an electron is more stable than when localized on an isolated atom. All the bonding orbitals are normally doubly occupied in stable neutral molecules.

G-5 GLOSSARY

**Bond-line formula** (Section 1.7): Formula in which connections between carbons are shown but individual carbons and hydrogens are not. The bond-line formula



represents the compound (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub>.

**Boundary surface** (Section 1.1): The surface that encloses the region where the probability of finding an electron is high (90–95%).

**Branched-chain carbohydrate** (Section 25.12): Carbohydrate in which the main carbon chain bears a carbon substituent in place of a hydrogen or hydroxyl group.

**Bromohydrin** (Section 6.17): A halohydrin in which the halogen is bromine (see *halohydrin*).

**Bromonium ion** (Section 6.16): A halonium ion in which the halogen is bromine (see *halonium ion*).

Brønsted acid See acid.

Brønsted base See base.

**Buckminsterfullerene** (Chapter 11, box, "Carbon Clusters, Fullerenes, and Nanotubes"): Name given to the C<sub>60</sub> cluster with structure resembling the geodesic domes of R. Buckminster Fuller; see front cover.

*n***-Butane** (Section 2.5): Common name for butane  $CH_3CH_2CH_2CH_3$ .

*n*-Butyl group (Section 2.10): The group  $CH_3CH_2CH_2CH_2$ —. sec-Butyl group (Section 2.10): The group

tert-Butyl group (Section 2.10): The group  $(CH_3)_3C$ —.

**Cahn–Ingold–Prelog notation (**Section 7.6): System for specifying absolute configuration as *R* or *S* on the basis of the order in which atoms or groups are attached to a stereogenic center. Groups are ranked in order of precedence according to rules based on atomic number.

Carbamate (Section 20.17): An ester of carbamic acid (H<sub>2</sub>NCO<sub>2</sub>H); a compound of the type H<sub>2</sub>NCO<sub>2</sub>R.

**Carbanion** (Section 9.5): Anion in which the negative charge is borne by carbon. An example is acetylide ion.

**Carbene** (Section 14.13): A neutral species in which one of the carbon atoms is associated with six valence electrons.

**Carbinolamine** (Section 17.10): Compound of the type

$$HO-C-NR_2$$

Carbinolamines are formed by nucleophilic addition of an amine to a carbonyl group and are intermediates in the formation of imines and enamines.

Carbocation (Section 4.9): Positive ion in which the charge resides on carbon. An example is *tert*-butyl cation, (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup>. Carbocations are unstable species that, though they cannot normally be isolated, are believed to be intermediates in certain reactions.

Carboxylate ion (Section 19.5): The conjugate base of a carboxylic acid, an ion of the type RCO<sub>2</sub><sup>-</sup>.

**Carboxylation** (Section 19.11): In the preparation of a carboxylic acid, the reaction of a carbanion with carbon dioxide. Typically, the carbanion source is a Grignard reagent.

$$RMgX \xrightarrow{1. CO_2} RCO_2H$$

Carboxylic acid (Sections 2.3 and 19.1): Compound of the type  $\bigcup_{\parallel}$ 

RCOH, also written as RCO<sub>2</sub>H.

Carboxylic acid derivative (Section 20.1): Compound that yields a carboxylic acid on hydrolysis. Carboxylic acid derivatives include acyl chlorides, anhydrides, esters, and amides.

Carotenoids (Section 26.16): Naturally occurring tetraterpenoid plant pigments.

**Cation** (Section 1.2): Positively charged ion.

**Cellobiose** (Section 25.14): A disaccharide in which two glucose units are joined by a  $\beta(1,4)$  linkage. Cellobiose is obtained by the hydrolysis of cellulose.

**Cellulose** (Section 25.15): A polysaccharide in which thousands of glucose units are joined by  $\beta(1,4)$  linkages.

Center of symmetry (Section 7.3): A point in the center of a structure located so that a line drawn from it to any element of the structure, when extended an equal distance in the opposite direction, encounters an identical element. Benzene, for example, has a center of symmetry.

Chain reaction (Section 4.18): Reaction mechanism in which a sequence of individual steps repeats itself many times, usually because a reactive intermediate consumed in one step is regenerated in a subsequent step. The halogenation of alkanes is a chain reaction proceeding via free-radical intermediates.

**Chair conformation** (Section 3.5): The most stable conformation of cyclohexane:



Chemical shift (Section 13.4): A measure of how shielded the nucleus of a particular atom is. Nuclei of different atoms have different chemical shifts, and nuclei of the same atom have chemical shifts that are sensitive to their molecular environment. In proton and carbon-13 NMR, chemical shifts are cited as δ, or parts per million (ppm), from the hydrogens or carbons, respectively, of tetramethylsilane.

**Chiral** (Section 7.1): Term describing an object that is not superposable on its mirror image.

**Chiral carbon atom** (Section 7.2): A carbon that is bonded to four groups, all of which are different from one another. Also called an *asymmetric carbon atom*. A more modern term is *stereogenic center*.

**Chiral center** (Section 7.2): See *stereogenic center*.

**Chlorohydrin** (Section 6.17): A halohydrin in which the halogen is chlorine (see *halohydrin*).

- **Chloronium ion** (Section 6.16): A halonium ion in which the halogen is chlorine (see *halonium ion*).
- **Cholesterol** (Section 26.11): The most abundant steroid in animals and the biological precursor to other naturally occurring steroids, including the bile acids, sex hormones, and corticosteroids.
- **Chromatography** (Section 13.21): A method for separation and analysis of mixtures based on the different rates at which different compounds are removed from a stationary phase by a moving phase.
- **Chromophore** (Section 13.20): The structural unit of a molecule principally responsible for absorption of radiation of a particular frequency; a term usually applied to ultravioletvisible spectroscopy.
- Chymotrypsin (Section 27.10): A digestive enzyme that catalyzes the hydrolysis of proteins. Chymotrypsin selectively catalyzes the cleavage of the peptide bond between the carboxyl group of phenylalanine, tyrosine, or tryptophan and some other amino acid.
- **cis-** (Section 3.12): Stereochemical prefix indicating that two substituents are on the same side of a ring or double bond. (Contrast with the prefix *trans-*.)
- Claisen condensation (Section 21.1): Reaction in which a  $\beta$ -keto ester is formed by condensation of two moles of an ester in base:

$$\begin{array}{c} O \\ \parallel \\ RCH_2COR' \xrightarrow{1. \ NaOR'} RCH_2CCHCOR' \ + \ R'OH \\ \parallel \\ R \end{array}$$

**Claisen rearrangement** (Section 24.13): Thermal conversion of an allyl phenyl ether to an *o*-allyl phenol. The rearrangement proceeds via a cyclohexadienone intermediate.

$$\begin{array}{c}
O \\
CH_2 \\
CH
\end{array}$$

$$\begin{array}{c}
CH_2 \\
CH_2$$

- Claisen—Schmidt condensation (Section 18.10): A mixed aldol condensation involving a ketone enolate and an aromatic aldehyde or ketone.
- **Clathrate** (Section 2.4): A mixture of two substances in which molecules of the minor component are held by van der Waals forces within a framework of molecules of the major component.
- Clemmensen reduction (Section 12.8): Method for reducing the carbonyl group of aldehydes and ketones to a methylene group (C=O → CH<sub>2</sub>) by treatment with zinc amalgam [Zn(Hg)] in concentrated hydrochloric acid.
- Closed-shell electron configuration (Sections 1.1 and 11.6): Stable electron configuration in which all the lowest energy orbitals of an atom (in the case of the noble gases), an ion (e.g., Na<sup>+</sup>), or a molecule (e.g., benzene) are filled.
- <sup>13</sup>C NMR (Section 13.14): Nuclear magnetic resonance spectroscopy in which the environments of individual carbon atoms are examined via their mass 13 isotope.

- **Codon** (Section 27.28): Set of three successive nucleotides in mRNA that is unique for a particular amino acid. The 64 codons possible from combinations of A, T, G, and C code for the 20 amino acids from which proteins are constructed.
- **Coenzyme** (Section 27.21): Molecule that acts in combination with an enzyme to bring about a reaction.
- **Coenzyme Q** (Section 24.14): Naturally occurring group of related quinones involved in the chemistry of cellular respiration. Also known as *ubiquinone*.
- **Combinatorial chemistry** (Section 27.18): A method for carrying out a large number of reactions on a small scale in the solid phase so as to generate a "library" of related compounds for further study, such as biological testing.
- **Combustion** (Section 2.15): Burning of a substance in the presence of oxygen. All hydrocarbons yield carbon dioxide and water when they undergo combustion.
- **Common nomenclature** (Section 2.8): Names given to compounds on some basis other than a comprehensive, systematic set of rules.
- **Concerted reaction** (Section 4.7): Reaction that occurs in a single elementary step.
- Condensation polymer (Section 20.16): Polymer in which the bonds that connect the monomers are formed by condensation reactions. Typical condensation polymers include polyesters and polyamides.
- **Condensation reaction** (Section 15.7): Reaction in which two molecules combine to give a product accompanied by the expulsion of some small stable molecule (such as water). An example is acid-catalyzed ether formation:

$$2ROH \xrightarrow{H_2SO_4} ROR + H_2O$$

- Condensed structural formula (Section 1.7): A standard way of representing structural formulas in which subscripts are used to indicate replicated atoms or groups, as in (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub>.
- **Conformational analysis** (Section 3.1): Study of the conformations available to a molecule, their relative stability, and the role they play in defining the properties of the molecule.
- **Conformations** (Section 3.1): Nonidentical representations of a molecule generated by rotation about single bonds.
- **Conformers** (Section 3.1): Different conformations of a single molecule.
- **Conjugate acid** (Section 4.6): The species formed from a Brønsted base after it has accepted a proton.
- Conjugate addition (Sections 10.10 and 18.12): Addition reaction in which the reagent adds to the termini of the conjugated system with migration of the double bond; synonymous with 1,4 addition. The most common examples include conjugate addition to 1,3-dienes and to  $\alpha,\beta$ -unsaturated carbonyl compounds.
- **Conjugate base** (Section 4.6): The species formed from a Brønsted acid after it has donated a proton.
- **Conjugated diene** (Section 10.5): System of the type C=C-C=C, in which two pairs of doubly bonded carbons are joined by a single bond. The  $\pi$  electrons are delocalized over the unit of four consecutive  $sp^2$ -hybridized carbons.

G-7 GLOSSARY

**Connectivity** (Section 1.7): Order in which a molecule's atoms are connected. Synonymous with *constitution*.

**Constitution** (Section 1.7): Order of atomic connections that defines a molecule.

Constitutional isomers (Section 1.8): Isomers that differ in respect to the order in which the atoms are connected. Butane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) and isobutane [(CH<sub>3</sub>)<sub>3</sub>CH] are constitutional isomers.

**Copolymer** (Section 10.11): Polymer formed from two or more different monomers.

**Coupling constant** *J* (Section 13.7): A measure of the extent to which two nuclear spins are coupled. In the simplest cases, it is equal to the distance between adjacent peaks in a split NMR signal.

**Covalent bond** (Section 1.3): Chemical bond between two atoms that results from their sharing of two electrons.

Cracking (Section 2.13): A key step in petroleum refining in which high-molecular-weight hydrocarbons are converted to lower molecular-weight ones by thermal or catalytic carbon—earbon bond cleavage.

Critical micelle concentration (Section 19.5): Concentration above which substances such as salts of fatty acids aggregate to form micelles in aqueous solution.

Crown ether (Section 16.4): A cyclic polyether that, via ion—dipole attractive forces, forms stable complexes with metal ions. Such complexes, along with their accompanying anion, are soluble in nonpolar solvents.

**C terminus** (Section 27.7): The amino acid at the end of a peptide or protein chain that has its carboxyl group intact that is, in which the carboxyl group is not part of a peptide bond.

**Cumulated diene** (Section 10.5): Diene of the type C=C=C, in which a single carbon atom participates in double bonds with two others.

**Cyanohydrin** (Section 17.7): Compound of the type

Cyanohydrins are formed by nucleophilic addition of HCN to the carbonyl group of an aldehyde or a ketone.

**Cycloaddition** (Section 10.12): Addition, such as the Diels—Alder reaction, in which a ring is formed via a cyclic transition state.

**Cycloalkane** (Section 2.12): An alkane in which a ring of carbon atoms is present.

**Cycloalkene** (Section 5.1): A cyclic hydrocarbon characterized by a double bond between two of the ring carbons.

**Cycloalkyne** (Section 9.4): A cyclic hydrocarbon characterized by a triple bond between two of the ring carbons.

**Cyclohexadienyl anion** (Section 23.6): The key intermediate in nucleophilic aromatic substitution by the addition—elimination mechanism. It is represented by the general structure shown, where Y is the nucleophile and X is the leaving group.

$$H \xrightarrow{Y X} H$$

**Cyclohexadienyl cation** (Section 12.2): The key intermediate in electrophilic aromatic substitution reactions. It is represented by the general structure

where E is derived from the electrophile that attacks the ring.

**Deactivating substituent** (Sections 12.11 and 12.13): A group that when present in place of a hydrogen substituent causes a particular reaction to occur more slowly. The term is most often applied to the effect of substituents on the rate of electrophilic aromatic substitution.

**Debye unit (D)** (Section 1.5): Unit customarily used for measuring dipole moments:

$$1 D = 1 \times 10^{-18} \text{ esu} \cdot \text{cm}$$

**Decarboxylation** (Section 19.17): Reaction of the type  $RCO_2H \longrightarrow RH + CO_2$ , in which carbon dioxide is lost from a carboxylic acid. Decarboxylation normally occurs readily only when the carboxylic acid is a 1,3-dicarboxylic acid or a β-keto acid.

Decoupling (Section 13.17): In NMR spectroscopy, any process that destroys the coupling of nuclear spins between two nuclei. Two types of decoupling are employed in <sup>13</sup>C NMR spectroscopy. Broadband decoupling removes all the <sup>1</sup>H—<sup>13</sup>C couplings; off-resonance decoupling removes all of <sup>1</sup>H—<sup>13</sup>C couplings except those between directly bonded atoms.

**Dehydration** (Section 5.9): Removal of H and OH from adjacent atoms. The term is most commonly employed in the preparation of alkenes by heating alcohols in the presence of an acid catalyst.

Dehydrogenation (Section 5.1): Removal of the elements of H<sub>2</sub> from adjacent atoms. The term is most commonly encountered in the industrial preparation of ethylene from ethane, propene from propane, 1,3-butadiene from butane, and styrene from ethylbenzene.

**Dehydrohalogenation** (Section 5.14): Reaction in which an alkyl halide, on being treated with a base such as sodium ethoxide, is converted to an alkene by loss of a proton from one carbon and the halogen from the adjacent carbon.

**Delocalization** (Section 1.9): Association of an electron with more than one atom. The simplest example is the shared

electron pair (covalent) bond. Delocalization is important in conjugated  $\pi$  electron systems, where an electron may be associated with several carbon atoms.

**Deoxy sugar** (Section 25.10): A carbohydrate in which one of the hydroxyl groups has been replaced by a hydrogen.

**DEPT** (Section 13.18): Abbreviation for distortionless enhancement of polarization transfer. DEPT is an NMR technique that reveals the number of hydrogens directly attached to a carbon responsible for a particular signal.

**Detergents** (Section 19.5): Substances that clean by micellar action. Although the term usually refers to a synthetic detergent, soaps are also detergents.

**Diastereomers** (Section 7.10): Stereoisomers that are not enantiomers stereoisomers that are not mirror images of one another.

Diastereotopic (Section 13.6): Describing two atoms or groups in a molecule that are attached to the same atom but are in stereochemically different environments that are not mirror images of each other. The two protons shown in bold in CH<sub>2</sub>=CHCl, for example, are diastereotopic. One is cis to chlorine, the other is trans.

**1,3-Diaxial repulsion** (Section 3.8): Repulsive forces between axial substituents on the same side of a cyclohexane ring.

Diazonium ion (Sections 22.16—22.17): Ion of the type R—N≡N: Aryl diazonium ions are formed by treatment of primary aromatic amines with nitrous acid. They are extremely useful in the preparation of aryl halides, phenols,

**Diazotization** (Section 22.17): The reaction by which a primary arylamine is converted to the corresponding diazonium ion by nitrosation.

**Dieckmann reaction** (Section 21.2): An intramolecular version of the Claisen condensation.

**Dielectric constant** (Section 8.12): A measure of the ability of a material to disperse the force of attraction between oppositely charged particles. The symbol for dielectric constant is  $\epsilon$ .

**Diels—Alder reaction** (Section 10.12): Conjugate addition of an alkene to a conjugated diene to give a cyclohexene derivative. Diels—Alder reactions are extremely useful in synthesis.

**Dienophile** (Section 10.12): The alkene that adds to the diene in a Diels—Alder reaction.

**β-Diketone** (Section 18.5): Compound of the type

$$R$$
 $R$ 
 $R$ 

also referred to as a 1,3-diketone.

and aryl cyanides.

**Dimer** (Section 6.21): Molecule formed by the combination of two identical molecules.

**Dipeptide** (Section 27.7): A compound in which two  $\alpha$ -amino acids are linked by an amide bond between the amino group of one and the carboxyl group of the other:

**Dipole—dipole attraction** (Section 2.14): A force of attraction between oppositely polarized atoms.

**Dipole/induced-dipole attraction** (Section 4.5): A force of attraction that results when a species with a permanent dipole induces a complementary dipole in a second species.

Dipole moment (Section 1.5): Product of the attractive force between two opposite charges and the distance between them. Dipole moment has the symbol  $\mu$  and is measured in Debye units (D).

**Disaccharide** (Sections 25.1 and 25.14): A carbohydrate that yields two monosaccharide units (which may be the same or different) on hydrolysis.

**Dispersion force** (Section 2.14): See *induced-dipole/induced-dipole attraction*.

**Disubstituted alkene** (Section 5.6): Alkene of the type R<sub>2</sub>C=CH<sub>2</sub> or RCH=CHR. The groups R may be the same or different, they may be any length, and they may be branched or unbranched. The significant point is that there are two carbons *directly* bonded to the carbons of the double bond.

**Disulfide bridge** (Section 27.7): An S—S bond between the sulfur atoms of two cysteine residues in a peptide or protein.

**DNA** (deoxyribonucleic acid) (Section 27.26): A polynucleotide of 2'-deoxyribose present in the nuclei of cells that serves to store and replicate genetic information. Genes are DNA.

**Double bond** (Section 1.4): Bond formed by the sharing of four electrons between two atoms.

**Double dehydrohalogenation** (Section 9.7): Reaction in which a geminal dihalide or vicinal dihalide, on being treated with a very strong base such as sodium amide, is converted to an alkyne by loss of two protons and the two halogen substituents.

**Double helix** (Section 27.27) The form in which DNA normally occurs in living systems. Two complementary strands of DNA are associated with each other by hydrogen bonds between their base pairs, and each DNA strand adopts a helical shape.

**Downfield** (Section 13.4): The low-field region of an NMR spectrum. A signal that is downfield with respect to another lies to its left on the spectrum.

**Eclipsed conformation** (Section 3.1): Conformation in which bonds on adjacent atoms are aligned with one another. For example, the C—H bonds indicated in the structure shown are eclipsed.

Edman degradation (Section 27.13): Method for determining the N-terminal amino acid of a peptide or protein. It involves treating the material with phenyl isothiocyanate (C<sub>6</sub>H<sub>5</sub>N=C=S), cleaving with acid, and then identifying the phenylthiohydantoin (PTH derivative) produced.

G-9 GLOSSARY

**Elastomer** (Section 10.11): A synthetic polymer that possesses elasticity.

**Electromagnetic radiation** (Section 13.1): Various forms of radiation propagated at the speed of light. Electromagnetic radiation includes (among others) visible light; infrared, ultraviolet, and microwave radiation; and radio waves, cosmic rays, and X-rays.

**Electron affinity** (Section 1.2): Energy change associated with the capture of an electron by an atom.

**Electronegativity** (Section 1.5): A measure of the ability of an atom to attract the electrons in a covalent bond toward itself. Fluorine is the most electronegative element.

**Electronic effect** (Section 5.6): An effect on structure or reactivity that is attributed to the change in electron distribution that a substituent causes in a molecule.

**Electron impact** (Section 13.21): Method for producing positive ions in mass spectrometry whereby a molecule is bombarded by high-energy electrons.

**18-Electron rule** (Section 14.14): The number of ligands that can be attached to a transition metal are such that the sum of the electrons brought by the ligands plus the valence electrons of the metal equals 18.

**Electrophile** (Section 4.10): A species (ion or compound) that can act as a Lewis acid, or electron pair acceptor; an "electron seeker." Carbocations are one type of electrophile.

**Electrophilic addition** (Section 6.4): Mechanism of addition in which the species that first attacks the multiple bond is an electrophile ("electron seeker").

**Electrophilic aromatic substitution** (Section 12.1): Fundamental reaction type exhibited by aromatic compounds. An electrophilic species (E<sup>+</sup>) attacks an aromatic ring and replaces one of the hydrogens.

$$Ar-H + E-Y \longrightarrow Ar-E + H-Y$$

**Electrophoresis** (Section 27.3): Method for separating substances on the basis of their tendency to migrate to a positively or negatively charged electrode at a particular pH.

**Electrostatic attraction** (Section 1.2): Force of attraction between oppositely charged particles.

Electrostatic potential (Section 1.10): The energy of interaction between a point positive charge and the charge field of a molecule. The electrostatic potential is positive for the interaction between the point positive charge and the molecule's electrons and negative for the interaction with the nuclei

**Elementary step** (Section 4.7): A step in a reaction mechanism in which each species shown in the equation for this step participates in the same transition state. An elementary step is characterized by a single transition state.

**Elements of unsaturation:** See *index of hydrogen deficiency*.

**β-Elimination** (Section 5.8): Reaction in which a double or triple bond is formed by loss of atoms or groups from adjacent atoms. (See *dehydration*, *dehydrogenation*, *dehydrohalogenation*, and *double dehydrohalogenation*.)

**Elimination—addition mechanism** (Section 23.8): Two-stage mechanism for nucleophilic aromatic substitution. In the first stage, an aryl halide undergoes elimination to form an

aryne intermediate. In the second stage, nucleophilic addition to the aryne yields the product of the reaction.

**Elimination bimolecular (E2) mechanism** (Section 5.15): Mechanism for elimination of alkyl halides characterized by a transition state in which the attacking base removes a proton at the same time that the bond to the halide leaving group is broken.

**Elimination unimolecular (E1) mechanism** (Section 5.17): Mechanism for elimination characterized by the slow formation of a carbocation intermediate followed by rapid loss of a proton from the carbocation to form the alkene.

**Enamine** (Section 17.11): Product of the reaction of a secondary amine and an aldehyde or a ketone. Enamines are characterized by the general structure

$$R_2C = CR$$
 $|$ 
 $NR'_2$ 

Enantiomeric excess (Section 7.4): Difference between the percentage of the major enantiomer present in a mixture and the percentage of its mirror image. An optically pure material has an enantiomeric excess of 100%. A racemic mixture has an enantiomeric excess of zero.

**Enantiomers** (Section 7.1): Stereoisomers that are related as an object and its nonsuperimposable mirror image.

Enantioselective synthesis (Section 27.4): Reaction that converts an achiral or racemic starting material to a chiral product in which one enantiomer is present in excess of the other.

**Enantiotopic** (Section 13.6): Describing two atoms or groups in a molecule whose environments are nonsuperposable mirror images of each other. The two protons shown in bold in CH<sub>3</sub>CH<sub>2</sub>Cl, for example, are enantiotopic. Replacement of first one, then the other, by some arbitrary test group yields compounds that are enantiomers of each other.

**Endothermic** (Section 1.2): Term describing a process or reaction that absorbs heat.

Enediyne antibiotics (Section 9.4): A family of tumor-inhibiting substances that is characterized by the presence of a C≡C−C≡C unit as part of a nine- or tenmembered ring.

**Energy of activation** (Section 3.2): Minimum energy that a reacting system must possess above its most stable state in order to undergo a chemical or structural change.

**Enol** (Section 9.12): Compound of the type

$$\begin{array}{c} OH \\ | \\ RC = CR_2 \end{array}$$

Enols are in equilibrium with an isomeric aldehyde or ketone, but are normally much less stable than aldehydes and ketones

**Enolate ion** (Section 18.6): The conjugate base of an enol. Enolate ions are stabilized by electron delocalization.

$$\begin{array}{ccc}
O^{-} & O \\
| & | \\
RC = CR_{2} \longleftrightarrow RC - \bar{C}R_{2}
\end{array}$$

**Enthalpy** (Section 2.15): The heat content of a substance; symbol, H

**Envelope** (Section 3.10): One of the two most stable conformations of cyclopentane. Four of the carbons in the envelope conformation are coplanar; the fifth carbon lies above or below this plane.

**Enzyme** (Section 27.20): A protein that catalyzes a chemical reaction in a living system.

**Epimers** (Section 25.21): Diastereomers that differ in configuration at only one of their stereogenic centers.

**Epoxidation** (Section 6.18): Conversion of an alkene to an epoxide by treatment with a peroxy acid.

**Epoxide** (Section 6.18): Compound of the type

$$R_2C$$
  $CR_2$ 

**Equatorial bond** (Section 3.6): A bond to a carbon in the chair conformation of cyclohexane oriented approximately along the equator of the molecule.

**Erythro** (Section 7.11): Term applied to the relative configuration of two stereogenic centers within a molecule. The erythro stereoisomer has like substituents on the same side of a Fischer projection.

**Essential amino acids** (Section 27.1): Amino acids that must be present in the diet for normal growth and good health.

**Essential fatty acids** (Section 26.6): Fatty acids that must be present in the diet for normal growth and good health.

**Essential oils** (Section 26.7): Pleasant-smelling oils of plants consisting of mixtures of terpenes, esters, alcohols, and other volatile organic substances.

**Ester** (Sections 2.3 and 20.1): Compound of the type



**Estrogen** (Section 26.15): A female sex hormone.

**Ethene** (Section 5.1): IUPAC name for CH<sub>2</sub>=CH<sub>2</sub>. The common name *ethylene*, however, is used far more often, and the IUPAC rules permit its use.

Ether (Section 16.1): Molecule that contains a C—O—C unit such as ROR', ROAr, or ArOAr. When the two groups bonded to oxygen are the same, the ether is described as a *symmetrical ether*. When the groups are different, it is called a *mixed ether*.

**Ethylene** (Section 5.1): CH<sub>2</sub>=CH<sub>2</sub>, the simplest alkene and the most important industrial organic chemical.

**Ethyl group** (Section 2.10): The group  $CH_3CH_2$ —.

**Exothermic** (Section 1.2): Term describing a reaction or process that gives off heat.

**Extinction coefficient:** See *molar absorptivity*.

**E—Z** notation for alkenes (Section 5.4): System for specifying double-bond configuration that is an alternative to cis—trans

notation. When higher ranked substituents are on the same side of the double bond, the configuration is *Z*. When higher ranked substituents are on opposite sides, the configuration is *E*. Rank is determined by the Cahn—Ingold—Prelog system.

**Fats and oils** (Section 26.2): Triesters of glycerol. Fats are solids at room temperature, oils are liquids.

Fatty acid (Section 26.2): Carboxylic acids obtained by hydrolysis of fats and oils. Fatty acids typically have unbranched chains and contain an even number of carbon atoms in the range of 12—20 carbons. They may include one or more double bonds.

Fatty acid synthetase (Section 26.3): Complex of enzymes that catalyzes the biosynthesis of fatty acids from acetate.

**Field effect** (Section 19.6): An electronic effect in a molecule that is transmitted from a substituent to a reaction site via the medium (e.g., solvent).

Fingerprint region (Section 13.19): The region 1400–625 cm<sup>-1</sup> of an infrared spectrum. This region is less characteristic of functional groups than others, but varies so much from one molecule to another that it can be used to determine whether two substances are identical or not.

**Fischer esterification** (Sections 15.8 and 19.14): Acid-catalyzed ester formation between an alcohol and a carboxylic acid:

$$\begin{matrix} O & & O \\ \parallel & \parallel & \parallel \\ RCOH + R'OH \xrightarrow{H^+} RCOR' + H_2O \end{matrix}$$

**Fischer projection** (Section 7.7): Method for representing stereochemical relationships. The four bonds to a stereogenic carbon are represented by a cross. The horizontal bonds are understood to project toward the viewer and the vertical bonds away from the viewer.

$$\begin{array}{ccc}
x & & & & \\
 & & & \\
 & & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & &$$

**Formal charge** (Section 1.6): The charge, either positive or negative, on an atom calculated by subtracting from the number of valence electrons in the neutral atom a number equal to the sum of its unshared electrons plus half the electrons in its covalent bonds.

**Fragmentation pattern** (Section 13.21): In mass spectrometry, the ions produced by dissociation of the molecular ion.

**Free energy** (Section 3.8): The available energy of a system; symbol. *G*.

**Free radical** (Section 4.17): Neutral species in which one of the electrons in the valence shell of carbon is unpaired. An example is methyl radical, 'CH<sub>3</sub>.

**Frequency** (Section 13.1): Number of waves per unit time. Although often expressed in hertz (Hz), or cycles per second, the SI unit for frequency is  $s^{-1}$ .

G-11 GLOSSARY

Friedel—Crafts acylation (Section 12.7): An electrophilic aromatic substitution in which an aromatic compound reacts with an acyl chloride or a carboxylic acid anhydride in the presence of aluminum chloride. An acyl group becomes bonded to the ring.

$$Ar-H + RC-Cl \xrightarrow{AlCl_3} Ar-CR$$

Friedel—Crafts alkylation (Section 12.6): An electrophilic aromatic substitution in which an aromatic compound reacts with an alkyl halide in the presence of aluminum chloride. An alkyl group becomes bonded to the ring.

$$Ar-H + R-X \xrightarrow{AlCl_3} Ar-R$$

**Fries rearrangement** (Section 24.9): Aluminum chloride-promoted rearrangement of an aryl ester to a ring-acylated derivative of phenol.

$$\begin{array}{c}
O \\
\parallel \\
OCR \xrightarrow{AlCl_3}
\end{array}$$

$$\begin{array}{c}
O \\
\parallel \\
OCH
\end{array}$$

Frontier orbitals (Section 10.14): Orbitals involved in a chemical reaction, usually the highest-occupied molecular orbital of one reactant and the lowest-unoccupied molecular orbital of the other.

Functional class nomenclature (Section 4.1): Type of IUPAC nomenclature in which compounds are named according to functional group families. The last word in the name identifies the functional group; the first word designates the alkyl or aryl group that bears the functional group. *Methyl bromide*, *ethyl alcohol*, and *diethyl ether* are examples of functional class names.

**Functional group** (Section 2.2): An atom or a group of atoms in a molecule responsible for its reactivity under a given set of conditions.

**Furanose form** (Section 25.6): Five-membered ring arising via cyclic hemiacetal formation between the carbonyl group and a hydroxyl group of a carbohydrate.

Gabriel synthesis (Section 22.9): Method for the synthesis of primary alkylamines in which a key step is the formation of a carbon—nitrogen bond by alkylation of the potassium salt of phthalimide.

**Gauche** (Section 3.1): Term describing the position relative to each other of two substituents on adjacent atoms when the

angle between their bonds is on the order of  $60^{\circ}$ . Atoms X and Y in the structure shown are gauche to each other.

**Geminal dihalide** (Section 9.7): A dihalide of the form  $R_2CX_2$ , in which the two halogen substituents are located on the same carbon.

**Geminal diol** (Section 17.6): The hydrate  $R_2C(OH)_2$  of an aldehyde or a ketone.

**Genome** (Section 27.29): The aggregate of all the genes that determine what an organism becomes.

**Globular protein** (Section 27.20): An approximately spherically shaped protein that forms a colloidal dispersion in water. Most enzymes are globular proteins.

**Glycogen** (Section 25.15): A polysaccharide present in animals that is derived from glucose. Similar in structure to amylopectin.

**Glycolysis** (Section 25.21): Biochemical process in which glucose is converted to pyruvate with release of energy.

**Glycoprotein** (Section 25.16): A protein to which carbohydrate molecules are attached by covalent bonds.

**Glycoside** (Section 25.13): A carbohydrate derivative in which the hydroxyl group at the anomeric position has been replaced by some other group. An *O*-glycoside is an ether of a carbohydrate in which the anomeric position bears an alkoxy group.

**Grain alcohol** (Section 4.2): A common name for ethanol (CH<sub>2</sub>CH<sub>2</sub>OH).

**Grignard reagent** (Section 14.4): An organomagnesium compound of the type RMgX formed by the reaction of magnesium with an alkyl or aryl halide.

**Half-chair** (Section 3.10): One of the two most stable conformations of cyclopentane. Three consecutive carbons in the half-chair conformation are coplanar. The fourth and fifth carbon lie, respectively, above and below the plane.

**Haloform reaction** (Section 18.7): The formation of  $CHX_3$  (X = Br, Cl, or I) brought about by cleavage of a methyl ketone on treatment with  $Br_2$ ,  $Cl_2$ , or  $I_2$  in aqueous base.

$$\begin{array}{ccc}
O & O \\
\parallel & X_2 \\
RCCH_3 \xrightarrow{X_2} & RCO^- + CHX_3
\end{array}$$

Halogenation (Sections 4.15 and 12.5): Replacement of a hydrogen by a halogen. The most frequently encountered examples are the free-radical halogenation of alkanes and the halogenation of arenes by electrophilic aromatic substitution.

**Halohydrin** (Section 6.17): A compound that contains both a halogen atom and a hydroxyl group. The term is most often used for compounds in which the halogen and the hydroxyl

group are on adjacent atoms (vicinal halohydrins). The most commonly encountered halohydrins are chlorohydrins and bromohydrins.

- **Halonium ion** (Section 6.16): A species that incorporates a positively charged halogen. Bridged halonium ions are intermediates in the addition of halogens to the double bond of an alkene.
- **Hammond's postulate** (Section 4.12): Principle used to deduce the approximate structure of a transition state. If two states, such as a transition state and an unstable intermediate derived from it, are similar in energy, they are believed to be similar in structure.
- **Haworth formulas** (Section 25.6): Planar representations of furanose and pyranose forms of carbohydrates.
- **Heat of combustion** (Section 2.15): Heat evolved on combustion of a substance. It is the value of  $-\Delta H^{\circ}$  for the combustion reaction.
- **Heat of formation** (Section 2.15): The value of  $\Delta H^{\circ}$  for formation of a substance from its elements.
- **Heat of hydrogenation** (Section 6.1): Heat evolved on hydrogenation of a substance. It is the value of  $-\Delta H^{\circ}$  for the addition of  $H_2$  to a multiple bond.
- α Helix (Section 27.19): One type of protein secondary structure. It is a right-handed helix characterized by hydrogen bonds between NH and C=O groups. It contains approximately 3.6 amino acids per turn.
- **Hell—Volhard—Zelinsky reaction** (Section 19.16): The phosphorus trihalide-catalyzed α halogenation of a carboxylic acid:

**Hemiacetal** (Section 17.8): Product of nucleophilic addition of one molecule of an alcohol to an aldehyde or a ketone. Hemiacetals are compounds of the type

- **Hemiketal** (Section 17.8): An old name for a hemiacetal derived from a ketone.
- **Henderson—Hasselbalch equation** (Section 19.4): An equation that relates degree of dissociation of an acid at a particular pH to its  $pK_a$ .

$$pH = pK_a + log \frac{[conjugate base]}{[acid]}$$

- **Heteroatom** (Section 1.7): An atom in an organic molecule that is neither carbon nor hydrogen.
- **Heterocyclic compound** (Section 3.15): Cyclic compound in which one or more of the atoms in the ring are elements other than carbon. Heterocyclic compounds may or may not be aromatic.
- **Heterogeneous reaction** (Section 6.1): A reaction involving two or more substances present in different phases. Hydro-

genation of alkenes is a heterogeneous reaction that takes place on the surface of an insoluble metal catalyst.

- **Heterolytic cleavage** (Section 4.17): Dissociation of a twoelectron covalent bond in such a way that both electrons are retained by one of the initially bonded atoms.
- **Hexose** (Section 25.4): A carbohydrate with six carbon atoms. **High-density lipoprotein (HDL)** (Section 26.11): A protein that carries cholesterol from the tissues to the liver where it is metabolized. HDL is often called "good cholesterol."
- Hofmann elimination (Section 22.14): Conversion of a quaternary ammonium hydroxide, especially an alkyltrimethylammonium hydroxide, to an alkene on heating. Elimination occurs in the direction that gives the less substituted double bond.

$$R_2CH$$
— $CR'_2HO^- \xrightarrow{heat} R_2C$ = $CR'_2+N(CH_3)_3+H_2O$   
 $+N(CH_3)_3$ 

**Hofmann rearrangement** (Section 20.17): Reaction in which an amide reacts with bromine in basic solution to give a primary amine having one less carbon atom than the amide.

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCNH}_2 \xrightarrow[\text{NaOH, H}_2O]{} \end{array} RNH_2$$

- **HOMO** (Section 10.13): Highest occupied molecular orbital (the orbital of highest energy that contains at least one of a molecule's electrons).
- **Homologous series** (Section 2.6): Group of structurally related substances in which successive members differ by a CH<sub>2</sub> group.
- **Homolytic cleavage** (Section 4.17): Dissociation of a twoelectron covalent bond in such a way that one electron is retained by each of the initially bonded atoms.
- **Hückel's rule** (Section 11.19): Completely conjugated planar monocyclic hydrocarbons possess special stability when the number of their  $\pi$  electrons =4n + 2, where n is an integer.
- **Hund's rule** (Section 1.1): When two orbitals are of equal energy, they are populated by electrons so that each is half-filled before either one is doubly occupied.
- **Hybrid orbital** (Section 1.15): An atomic orbital represented as a mixture of various contributions of that atom's s,p,d, etc. orbitals.
- **Hydration** (Section 6.10): Addition of the elements of water (H, OH) to a multiple bond.
- **Hydride shift** (Section 5.13): Migration of a hydrogen with a pair of electrons (H:) from one atom to another. Hydride shifts are most commonly seen in carbocation rearrangements.
- **Hydroboration—exidation** (Section 6.11): Reaction sequence involving a separate hydroboration stage and oxidation stage. In the hydroboration stage, diborane adds to an alkene to give an alkylborane. In the oxidation stage, the alkylborane is oxidized with hydrogen peroxide to give an alcohol. The reaction product is an alcohol corresponding to the anti-Markovnikov, syn hydration of an alkene.

G-13 GLOSSARY

**Hydrocarbon** (Section 2.1): A compound that contains only carbon and hydrogen.

**Hydroformylation** (Section 17.5): An industrial process for preparing aldehydes (RCH<sub>2</sub>CH<sub>2</sub>CH=O) by the reaction of terminal alkenes (RCH=CH<sub>2</sub>) with carbon monoxide.

**Hydrogenation** (Section 6.1): Addition of H<sub>2</sub> to a multiple bond

**Hydrogen bonding** (Section 4.5): Type of dipole—dipole attractive force in which a positively polarized hydrogen of one molecule is weakly bonded to a negatively polarized atom of an adjacent molecule. Hydrogen bonds typically involve the hydrogen of one —OH group and the oxygen of another.

**Hydrolysis** (Section 6.9): Water-induced cleavage of a bond. **Hydronium ion** (Section 4.6): The species  $H_3O^+$ .

**Hydrophilic** (Section 19.5): Literally, "water-loving"; a term applied to substances that are soluble in water, usually because of their ability to form hydrogen bonds with water.

**Hydrophobic** (Section 19.5): Literally, "water-hating"; a term applied to substances that are not soluble in water, but are soluble in nonpolar, hydrocarbon-like media.

**Hydroxylation** (Section 15.5): Reaction or sequence of reactions in which an alkene is converted to a vicinal diol.

**Imide** (Section 20.15): Compound of the type

in which two acyl groups are bonded to the same nitrogen. **Imine** (Section 17.10): Compound of the type  $R_2C = NR'$  formed by the reaction of an aldehyde or a ketone with a primary amine (R'NH<sub>2</sub>). Imines are sometimes called *Schiff's bases*.

**Index of hydrogen deficiency** (Section 13.22): A measure of the total double bonds and rings a molecule contains. It is determined by comparing the molecular formula  $C_nH_x$  of the compound to that of an alkane that has the same number of carbons according to the equation:

Index of hydrogen deficiency =  $\frac{1}{2}(C_nH_{2n+2} - C_nH_x)$ 

**Induced-dipole/induced-dipole attraction** (Section 2.14): Force of attraction resulting from a mutual and complementary polarization of one molecule by another. Also referred to as *London forces* or *dispersion forces*.

**Inductive effect** (Section 4.10): An electronic effect transmitted by successive polarization of the  $\sigma$  bonds within a molecule or an ion.

**Infrared (IR) spectroscopy** (Section 13.19): Analytical technique based on energy absorbed by a molecule as it vibrates by stretching and bending bonds. Infrared spectroscopy is useful for analyzing the functional groups in a molecule.

**Initiation step** (Section 4.18): A process which causes a reaction, usually a free-radical reaction, to begin but which by itself is not the principal source of products. The initiation step in the halogenation of an alkane is the dissociation of a halogen molecule to two halogen atoms.

Integrated area (Section 13.6): The relative area of a signal in an NMR spectrum. Areas are proportional to the number of equivalent protons responsible for the peak.

**Intermediate** (Section 3.7): Transient species formed during a chemical reaction. Typically, an intermediate is not stable under the conditions of its formation and proceeds further to form the product. Unlike a transition state, which corresponds to a maximum along a potential energy surface, an intermediate lies at a potential energy minimum.

**Intermolecular forces** (Section 2.14): Forces, either attractive or repulsive, between two atoms or groups in *separate* molecules

**Intramolecular forces** (Section 2.15): Forces, either attractive or repulsive, between two atoms or groups *within* the same molecule.

**Inversion of configuration** (Section 8.4): Reversal of the three-dimensional arrangement of the four bonds to  $sp^3$ -hybridized carbon. The representation shown illustrates inversion of configuration in a nucleophilic substitution where LG is the leaving group and Nu is the nucleophile.

$$V = V - LG \longrightarrow Nu - C$$

lonic bond (Section 1.2): Chemical bond between oppositely charged particles that results from the electrostatic attraction between them.

**lonization energy** (Section 1.2): Amount of energy required to remove an electron from some species.

**Isobutane** (Section 2.5): The common name for 2-methyl-propane, (CH<sub>3</sub>)<sub>3</sub>CH.

Isobutyl group (Section 2.10): The group  $(CH_3)_2CHCH_2$ —.

**Isoelectric point** (Section 27.3): pH at which the concentration of the zwitterionic form of an amino acid is a maximum. At a pH below the isoelectric point the dominant species is a cation. At higher pH, an anion predominates. At the isoelectric point the amino acid has no net charge.

**Isolated diene** (Section 10.5): Diene of the type

$$C = C - (C)_r - C = C$$

in which the two double bonds are separated by one or more  $sp^3$ -hybridized carbons. Isolated dienes are slightly less stable than isomeric conjugated dienes.

Isomers (Section 1.8): Different compounds that have the same molecular formula. Isomers may be either constitutional isomers or stereoisomers.

**Isopentane** (Section 2.7): The common name for 2-methylbutane, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub>.

**Isoprene unit** (Section 26.7): The characteristic five-carbon structural unit found in terpenes:

**Isopropyl group** (Section 2.10): The group  $(CH_3)_2CH$ —.

**Isotactic polymer** (Section 7.15): A stereoregular polymer in which the substituent at each successive stereogenic center is on the same side of the zigzag carbon chain.

**Isotopic cluster** (Section 13.21): In mass spectrometry, a group of peaks that differ in m/z because they incorporate different isotopes of their component elements.

**IUPAC nomenclature** (Section 2.8): The most widely used method of naming organic compounds. It uses a set of rules proposed and periodically revised by the International Union of Pure and Applied Chemistry.

**Kekulé structure** (Section 11.2): Structural formula for an aromatic compound that satisfies the customary rules of bonding and is usually characterized by a pattern of alternating single and double bonds. There are two Kekulé formulations for benzene:



A single Kekulé structure does not completely describe the actual bonding in the molecule.

**Ketal** (Section 17.8): An old name for an acetal derived from a ketone.

**Keto—enol tautomerism** (Section 18.4): Process by which an aldehyde or a ketone and its enol equilibrate:

$$\begin{array}{ccc}
O & OH \\
\parallel & \mid \\
RC-CHR_2 & \longrightarrow RC=CR_2
\end{array}$$

**β-Keto ester** (Section 21.1): A compound of the type

**Ketone** (Sections 2.3 and 17.1): A member of the family of compounds in which both atoms attached to a carbonyl group (C=O) are carbon, as in

**Ketose** (Section 25.1): A carbohydrate that contains a ketone carbonyl group in its open-chain form.

Kiliani—Fischer synthesis (Section 25.20): A synthetic method for carbohydrate chain extension. The new carbon—earbon bond is formed by converting an aldose to its cyanohydrin. Reduction of the cyano group to an aldehyde function completes the synthesis.

**Kinetically controlled reaction** (Section 10.10): Reaction in which the major product is the one that is formed at the fastest rate.

**Kolbe—Schmitt reaction** (Section 24.10): The high-pressure reaction of the sodium salt of a phenol with carbon dioxide to give an *ο*-hydroxybenzoic acid. The Kolbe—Schmitt

reaction is used to prepare salicylic acid in the synthesis of aspirin.

Lactam (Section 20.14): A cyclic amide.

Lactone (Section 19.15): A cyclic ester.

**Lactose** (Section 25.14): Milk sugar; a disaccharide formed by a β-glycosidic linkage between C-4 of glucose and C-1 of galactose

**LDA** (Section 21.10): Abbreviation for lithium diisopropylamide LiN[CH(CH<sub>3</sub>)<sub>2</sub>]. LDA is a strong, sterically hindered base, used to convert esters to their enolates.

**Leaving group** (Section 5.15): The group, normally a halide ion, that is lost from carbon in a nucleophilic substitution or elimination.

**Le Châtelier's principle** (Section 6.10): A reaction at equilibrium responds to any stress imposed on it by shifting the equilibrium in the direction that minimizes the stress.

Lewis acid: See *acid*. Lewis base: See *base*.

Lewis structure (Section 1.3): A chemical formula in which electrons are represented by dots. Two dots (or a line) between two atoms represent a covalent bond in a Lewis structure. Unshared electrons are explicitly shown, and stable Lewis structures are those in which the octet rule is satisfied.

**Lindlar catalyst** (Section 9.9): A catalyst for the hydrogenation of alkynes to *cis*-alkenes. It is composed of palladium, which has been "poisoned" with lead(II) acetate and quinoline, supported on calcium carbonate.

**Lipid bilayer** (Section 26.4): Arrangement of two layers of phospholipids that constitutes cell membranes. The polar termini are located at the inner and outer membrane—water interfaces, and the lipophilic hydrocarbon tails cluster on the inside.

**Lipids** (Section 26.1): Biologically important natural products characterized by high solubility in nonpolar organic solvents.

**Lipophilic** (Section 19.5): Literally, "fat-loving"; synonymous in practice with *hydrophobic*.

**Locant** (Section 2.9): In IUPAC nomenclature, a prefix that designates the atom that is associated with a particular structural unit. The locant is most often a number, and the structural unit is usually an attached substituent as in 2-chlorobutane.

**London force** (Section 2.14): See *induced-dipole/induced-dipole attraction*.

**Low-density lipopropein (LDL)** (Section 26.11): A protein which carries cholesterol from the liver through the blood to the tissues. Elevated LDL levels are a risk factor for heart disease; LDL is often called "bad cholesterol."

**LUMO** (Section 10.13): The orbital of lowest energy that contains none of a molecule's electrons; the lowest unoccupied molecular orbital.

Magnetic resonance imaging (MRI): (Section 13.18): A diagnostic method in medicine in which tissues are examined by NMR.

G-15 GLOSSARY

Malonic ester synthesis (Section 21.7): Synthetic method for the preparation of carboxylic acids involving alkylation of the enolate of diethyl malonate

as the key carbon—earbon bond-forming step.

**Maltose** (Section 25.14): A disaccharide obtained from starch in which two glucose units are joined by an  $\alpha(1,4)$ -glycosidic link.

**Markovnikov's rule** (Section 6.5): An unsymmetrical reagent adds to an unsymmetrical double bond in the direction that places the positive part of the reagent on the carbon of the double bond that has the greater number of hydrogens.

Mass spectrometry (Section 13.21): Analytical method in which a molecule is ionized and the various ions are examined on the basis of their mass-to-charge ratio.

**Mechanism** (Section 4.7): The sequence of steps that describes how a chemical reaction occurs; a description of the intermediates and transition states that are involved during the transformation of reactants to products.

**Mercaptan** (Section 15.13): An old name for the class of compounds now known as *thiols*.

Merrifield method: See solid-phase peptide synthesis.

**Meso stereoisomer** (Section 7.11): An achiral molecule that has stereogenic centers. The most common kind of *meso* compound is a molecule with two stereogenic centers and a plane of symmetry.

Messenger RNA (mRNA): (Section 27.28): A polynucleotide of ribose that "reads" the sequence of bases in DNA and interacts with tRNAs in the ribosomes to promote protein biosynthesis.

**Meta** (Section 11.7): Term describing a 1,3 relationship between substituents on a benzene ring.

**Meta director** (Section 12.9): A group that when present on a benzene ring directs an incoming electrophile to a position meta to itself.

**Metallocene** (Section 14.14): A transition metal complex that bears a cyclopentadienyl ligand.

**Metalloenzyme** (Section 27.20): An enzyme in which a metal ion at the active site contributes in a chemically significant way to the catalytic activity.

**Methanogen** (Section 2.4): An organism that produces methane.

Methine group (Section 2.5): The group CH.

**Methylene group** (Section 2.4): The group  $-CH_2$ .

**Methyl group** (Section 1.16): The group CH<sub>3</sub>—.

**Mevalonic acid** (Section 26.10): An intermediate in the biosynthesis of steroids from acetyl coenzyme A.

Micelle (Section 19.5): A spherical aggregate of species such as carboxylate salts of fatty acids that contain a lipophilic end and a hydrophilic end. Micelles containing 50—100 carboxylate salts of fatty acids are soaps.

Michael addition (Sections 18.13 and 21.9): The conjugate addition of a carbanion (usually an enolate) to an  $\alpha$ ,β-unsaturated carbonyl compound.

**Microscopic reversibility** (Section 6.10): The principle that the intermediates and transition states in the forward and backward stages of a reversible reaction are identical, but are encountered in the reverse order.

**Molar absorptivity** (Section 13.20): A measure of the intensity of a peak, usually in UV-VIS spectroscopy.

**Molecular dipole moment** (Section 1.11): The overall measured dipole moment of a molecule. It can be calculated as the resultant (or vector sum) of all the individual bond dipole moments.

**Molecular formula** (Section 1.7): Chemical formula in which subscripts are used to indicate the number of atoms of each element present in one molecule. In organic compounds, carbon is cited first, hydrogen second, and the remaining elements in alphabetical order.

**Molecular ion** (Section 13.21): In mass spectrometry, the species formed by loss of an electron from a molecule.

Molecular orbital theory (Section 1.14): Theory of chemical bonding in which electrons are assumed to occupy orbitals in molecules much as they occupy orbitals in atoms. The molecular orbitals are described as combinations of the orbitals of all of the atoms that make up the molecule.

**Monomer** (Section 6.21): The simplest stable molecule from which a particular polymer may be prepared.

**Monosaccharide** (Section 25.1): A carbohydrate that cannot be hydrolyzed further to yield a simpler carbohydrate.

Monosubstituted alkene (Section 5.6): An alkene of the type RCH=CH<sub>2</sub>, in which there is only one carbon *directly* bonded to the carbons of the double bond.

**Multiplicity** (Section 13.7): The number of peaks into which a signal is split in nuclear magnetic resonance spectroscopy. Signals are described as *singlets, doublets, triplets,* and so on, according to the number of peaks into which they are split.

**Mutarotation** (Section 25.8): The change in optical rotation that occurs when a single form of a carbohydrate is allowed to equilibrate to a mixture of isomeric hemiacetals.

**Nanotube** (Section 11.8): A form of elemental carbon composed of a cylindrical cluster of carbon atoms.

**Neopentane** (Section 2.7): The common name for 2,2-dimethylpropane, (CH<sub>3</sub>)<sub>4</sub>C.

**Neurotransmitter** (Section 22.5): Substance, usually a naturally occurring amine, that mediates the transmission of nerve impulses.

Newman projection (Section 3.1): Method for depicting conformations in which one sights down a carbon—earbon bond and represents the front carbon by a point and the back carbon by a circle.

**Nitration** (Section 12.3): Replacement of a hydrogen substituent by an —NO<sub>2</sub> group. The term is usually used in connection with electrophilic aromatic substitution.

$$Ar-H \xrightarrow{HNO_3} Ar-NO_2$$

Nitrile (Sections 2.3 and 20.1): A compound of the type RC≡N. R may be alkyl or aryl. Also known as *alkyl* or *aryl cyanides*.

Nitrosamine See *N-nitroso amine*.

N-Nitroso amine (Section 22.16): A compound of the type R<sub>2</sub>N—N=O. R may be alkyl or aryl groups, which may be the same or different. N-Nitroso amines are formed by nitrosation of secondary amines.

**Nitrosation** (Section 22.16): The reaction of a substance, usually an amine, with nitrous acid. Primary amines yield diazonium ions; secondary amines yield *N*-nitroso amines. Tertiary aromatic amines undergo nitrosation of their aromatic ring.

**Noble gases** (Section 1.1): The elements in group VIIIA of the periodic table (helium, neon, argon, krypton, xenon, radon). Also known as the *rare gases*, they are, with few exceptions, chemically inert.

**Nodal surface** (Section 1.1): A plane drawn through an orbital where the algebraic sign of a wave function changes. The probability of finding an electron at a node is zero.

**N terminus** (Section 27.7): The amino acid at the end of a peptide or protein chain that has its  $\alpha$ -amino group intact; that is, the  $\alpha$ -amino group is not part of a peptide bond.

Nuclear magnetic resonance (NMR) spectroscopy (Section 13.3): A method for structure determination based on the effect of molecular environment on the energy required to promote a given nucleus from a lower energy spin state to a higher energy state.

**Nucleic acid** (Section 27.26): A polynucleotide present in the nuclei of cells.

**Nucleophile** (Section 4.10): An atom that has an unshared electron pair which can be used to form a bond to carbon. Nucleophiles are Lewis bases.

**Nucleophilic acyl substitution** (Section 20.3): Nucleophilic substitution at the carbon atom of an acyl group.

Nucleophilic addition (Section 17.6): The characteristic reaction of an aldehyde or a ketone. An atom possessing an unshared electron pair bonds to the carbon of the C=O group, and some other species (normally hydrogen) bonds to the oxygen.

$$\begin{matrix} O & OH \\ \parallel \\ RCR' + H-Y : \longrightarrow \begin{matrix} OH \\ \mid \\ RC-Y : \end{matrix}$$

Nucleophilic aliphatic substitution (Chapter 8): Reaction in which a nucleophile replaces a leaving group, usually a halide ion, from  $sp^3$ -hybridized carbon. Nucleophilic aliphatic substitution may proceed by either an  $S_N1$  or an  $S_N2$  mechanism.

Nucleophilic aromatic substitution (Chapter 23): A reaction in which a nucleophile replaces a leaving group as a substituent on an aromatic ring. Substitution may proceed by an addition—elimination mechanism or an elimination—addition mechanism.

**Nucleophilicity** (Section 8.7): A measure of the reactivity of a Lewis base in a nucleophilic substitution reaction.

Nucleoside (Section 27.24): The combination of a purine or pyrimidine base and a carbohydrate, usually ribose or 2-deoxyribose.

**Nucleotide** (Section 27.25): The phosphate ester of a nucleoside.

Octane rating (Section 2.13): The capacity of a sample of gasoline to resist "knocking," expressed as a number equal to the percentage of 2,2,4-trimethylpentane ("isooctane") in an isooctane—heptane mixture that has the same knocking characteristics.

Octet rule (Section 1.3): When forming compounds, atoms gain, lose, or share electrons so that the number of their valence electrons is the same as that of the nearest noble gas. For the elements carbon, nitrogen, oxygen, and the halogens, this number is 8.

**Oligomer** (Section 14.15): A molecule composed of too few monomer units for it to be classified as a polymer, but more than in a dimer, trimer, tetramer, etc.

**Oligosaccharide** (Section 25.1): A carbohydrate that gives three to ten monosaccharides on hydrolysis.

**Optical activity** (Section 7.4): Ability of a substance to rotate the plane of polarized light. To be optically active, a substance must be chiral, and one enantiomer must be present in excess of the other.

**Optically pure** (Section 7.4): Describing a chiral substance in which only a single enantiomer is present.

**Orbital** (Section 1.1): Strictly speaking, a wave function  $\psi$ . It is convenient, however, to think of an orbital in terms of the probability  $\psi^2$  of finding an electron at some point relative to the nucleus, as the volume inside the boundary surface of an atom, or the region in space where the probability of finding an electron is high.

 σ Orbital (Section 1.14): A bonding orbital characterized by rotational symmetry.

σ\* Orbital (Section 1.14): An antibonding orbital characterized by rotational symmetry.

Organometallic compound (Section 14.1): A compound that contains a carbon-to-metal bond.

**Ortho** (Section 11.7): Term describing a 1,2 relationship between substituents on a benzene ring.

**Ortho, para director** (Section 12.9): A group that when present on a benzene ring directs an incoming electrophile to the positions ortho and para to itself.

Oxidation (Section 2.16): A decrease in the number of electrons associated with an atom. In organic chemistry, oxidation of carbon occurs when a bond between carbon and an atom that is less electronegative than carbon is replaced by a bond to an atom that is more electronegative than carbon.

G-17 GLOSSARY

Oxime (Section 17.10): A compound of the type R<sub>2</sub>C=NOH, formed by the reaction of hydroxylamine (NH<sub>2</sub>OH) with an aldehyde or a ketone.

Oxonium ion (Section 4.6): Specific name for the species  $H_3O^+$  (also called *hydronium ion*). General name for species such as alkyloxonium ions  $ROH_2^+$  analogous to  $H_2O^+$ .

Ozonolysis (Section 6.19): Ozone-induced cleavage of a carbon–earbon double or triple bond.

Para (Section 11.7): Term describing a 1,4 relationship between substituents on a benzene ring.

Paraffin hydrocarbons (Section 2.15): An old name for alkanes and cycloalkanes.

Partial rate factor (Section 12.10): In electrophilic aromatic substitution, a number that compares the rate of attack at a particular ring carbon with the rate of attack at a single position of benzene.

Pauli exclusion principle (Section 1.1): No two electrons can have the same set of four quantum numbers. An equivalent expression is that only two electrons can occupy the same orbital, and then only when they have opposite spins.

PCC (Section 15.10): Abbreviation for pyridinium chlorochromate C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup> ClCrO<sub>3</sub><sup>-</sup>. When used in an anhydrous medium, PCC oxidizes primary alcohols to aldehydes and secondary alcohols to ketones.

**PDC** (Section 15.10): Abbreviation for pyridinium dichromate  $(C_5H_5NH)_2^{2+} Cr_2O_7^{2-}$ . Used in same manner and for same purposes as PCC (see preceding entry).

n-Pentane (Section 2.7): The common name for pentane, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

**Pentose** (Section 25.4): A carbohydrate with five carbon atoms.

**Peptide** (Section 27.7): Structurally, a molecule composed of two or more  $\alpha$ -amino acids joined by peptide bonds.

**Peptide bond** (Section 27.7): An amide bond between the carboxyl group of one α-amino acid and the amino group of another.

(The bond highlighted in yellow is the peptide bond.)

**Pericyclic reaction** (Section 10.12): A reaction that proceeds through a cyclic transition state.

**Period** (Section 1.1): A horizontal row of the periodic table.

**Peroxide** (Section 6.8): A compound of the type ROOR.

**Peroxide effect** (Section 6.8): Reversal of regioselectivity observed in the addition of hydrogen bromide to alkenes brought about by the presence of peroxides in the reaction mixture.

**Phase-transfer catalysis** (Section 22.6): Method for increasing the rate of a chemical reaction by transporting an ionic re-

actant from an aqueous phase where it is solvated and less reactive to an organic phase where it is not solvated and is more reactive. Typically, the reactant is an anion that is carried to the organic phase as its quaternary ammonium salt.

**Phenols** (Section 24.1): Family of compounds characterized by a hydroxyl substituent on an aromatic ring as in ArOH. *Phenol* is also the name of the parent compound, C<sub>6</sub>H<sub>5</sub>OH.

**Phenyl group** (Section 11.7): The group

It is often abbreviated C<sub>6</sub>H<sub>5</sub>—.

**Phospholipid** (Section 26.4): A diacylglycerol bearing a choline-phosphate "head group." Also known as *phosphatidylcholine*.

**Photochemical reaction** (Section 4.19): A chemical reaction that occurs when light is absorbed by a substance.

**Photon** (Section 13.1): Term for an individual "bundle" of energy, or particle, of electromagnetic radiation.

 $pK_a$  (Section 4.6): A measure of acid strength defined as  $-\log K_a$ . The stronger the acid, the smaller the value of  $pK_a$ .

**Planck's constant** (Section 13.1): Constant of proportionality (h) in the equation E = hv, which relates the energy (E) to the frequency (v) of electromagnetic radiation.

**Plane of symmetry** (Section 7.3): A plane that bisects an object, such as a molecule, into two mirror-image halves; also called a *mirror plane*. When a line is drawn from any element in the object perpendicular to such a plane and extended an equal distance in the opposite direction, a duplicate of the element is encountered.

Pleated β sheet (Section 27.19): Type of protein secondary structure characterized by hydrogen bonds between NH and C=O groups of adjacent parallel peptide chains. The individual chains are in an extended zigzag conformation.

**Polar covalent bond** (Section 1.5): A shared electron pair bond in which the electrons are drawn more closely to one of the bonded atoms than the other.

**Polarimeter** (Section 7.4): An instrument used to measure optical activity.

**Polarizability** (Section 4.5): A measure of the ease of distortion of the electric field associated with an atom or a group. A fluorine atom in a molecule, for example, holds its electrons tightly and is very nonpolarizable. Iodine is very polarizable.

**Polarized light** (Section 7.4): Light in which the electric field vectors vibrate in a single plane. Polarized light is used in measuring optical activity.

Polyamide (Section 20.16): A polymer in which individual structural units are joined by amide bonds. Nylon is a synthetic polyamide; proteins are naturally occurring polyamides.

Polyamine (Section 22.5): A compound that contains many amino groups. The term is usually applied to a group of naturally occurring substances, including spermine, spermidine, and putrescine, that are believed to be involved in cell differentiation and proliferation.

**Polycyclic aromatic hydrocarbon** (Section 11.8): An aromatic hydrocarbon characterized by the presence of two or more benzene-like rings.

**Polycyclic hydrocarbon** (Section 3.14): A hydrocarbon in which two carbons are common to two or more rings.

**Polyester** (Section 20.16): A polymer in which individual structural units are joined by ester bonds.

**Polyether** (Section 16.4): A molecule that contains many ether linkages. Polyethers occur naturally in a number of antibiotic substances.

**Polyethylene** (Section 6.21): A polymer of ethylene.

**Polymer** (Section 6.21): Large molecule formed by the repetitive combination of many smaller molecules (monomers).

**Polymerization** (Section 6.21): Process by which a polymer is prepared. The principal processes include *free-radical*, *cationic*, *coordination*, and *condensation polymerization*.

**Polypeptide** (Section 27.1): A polymer made up of "many" (more than eight to ten) amino acid residues.

**Polypropylene** (Section 6.21): A polymer of propene.

**Polysaccharide** (Sections 25.1 and 25.15): A carbohydrate that yields "many" monosaccharide units on hydrolysis.

**Potential energy** (Section 2.15): The energy a system has exclusive of its kinetic energy.

**Potential energy diagram** (Section 4.7): Plot of potential energy versus some arbitrary measure of the degree to which a reaction has proceeded (the reaction coordinate). The point of maximum potential energy is the transition state.

**Primary alkyl group** (Section 2.10): Structural unit of the type  $RCH_2$ —, in which the point of attachment is to a primary carbon.

**Primary amine** (Section 22.1): An amine with a single alkyl or aryl substituent and two hydrogens: an amine of the type RNH<sub>2</sub> (primary alkylamine) or ArNH<sub>2</sub> (primary arylamine).

**Primary carbon** (Section 2.10): A carbon that is directly attached to only one other carbon.

**Primary structure** (Section 27.8): The sequence of amino acids in a peptide or protein.

**Principal quantum number** (Section 1.1): The quantum number (n) of an electron that describes its energy level. An electron with n = 1 must be an s electron; one with n = 2 has s and p states available.

**Propagation steps** (Section 4.18): Elementary steps that repeat over and over again in a chain reaction. Almost all of the products in a chain reaction arise from the propagation steps.

**Protecting group** (Section 17.9): A temporary alteration in the nature of a functional group so that it is rendered inert under the conditions in which reaction occurs somewhere else in the molecule. To be synthetically useful, a protecting group must be stable under a prescribed set of reaction conditions, yet be easily introduced and removed.

**Protein** (Chapter 27): A naturally occurring polymer that typically contains 100–300 amino acid residues.

Protein Data Bank (Section 27.20): A central repository in which crystallographic coordinates for biological molecules, especially proteins, are stored. The data are accessible via the World-Wide Web and can be transformed into three-dimensional images with appropriate molecular-modeling software.

**Protic solvent** (Section 8.12): A solvent that has easily exchangeable protons, especially protons bonded to oxygen as in hydroxyl groups.

**Purine** (Section 27.23): The heterocyclic aromatic compound.

**Pyranose form** (Section 25.7): Six-membered ring arising via cyclic hemiacetal formation between the carbonyl group and a hydroxyl group of a carbohydrate.

**Pyrimidine** (Section 27.23): The heterocyclic aromatic compound.



**Quantum** (Section 13.1): The energy associated with a photon. **Quaternary ammonium salt** (Section 22.1): Salt of the type  $R_4N^+$   $X^-$ . The positively charged ion contains a nitrogen with a total of four organic substituents (any combination of alkyl and aryl groups).

**Quaternary carbon** (Section 2.10): A carbon that is directly attached to four other carbons.

Quaternary structure (Section 27.22): Description of the way in which two or more protein chains, not connected by chemical bonds, are organized in a larger protein.

**Quinone** (Section 24.14): The product of oxidation of an ortho or para dihydroxybenzene derivative. Examples of quinones include

**R** (Section 2.2): Symbol for an alkyl group.

**Racemic mixture** (Section 7.4): Mixture containing equal quantities of enantiomers.

**Rate-determining step** (Section 4.11): Slowest step of a multistep reaction mechanism. The overall rate of a reaction can be no faster than its slowest step.

**Rearrangement** (Section 5.13): Intramolecular migration of an atom, a group, or a bond from one atom to another.

**Reducing sugar** (Section 25.19): A carbohydrate that can be oxidized with substances such as Benedict's reagent. In general, a carbohydrate with a free hydroxyl group at the anomeric position.

**Reduction** (Section 2.16): Gain in the number of electrons associated with an atom. In organic chemistry, reduction of carbon occurs when a bond between carbon and an atom which is more electronegative than carbon is replaced by a bond to an atom which is less electronegative than carbon.

**Reductive amination** (Section 22.11): Method for the preparation of amines in which an aldehyde or a ketone is treated with ammonia or an amine under conditions of catalytic hydrogenation.

**Refining** (Section 2.13): Conversion of crude oil to useful materials, especially gasoline.

**Reforming** (Section 2.13): Step in oil refining in which the proportion of aromatic and branched-chain hydrocarbons in petroleum is increased so as to improve the octane rating of gasoline.

**Regioselective** (Section 5.10): Term describing a reaction that can produce two (or more) constitutional isomers but gives one of them in greater amounts than the other. A reaction that is 100% regioselective is termed regiospecific.

**Relative configuration** (Section 7.5): Stereochemical configuration on a comparative, rather than an absolute, basis. Terms such as D, L, erythro, threo,  $\alpha$ , and  $\beta$  describe relative configuration.

**Resolution** (Section 7.14): Separation of a racemic mixture into its enantiomers.

**Resonance** (Section 1.9): Method by which electron delocalization may be shown using Lewis structures. The true electron distribution in a molecule is regarded as a hybrid of the various Lewis structures that can be written for a molecule.

**Resonance energy** (Section 10.6): Extent to which a substance is stabilized by electron delocalization. It is the difference in energy between the substance and a hypothetical model in which the electrons are localized.

**Restriction enzymes** (Section 27.29): Enzymes that catalyze the cleavage of DNA at specific sites.

**Retention of configuration** (Section 6.13): Stereochemical pathway observed when a new bond is made that has the same spatial orientation as the bond that was broken.

Retrosynthetic analysis (Section 14.9): Technique for synthetic planning based on reasoning backward from the target molecule to appropriate starting materials. An arrow of the type  $\square$  designates a retrosynthetic step.

**Ring inversion** (Section 3.7): Process by which a chair conformation of cyclohexane is converted to a mirror-image chair. All of the equatorial substituents become axial, and vice versa. Also called *ring flipping*, or *chair—chair interconversion*.

**RNA** (ribonucleic acid) (Section 27.26): A polynucleotide of ribose.

**Robinson annulation** (Section 18.13): The combination of a Michael addition and an intramolecular aldol condensation used as a synthetic method for ring formation.

Rotamer (Section 3.1): Synonymous with conformer.

Sandmeyer reaction (Section 22.18): Reaction of an aryl diazonium ion with CuCl, CuBr, or CuCN to give, respectively, an aryl chloride, aryl bromide, or aryl cyanide (nitrile).

**Sanger's reagent** (Section 27.11): The compound 1-fluoro-2,4-dinitrobenzene, used in N-terminal amino acid identification.

**Saponification** (Section 20.10): Hydrolysis of esters in basic solution. The products are an alcohol and a carboxylate salt. The term means "soap making" and derives from the process whereby animal fats were converted to soap by heating with wood ashes.

**Saturated hydrocarbon** (Section 6.1): A hydrocarbon in which there are no multiple bonds.

**Sawhorse formula** (Section 3.1): A representation of the three-dimensional arrangement of bonds in a molecule by a drawing of the type shown.



**Schiemann reaction** (Section 22.18): Preparation of an aryl fluoride by heating the diazonium fluoroborate formed by addition of tetrafluoroboric acid (HBF<sub>4</sub>) to a diazonium ion.

Schiff's base (Section 17.10): Another name for an imine; a compound of the type  $R_2C = NR'$ .

**Scientific method** (Section 6.6): A systematic approach to establishing new knowledge in which observations lead to laws, laws to theories, theories to testable hypotheses, and hypotheses to experiments.

**Secondary alkyl group** (Section 2.10): Structural unit of the type R<sub>2</sub>CH—, in which the point of attachment is to a secondary carbon.

**Secondary amine** (Section 22.1): An amine with any combination of two alkyl or aryl substituents and one hydrogen on nitrogen; an amine of the type

RNHR' or RNHAr or ArNHAr'.

**Secondary carbon** (Section 2.10): A carbon that is directly attached to two other carbons.

Secondary structure (Section 27.19): The conformation with respect to nearest neighbor amino acids in a peptide or protein. The  $\alpha$  helix and the  $\beta$  pleated sheet are examples of protein secondary structures.

**Sequence rule** (Section 7.6): Foundation of the Cahn—Ingold—Prelog system. It is a procedure for ranking substituents on the basis of atomic number.

**Shielding** (Section 13.4): Effect of a molecule's electrons that decreases the strength of an external magnetic field felt by a proton or another nucleus.

- Sigmatropic rearrangement (Section 24.13): Migration of a  $\sigma$  bond from one end of a conjugated  $\pi$  electron system to the other. The Claisen rearrangement is an example.
- Simmons—Smith reaction (Section 14.12): Reaction of an alkene with iodomethylzinc iodide to form a cyclopropane derivative.
- **Skew boat** (Section 3.5): An unstable conformation of cyclohexane. It is slightly more stable than the boat conformation.
- **Soaps** (Section 19.5): Cleansing substances obtained by the hydrolysis of fats in aqueous base. Soaps are sodium or potassium salts of unbranched carboxylic acids having 12–48 carbon atoms.
- **Solid-phase peptide synthesis** (Section 27.18): Method for peptide synthesis in which the C-terminal amino acid is covalently attached to an inert solid support and successive amino acids are attached via peptide bond formation. At the completion of the synthesis the polypeptide is removed from the support.
- **Solvolysis reaction** (Section 8.7): Nucleophilic substitution in a medium in which the only nucleophiles present are the solvent and its conjugate base.
- **Space-filling model** (Section 1.9): A type of molecular model that attempts to represent the volume occupied by the atoms.
- **Specific rotation** (Section 7.4): Optical activity of a substance per unit concentration per unit path length:

$$[\alpha] = \frac{100\alpha}{cl}$$

where  $\alpha$  is the observed rotation in degrees, c is the concentration in g/100 mL, and l is the path length in decimeters.

- **Spectrometer** (Section 13.1): Device designed to measure absorption of electromagnetic radiation by a sample.
- Spectrum (Section 13.2): Output, usually in chart form, of a spectrometer. Analysis of a spectrum provides information about molecular structure.
- sp Hybridization (Section 1.18): Hybridization state adopted by carbon when it bonds to two other atoms as, for example, in alkynes. The s orbital and one of the 2p orbitals mix to form two equivalent sp-hybridized orbitals. A linear geometry is characteristic of sp hybridization.
- $sp^2$ -Hybridization (Section 1.17): A model to describe the bonding of a carbon attached to three other atoms or groups. The carbon 2s orbital and the two 2p orbitals are combined to give a set of three equivalent  $sp^2$  orbitals having 33.3% s character and 66.7% p character. One p orbital remains unhybridized. A trigonal planar geometry is characteristic of  $sp^2$  hybridization.
- sp³-Hybridization (Section 1.15): A model to describe the bonding of a carbon attached to four other atoms or groups. The carbon 2s orbital and the three 2p orbitals are combined to give a set of four equivalent orbitals having 25% s character and 75% p character. These orbitals are directed toward the corners of a tetrahedron.
- **Spin quantum number** (Section 1.1): One of the four quantum numbers that describe an electron. An electron may have either of two different spin quantum numbers,  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

**Spin—spin coupling** (Section 13.7): The communication of nuclear spin information between two nuclei.

- Spin—spin splitting (Section 13.7): The splitting of NMR signals caused by the coupling of nuclear spins. Only non-equivalent nuclei (such as protons with different chemical shifts) can split one another's signals.
- **Spirocyclic hydrocarbon** (Section 3.14): A hydrocarbon in which a single carbon is common to two rings.
- **Squalene** (Section 26.11): A naturally occurring triterpene from which steroids are biosynthesized.
- **Staggered conformation** (Section 3.1): Conformation of the type shown, in which the bonds on adjacent carbons are as far away from one another as possible.



- **Stereochemistry** (Chapter 7): Chemistry in three dimensions; the relationship of physical and chemical properties to the spatial arrangement of the atoms in a molecule.
- **Stereoelectronic effect** (Section 5.16): An electronic effect that depends on the spatial arrangement between the orbitals of the electron donor and acceptor.
- **Stereogenic axis** (Section 10.8): Line drawn through a molecule that is analogous to the long axis of a right-handed or left-handed screw or helix.
- **Stereogenic center** (Section 7.2): An atom that has four nonequivalent atoms or groups attached to it. At various times stereogenic centers have been called *asymmetric centers* or *chiral centers*.
- **Stereoisomers** (Section 3.12): Isomers which have the same constitution but which differ in respect to the arrangement of their atoms in space. Stereoisomers may be either *enantiomers* or *diastereomers*.
- **Stereoregular polymer** (Section 7.15): Polymer containing stereogenic centers according to a regular repeating pattern. Syndiotactic and isotactic polymers are stereoregular.
- **Stereoselective reaction** (Sections 5.11 and 6.3): Reaction in which a single starting material has the capacity to form two or more stereoisomeric products but forms one of them in greater amounts than any of its stereoisomers. Terms such as *addition to the less hindered side* describe stereoselectivity.
- **Stereospecific reaction** (Section 7.13): Reaction in which stereoisomeric starting materials give stereoisomeric products. Terms such as *syn addition, anti elimination,* and *inversion of configuration* describe stereospecific reactions.
- **Steric hindrance** (Sections 3.3, 6.3, and 8.6): An effect on structure or reactivity that depends on van der Waals repulsive forces.
- **Steric strain** (Section 3.2): Destabilization of a molecule as a result of van der Waals repulsion, distorted bond distances, bond angles, or torsion angles.

G-21 GLOSSARY

**Steroid** (Section 26.11): Type of lipid present in both plants and animals characterized by a nucleus of four fused rings (three are six-membered, one is five-membered). Cholesterol is the most abundant steroid in animals.

**Strecker synthesis** (Section 27.4): Method for preparing amino acids in which the first step is reaction of an aldehyde with ammonia and hydrogen cyanide to give an amino nitrile, which is then hydrolyzed.

$$\begin{array}{c}
O \\
RCH \xrightarrow{NH_3} RCHC = N \xrightarrow{hydrolysis} RCHCO_2^- \\
NH_2 \xrightarrow{hydrolysis} RCHCO_2^-
\end{array}$$

**Stretching vibration** (Section 13.19): A regular, repetitive motion of two atoms or groups along the bond that connects them.

**Structural isomer** (Section 1.8): Synonymous with *constitutional isomer*.

Substitution nucleophilic bimolecular (S<sub>N</sub>2) mechanism (Sections 4.13 and 8.3): Concerted mechanism for nucleophilic substitution in which the nucleophile attacks carbon from the side opposite the bond to the leaving group and assists the departure of the leaving group.

Substitution nucleophilic unimolecular (S<sub>N</sub>1) mechanism (Sections 4.11 and 8.8): Mechanism for nucleophilic substitution characterized by a two-step process. The first step is rate-determining and is the ionization of an alkyl halide to a carbocation and a halide ion.

**Substitution reaction** (Section 4.8): Chemical reaction in which an atom or a group of a molecule is replaced by a different atom or group.

**Substitutive nomenclature** (Section 4.1): Type of IUPAC nomenclature in which a substance is identified by a name ending in a suffix characteristic of the type of compound. 2-Methylbutanol, 3-pentanone, and 2-phenylpropanoic acid are examples of substitutive names.

**Sucrose** (Section 25.14): A disaccharide of glucose and fructose in which the two monosaccharides are joined at their anomeric positions.

**Sulfide** (Section 16.1): A compound of the type RSR'. Sulfides are the sulfur analogs of ethers.

**Sulfonation** (Section 12.4): Replacement of a hydrogen by an —SO<sub>3</sub>H group. The term is usually used in connection with electrophilic aromatic substitution.

$$Ar-H \xrightarrow{SO_3} Ar-SO_3H$$

Sulfone (Section 16.16): Compound of the type

$$\begin{array}{c} : \stackrel{\cdot}{O}:\\ R \stackrel{\mid}{-} S \stackrel{2^+}{-} R\\ : O: \end{array}$$

**Sulfoxide** (Section 16.16): Compound of the type

**Symmetry-allowed reaction** (Section 10.14): Concerted reaction in which the orbitals involved overlap in phase at all stages of the process. The conrotatory ring opening of cyclobutene to 1,3-butadiene is a symmetry-allowed reaction.

Symmetry-forbidden reaction (Section 10.14): Concerted reaction in which the orbitals involved do not overlap in phase at all stages of the process. The disrotatory ring opening of cyclobutene to 1,3-butadiene is a symmetry-forbidden reaction.

**Syn addition** (Section 6.3): Addition reaction in which the two portions of the reagent which add to a multiple bond add from the same side.

**Syndiotactic polymer** (Section 7.15): Stereoregular polymer in which the configuration of successive stereogenic centers alternates along the chain.

**Synthon** (Section 21.6): A structural unit in a molecule that is related to a synthetic operation.

**Systematic nomenclature** (Section 2.8): Names for chemical compounds that are developed on the basis of a prescribed set of rules. Usually the IUPAC system is meant when the term *systematic nomenclature* is used.

**Tautomerism** (Sections 9.12 and 18.4): Process by which two isomers are interconverted by an actual or formal movement of an atom or a group. Enolization is a form of tautomerism.

$$\begin{array}{ccc}
O & OH \\
\parallel & & \mid \\
RC-CHR_2 & \longrightarrow RC=CR_2
\end{array}$$

**Terminal alkyne** (Section 9.1): Alkyne of the type RC≡CH, in which the triple bond appears at the end of the chain.

**Termination steps** (Section 4.18): Reactions that halt a chain reaction. In a free-radical chain reaction, termination steps consume free radicals without generating new radicals to continue the chain.

**Terpenes** (Section 26.7): Compounds that can be analyzed as clusters of isoprene units. Terpenes with 10 carbons are classified as *monoterpenes*, those with 15 are *sesquiterpenes*, those with 20 are *diterpenes*, and those with 30 are *triterpenes*.

**Tertiary alkyl group** (Section 2.10): Structural unit of the type R<sub>3</sub>C—, in which the point of attachment is to a tertiary carbon.

**Tertiary amine** (Section 22.1): Amine of the type R<sub>3</sub>N with any combination of three alkyl or aryl substituents on nitrogen.

**Tertiary carbon** (Section 2.10): A carbon that is directly attached to three other carbons.

**Tertiary structure** (Section 27.20): A description of how a protein chain is folded.

Tesla (Section 13.3): SI unit for magnetic field strength.

- **Tetrahedral intermediate** (Section 19.14 and Chapter 20): The key intermediate in nucleophilic acyl substitution. Formed by nucleophilic addition to the carbonyl group of a carboxylic acid derivative.
- **Tetramethylsilane (TMS)** (Section 13.4): The molecule (CH<sub>3</sub>)<sub>4</sub>Si, used as a standard to calibrate proton and carbon-13 NMR spectra.
- **Tetrasubstituted alkene** (Section 5.6): Alkene of the type R<sub>2</sub>C=CR<sub>2</sub>, in which there are four carbons *directly* bonded to the carbons of the double bond. (The R groups may be the same or different.)
- **Tetrose** (Section 25.3): A carbohydrate with four carbon atoms. **Thermochemistry** (Section 2.15): The study of heat changes that accompany chemical processes.
- **Thermodynamically controlled reaction** (Section 10.10): Reaction in which the reaction conditions permit two or more products to equilibrate, giving a predominance of the most stable product.
- **Thioester** (Section 20.12): An *S*-acyl derivative of a thiol; a compound of the type



- **Thiol** (Section 15.13): Compound of the type RSH or ArSH.
- **Threo** (Section 7.11): Term applied to the relative configuration of two stereogenic centers within a molecule. The threo stereoisomer has like substituents on opposite sides of a Fischer projection.
- **Torsional strain** (Section 3.1): Decreased stability of a molecule that results from the eclipsing of bonds.
- **trans-** (Section 3.12): Stereochemical prefix indicating that two substituents are on opposite sides of a ring or a double bond. (Contrast with the prefix cis-.)
- **Transcription** (Section 27.28): Construction of a strand of mRNA complementary to a DNA template.
- **Transfer RNA (tRNA)** (Section 27.28): A polynucleotide of ribose that is bound at one end to a unique amino acid. This amino acid is incorporated into a growing peptide chain.
- **Transition state** (Section 3.1): The point of maximum energy in an elementary step of a reaction mechanism.
- **Translation** (Section 27.28): The "reading" of mRNA by various tRNAs, each one of which is unique for a particular amino acid.
- **Triacylglycerol** (Section 26.2): A derivative of glycerol (1,2,3-propanetriol) in which the three oxygens bear acyl groups derived from fatty acids.
- **Tripeptide** (Section 27.1): A compound in which three  $\alpha$ -amino acids are linked by peptide bonds.
- **Triple bond** (Section 1.4): Bond formed by the sharing of six electrons between two atoms.
- **Trisubstituted alkene** (Section 5.6): Alkene of the type R<sub>2</sub>C=CHR, in which there are three carbons *directly* bonded to the carbons of the double bond. (The R groups may be the same or different.)
- **Trivial nomenclature** (Section 2.8): Term synonymous with *common nomenclature*.

**Trypsin** (Section 27.10): A digestive enzyme that catalyzes the hydrolysis of proteins. Trypsin selectively catalyzes the cleavage of the peptide bond between the carboxyl group of lysine or arginine and some other amino acid.

**Twist boat** (Section 3.5): Synonymous with *skew boat*.

- **Ultraviolet-visible (UV-VIS) spectroscopy** (Section 13.20): Analytical method based on transitions between electronic energy states in molecules. Useful in studying conjugated systems such as polyenes.
- Unimolecular (Section 4.11): Describing a step in a reaction mechanism in which only one particle undergoes a chemical change at the transition state.
- $\alpha$ , $\beta$ -Unsaturated aldehyde or ketone (Section 18.11): Aldehyde or ketone that bears a double bond between its  $\alpha$  and  $\beta$  carbons as in

$$O$$
 $\parallel$ 
 $R_2C = CHCR'$ 

- **Unsaturated hydrocarbon** (Section 6.1): A hydrocarbon that can undergo addition reactions; that is, one that contains multiple bonds.
- **Upfield** (Section 13.4): The high-field region of an NMR spectrum. A signal that is upfield with respect to another lies to its right on the spectrum.
- **Urethan** (Section 20.17): Another name for a carbamate ester; a compound of the type (H<sub>2</sub>NCO<sub>2</sub>R).
- **Uronic acids** (Section 25.19): Carbohydrates that have an aldehyde function at one end of their carbon chain and a carboxylic acid group at the other.
- Valence bond theory (Section 1.13): Theory of chemical bonding based on overlap of half-filled atomic orbitals between two atoms. Orbital hybridization is an important element of valence bond theory.
- **Valence electrons** (Section 1.1): The outermost electrons of an atom. For second-row elements these are the 2s and 2p electrons.
- Valence shell electron-pair repulsion (VSEPR) model (Section 1.10): Method for predicting the shape of a molecule based on the notion that electron pairs surrounding a central atom repel one another. Four electron pairs will arrange themselves in a tetrahedral geometry, three will assume a trigonal planar geometry, and two electron pairs will adopt a linear arrangement.
- Van der Waals forces (Section 2.15): Intermolecular forces that do not involve ions (dipole—dipole, dipole/induced-dipole, and induced-dipole/induced-dipole forces).
- Van der Waals radius (Section 2.15): A measure of the effective size of an atom or a group. The repulsive force between two atoms increases rapidly when they approach each other at distances less than the sum of their van der Waals radii.
- Van der Waals strain (Section 3.2): Destabilization that results when two atoms or groups approach each other too closely. Also known as *van der Waals repulsion*.

G-23 GLOSSARY

**Vicinal** (Section 6.14): Describing two substituents that are located on adjacent atoms.

**Vicinal coupling** (Section 13.7): Coupling of the nuclear spins of atoms X and Y when they are substituents on adjacent atoms as in X—A—B—Y. Vicinal coupling is the most common cause of spin—spin splitting in <sup>1</sup>H NMR spectroscopy.

Vicinal diol (Section 15.5): Compound that has two hydroxyl (—OH) groups which are on adjacent sp<sup>3</sup>-hybridized carbons

Vinyl group (Section 5.1): The group  $CH_2 = CH - ...$ 

Vitalism (Introduction): A nineteenth-century theory that divided chemical substances into two main classes, organic and inorganic, according to whether they originated in living (animal or vegetable) or nonliving (mineral) matter, respectively. Vitalist doctrine held that the conversion of inorganic substances to organic ones could be accomplished only through the action of some "vital force."

Walden inversion (Section 8.4): Originally, a reaction sequence developed by Paul Walden whereby a chiral starting material was transformed to its enantiomer by a series of stereospecific reactions. Current usage is more general and refers to the inversion of configuration that attends any bimolecular nucleophilic substitution.

**Wave functions** (Section 1.1): The solutions to arithmetic expressions that express the energy of an electron in an atom.

**Wavelength** (Section 13.1): Distance between two successive maxima (peaks) or two successive minima (troughs) of a wave.

**Wave numbers** (Section 13.19): Conventional units in infrared spectroscopy that are proportional to frequency. Wave numbers are in reciprocal centimeters (cm<sup>-1</sup>).

Wax (Section 26.5): A mixture of water-repellent substances that form a protective coating on the leaves of plants, the fur of animals, and the feathers of birds, among other things. A principal component of a wax is often an ester in which both the acyl portion and the alkyl portion are characterized by long carbon chains.

Williamson ether synthesis (Section 16.6): Method for the preparation of ethers involving an  $S_N2$  reaction between an alkoxide ion and a primary alkyl halide:

$$RONa + R'CH_2Br \longrightarrow R'CH_2OR + NaBr$$

**Wittig reaction** (Section 17.12): Method for the synthesis of alkenes by the reaction of an aldehyde or a ketone with a phosphorus ylide.

$$\begin{array}{c}
O \\
RCR' + (C_6H_5)_3\overset{+}{P} - \overset{-}{C}R_2'' \longrightarrow \\
R' & C = C \\
R'' + (C_6H_5)_3\overset{+}{P} - O^{-}
\end{array}$$

Wolff—Kishner reduction (Section 12.8): Method for reducing the carbonyl group of aldehydes and ketones to a methylene group (C=O → CH<sub>2</sub>) by treatment with hydrazine (H<sub>2</sub>NNH<sub>2</sub>) and base (KOH) in a high-boiling alcohol solvent.

**Wood alcohol** (Section 4.2): A common name for methanol, CH<sub>3</sub>OH.

**Ylide** (Section 17.12): A neutral molecule in which two oppositely charged atoms, each with an octet of electrons, are directly bonded to each other. The compound

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2$$

is an example of an ylide.

**Zaitsev's rule** (Section 5.10): When two or more alkenes are capable of being formed by an elimination reaction, the one with the more highly substituted double bond (the more stable alkene) is the major product.

**Zwitterion** (Section 27.3): The form in which neutral amino acids actually exist. The amino group is in its protonated form and the carboxyl group is present as a carboxylate