

## Appendix C - Glossary

- **Absolute configuration:** The exact three-dimensional structure of a chiral molecule. Absolute configurations are specified verbally by the Cahn–Ingold–Prelog *R,S* convention.
- **Absorbance (A):** In optical spectroscopy, the logarithm of the intensity of the incident light divided by the intensity of the light transmitted through a sample;  $A = \log I_0/I$ .
- **Absorption spectrum:** A plot of wavelength of incident light versus amount of light absorbed. Organic molecules show absorption spectra in both the infrared and the ultraviolet regions of the electromagnetic spectrum.
- **Acetals,  $R_2C(OR')_2$ :** A type of functional group consisting of two –OR groups bonded to the same carbon,  $R_2C(OR')_2$ . Acetals are often used as protecting groups for ketones and aldehydes.
- **Acetoacetic ester synthesis:** The synthesis of a methyl ketone by alkylation of an alkyl halide with ethyl acetoacetate, followed by hydrolysis and decarboxylation.
- **Acetyl group:** The  $CH_3CO-$  group.
- **Acetylide anion:** The anion formed by removal of a proton from a terminal alkyne,  $R-C \equiv C:^-$ .
- **Achiral:** Having a lack of handedness. A molecule is achiral if it has a plane of symmetry and is thus superimposable on its mirror image.
- **Acid anhydrides:** A type of functional group with two acyl groups bonded to a common oxygen atom,  $RCO_2COR'$ .
- **Acid halides:** A type of functional group with an acyl group bonded to a halogen atom,  $RCOX$ .
- **Acidity constant,  $K_a$ :** A measure of acid strength. For any acid HA, the acidity constant is given by the expression 
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}.$$
- **Activating groups:** Electron-donating groups such as hydroxyl (–OH) or amino (–NH<sub>2</sub>) that increase the reactivity of an aromatic ring toward electrophilic aromatic substitution.
- **Activation energy:** The difference in energy between ground state and transition state in a reaction. The amount of activation energy determines the rate at which the reaction proceeds. Most organic reactions have activation energies of 40–100 kJ/mol.
- **Active site:** The pocket in an enzyme where a substrate is bound and undergoes reaction.
- **Acyclic diene metathesis (ADMET):** A method of polymer synthesis that uses the olefin metathesis reaction of an open-chain diene.
- **Acyl group:** A –COR group.
- **Acyl phosphates:** A type of functional group with an acyl group bonded to a phosphate,  $RCO_2PO_3^{2-}$ .
- **Acylation:** The introduction of an acyl group, –COR, onto a molecule. For example, acylation of an alcohol yields an ester, acylation of an amine yields an amide, and acylation of an aromatic ring yields an alkyl aryl ketone.
- **Acylium ion:** A resonance-stabilized carbocation in which the positive charge is located at a carbonyl-group carbon,  $R-\overset{+}{C}=O \leftrightarrow R-C \equiv O^+$ . Acylium ions are intermediates in Friedel–Crafts acylation reactions.
- **Adams' catalyst:** The  $PtO_2$  catalyst used for alkene hydrogenations.
- **1,2-Addition:** Addition of a reactant to the two ends of a double bond.
- **1,4-Addition:** Addition of a reactant to the ends of a conjugated  $\pi$  system. Conjugated dienes yield 1,4 adducts when treated with electrophiles such as HCl. Conjugated enones yield 1,4 adducts when treated with nucleophiles such as amines.
- **Addition reactions:** Occur when two reactants add together to form a single product with no atoms left over.
- **Adrenocortical hormones:** Steroid hormones secreted by the adrenal glands. There are two types of these hormones: mineralocorticoids and glucocorticoids.
- **Alcohols:** A class of compounds with an –OH group bonded to a saturated,  $sp^3$ -hybridized carbon, ROH.
- **Aldaric acid:** The dicarboxylic acid resulting from oxidation of an aldose.
- **Aldehydes (RCHO):** A class of compounds containing the –CHO functional group.
- **Alditol:** The polyalcohol resulting from reduction of the carbonyl group of a sugar.
- **Aldol reaction:** The carbonyl condensation reaction of an aldehyde or ketone to give a  $\beta$ -hydroxy carbonyl compound.
- **Aldonic acids:** Monocarboxylic acids resulting from oxidation of the –CHO group of an aldose.
- **Aldoses:** A type of carbohydrate with an aldehyde functional group.
- **Alicyclic:** A nonaromatic cyclic hydrocarbon such as a cycloalkane or cycloalkene.
- **Aliphatic:** A nonaromatic hydrocarbon such as a simple alkane, alkene, or alkyne.
- **Alkaloids:** Naturally occurring organic bases, such as morphine.
- **Alkanes:** A class of compounds of carbon and hydrogen that contains only single bonds.

- **Alkene:** A hydrocarbon that contains a carbon–carbon double bond,  $R_2C=$ .
- **Alkoxide ion,  $RO^-$ :** The anion formed by deprotonation of an alcohol.
- **Alkoxymercuration:** A method for synthesizing ethers by mercuric-ion catalyzed addition of an alcohol to an alkene followed by demercuration on treatment with  $NaBH_4$ .
- **Alkyl group:** The partial structure that remains when a hydrogen atom is removed from an alkane.
- **Alkyl halide:** A compound with a halogen atom bonded to a saturated,  $sp^3$ -hybridized carbon atom.
- **Alkylamines:** Amino-substituted alkanes  $RNH_2$ ,  $R_2NH$ , or  $R_3N$ .
- **Alkylation:** Introduction of an alkyl group onto a molecule. For example, aromatic rings can be alkylated to yield arenes, and enolate anions can be alkylated to yield  $\alpha$ -substituted carbonyl compounds.
- **Alkyne:** A hydrocarbon that contains a carbon–carbon triple bond,  $RC\equiv$ .
- **Allyl group:** A  $H_2C=CHCH_2-$  substituent.
- **Allylic:** The position next to a double bond. For example,  $H_2C=$  is an allylic bromide.
- **$\alpha$ -Amino acids:** A type of difunctional compound with an amino group on the carbon atom next to a carboxyl group,  $RCH(NH_2)CO_2H$ .
- **$\alpha$  Anomer:** The cyclic hemiacetal form of a sugar that has the hemiacetal  $-OH$  group cis to the  $-OH$  at the lowest chirality center in a Fischer projection.
- **$\alpha$  Helix:** The coiled secondary structure of a protein.
- **$\alpha$  Position:** The position next to a carbonyl group.
- **$\alpha$ -Substitution reaction:** The substitution of the  $\alpha$  hydrogen atom of a carbonyl compound by reaction with an electrophile.
- **Amides:** A class of compounds containing the  $-CONR_2$  functional group.
- **Amidomalonate synthesis:** A method for preparing  $\alpha$ -amino acids by alkylation of diethyl amidomalonate with an alkyl halide followed by deprotection and decarboxylation.
- **Amines:** A class of compounds containing one or more organic substituents bonded to a nitrogen atom,  $RNH_2$ ,  $R_2NH$ , or  $R_3N$ .
- **Amino acid:** See  $\alpha$ -Amino acid.
- **Amino sugar:** A sugar with one of its  $-OH$  groups replaced by  $-NH_2$ .
- **Amphiprotic:** Capable of acting either as an acid or as a base. Amino acids are amphiprotic.
- **Amplitude:** The height of a wave measured from the midpoint to the maximum. The intensity of radiant energy is proportional to the square of the wave's amplitude.
- **Anabolic steroids:** Synthetic androgens that mimic the tissue-building effects of natural testosterone.
- **Anabolism:** The group of metabolic pathways that build up larger molecules from smaller ones.
- **Androgen:** A male steroid sex hormone.
- **Angle strain:** The strain introduced into a molecule when a bond angle is deformed from its ideal value. Angle strain is particularly important in small-ring cycloalkanes, where it results from compression of bond angles to less than their ideal tetrahedral values.
- **Annulation:** The building of a new ring onto an existing molecule.
- **Anomeric center:** The hemiacetal carbon atom in the cyclic pyranose or furanose form of a sugar.
- **Anomers:** Cyclic stereoisomers of sugars that differ only in their configuration at the hemiacetal (anomeric) carbon.
- **Antarafacial:** A pericyclic reaction that takes place on opposite faces of the two ends of a  $\pi$  electron system.
- **Anti conformation:** The geometric arrangement around a carbon–carbon single bond in which the two largest substituents are  $180^\circ$  apart as viewed in a Newman projection.
- **Anti periplanar:** Describing the stereochemical relationship in which two bonds on adjacent carbons lie in the same plane at an angle of  $180^\circ$ .
- **Anti stereochemistry:** The opposite of syn. An anti addition reaction is one in which the two ends of the double bond are attacked from different sides. An anti elimination reaction is one in which the two groups leave from opposite sides of the molecule.
- **Antiaromatic:** Referring to a planar, conjugated molecule with  $4n$   $\pi$  electrons. Delocalization of the  $\pi$  electrons leads to an increase in energy.
- **Antibonding MO:** A molecular orbital that is higher in energy than the atomic orbitals from which it is formed.
- **Anticodon:** A sequence of three bases on tRNA that reads the codons on mRNA and brings the correct amino acids into position for protein synthesis.
- **Antisense strand:** The template, noncoding strand of double-helical DNA that does not contain the gene.
- **Arene:** An alkyl-substituted benzene.

- **Arenediazonium salt:** An aromatic compound  $\text{Ar}-\text{N}^+\equiv\text{N X}^-$ ; used in the Sandmeyer reaction.
- **Aromaticity:** The special characteristics of cyclic conjugated molecules, including unusual stability and a tendency to undergo substitution reactions rather than addition reactions on treatment with electrophiles. Aromatic molecules are planar, cyclic, conjugated species with  $4n + 2 \pi$  electrons.
- **Arylamines:** Amino-substituted aromatic compounds,  $\text{ArNH}_2$ .
- **Atactic:** A chain-growth polymer in which the stereochemistry of the substituents is oriented randomly along the backbone.
- **Atomic mass:** The weighted average mass of an element's naturally occurring isotopes.
- **Atomic number, Z:** The number of protons in the nucleus of an atom.
- **ATZ Derivative:** An anilinothiazolinone, formed from an amino acid during Edman degradation of a peptide.
- **Aufbau principle:** The rules for determining the electron configuration of an atom.
- **Axial bonds:** Bonds or positions in chair cyclohexane that lie along the ring axis, perpendicular to the rough plane of the ring.
- **Azide synthesis:** A method for preparing amines by  $\text{S}_{\text{N}}2$  reaction of an alkyl halide with azide ion, followed by reduction.
- **Azo compounds:** A class of compounds with the general structure  $\text{R}-\text{N}=\text{N}-\text{R}'$ .
- **Backbone:** The continuous chain of atoms running the length of a protein or other polymer.
- **Base peak:** The most intense peak in a mass spectrum.
- **Basicity constant,  $K_{\text{b}}$ :** A measure of base strength in water. For any base B, the basicity constant is given by the expression  

$$\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$$

$$K_{\text{b}} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$
- **Bent bonds:** The bonds in small rings such as cyclopropane that bend away from the internuclear line and overlap at a slight angle, rather than head-on. Bent bonds are highly strained and highly reactive.
- **Benzoyl:** The  $\text{C}_6\text{H}_5\text{CO}-$  group.
- **Benzyl:** The  $\text{C}_6\text{H}_5\text{CH}_2-$  group.
- **Benzylic:** The position next to an aromatic ring.
- **Benzyne:** An unstable compound having a triple bond in a benzene ring.
- **$\beta$  Anomer:** The cyclic hemiacetal form of a sugar that has the hemiacetal  $-\text{OH}$  group trans to the  $-\text{OH}$  at the lowest chirality center in a Fischer projection.
- **$\beta$  Diketone:** A 1,3-diketone.
- **$\beta$ -Keto ester:** A 3-oxoester.
- **$\beta$  Lactam:** A four-membered lactam, or cyclic amide. Penicillin and cephalosporin antibiotics contain  $\beta$ -lactam rings.
- **$\beta$ -Oxidation pathway:** The metabolic pathway for degrading fatty acids.
- **$\beta$ -Pleated sheet:** A type of secondary structure of a protein.
- **Betaine:** A neutral dipolar molecule with nonadjacent positive and negative charges. For example, the adduct of a Wittig reagent with a carbonyl compound is a betaine.
- **Bicycloalkane:** A cycloalkane that contains two rings.
- **Bimolecular reaction:** A reaction whose rate-limiting step occurs between two reactants.
- **Block copolymers:** Polymers in which different blocks of identical monomer units alternate with one another.
- **Boat cyclohexane:** A conformation of cyclohexane that bears a slight resemblance to a boat. Boat cyclohexane has no angle strain but has a large number of eclipsing interactions that make it less stable than chair cyclohexane.
- **Boc derivative:** A butyloxycarbonyl N-protected amino acid.
- **Bond angle:** The angle formed between two adjacent bonds.
- **Bond dissociation energy, D:** The amount of energy needed to break a bond and produce two radical fragments.
- **Bond length:** The equilibrium distance between the nuclei of two atoms that are bonded to each other.
- **Bond strength:** An alternative name for bond dissociation energy.
- **Bonding MO:** A molecular orbital that is lower in energy than the atomic orbitals from which it is formed.
- **Branched-chain alkanes:** Alkanes that contain a branching connection of carbons as opposed to straight-chain alkanes.
- **Bridgehead:** An atom that is shared by more than one ring in a polycyclic molecule.
- **Bromohydrin:** A 1,2-bromoalcohol; obtained by addition of  $\text{HOBr}$  to an alkene.
- **Bromonium ion:** A species with a divalent, positively charged bromine,  $\text{R}_2\text{Br}^+$ .
- **Brønsted–Lowry acid:** A substance that donates a hydrogen ion (proton;  $\text{H}^+$ ) to a base.
- **Brønsted–Lowry base:** A substance that accepts  $\text{H}^+$  from an acid.
- **C-terminal amino acid:** The amino acid with a free  $-\text{CO}_2\text{H}$  group at the end of a protein chain.

- **Cahn–Ingold–Prelog sequence rules:** A series of rules for assigning relative rankings to substituent groups on a chirality center or a double-bond carbon atom.
- **Cannizzaro reaction:** The disproportionation reaction of an aldehyde on treatment with base to yield an alcohol and a carboxylic acid.
- **Carbanion:** A carbon anion, or substance that contains a trivalent, negatively charged carbon atom ( $R_3C^-$ ). Alkyl carbanions are  $sp^3$ -hybridized and have eight electrons in the outer shell of the negatively charged carbon.
- **Carbene,  $R_2C$ :** A neutral substance that contains a divalent carbon atom having only six electrons in its outer shell ( $R_2C:$ ).
- **Carbinolamine:** A molecule that contains the  $R_2C(OH)NH_2$  functional group. Carbinolamines are produced as intermediates during the nucleophilic addition of amines to carbonyl compounds.
- **Carbocation:** A carbon cation, or substance that contains a trivalent, positively charged carbon atom having six electrons in its outer shell ( $R_3C^+$ ).
- **Carbohydrates:** Polyhydroxy aldehydes or ketones. Carbohydrates can be either simple sugars, such as glucose, or complex sugars, such as cellulose.
- **Carbonyl condensation reactions:** A type of reaction that joins two carbonyl compounds together by a combination of  $\alpha$ -substitution and nucleophilic addition reactions.
- **Carbonyl group:** The  $C=O$  functional group.
- **Carboxyl group:** The  $-CO_2H$  functional group.
- **Carboxylation:** The addition of  $CO_2$  to a molecule.
- **Carboxylic acids,  $RCO_2H$ :** Compounds containing the  $-CO_2H$  functional group.
- **Carboxylic acid derivative:** A compound in which an acyl group is bonded to an electronegative atom or substituent that can act as a leaving group in a substitution reaction. Esters, amides, and acid halides are examples.
- **Catabolism:** The group of metabolic pathways that break down larger molecules into smaller ones.
- **Catalyst:** A substance that increases the rate of a chemical transformation by providing an alternative mechanism but is not itself changed in the reaction.
- **Cation radical:** A reactive species, typically formed in a mass spectrometer by loss of an electron from a neutral molecule and having both a positive charge and an odd number of electrons.
- **Chain-growth polymers:** Polymers whose bonds are produced by chain reaction mechanisms. Polyethylene and other alkene polymers are examples.
- **Chain reaction:** A reaction that, once initiated, sustains itself in an endlessly repeating cycle of propagation steps. The radical chlorination of alkanes is an example of a chain reaction that is initiated by irradiation with light and then continues in a series of propagation steps.
- **Chair conformation:** A three-dimensional conformation of cyclohexane that resembles the rough shape of a chair. The chair form of cyclohexane is the lowest-energy conformation of the molecule.
- **Chemical shift:** The position on the NMR chart where a nucleus absorbs. By convention, the chemical shift of tetramethylsilane (TMS) is set at zero, and all other absorptions usually occur downfield (to the left on the chart). Chemical shifts are expressed in delta units ( $\delta$ ), where 1  $\delta$  equals 1 ppm of the spectrometer operating frequency.
- **Chiral:** Having handedness. Chiral molecules are those that do not have a plane of symmetry and are therefore not superimposable on their mirror image. A chiral molecule thus exists in two forms, one right-handed and one left-handed. The most common cause of chirality in a molecule is the presence of a carbon atom that is bonded to four different substituents.
- **Chiral environment:** The chiral surroundings or conditions in which a molecule resides.
- **Chirality center:** An atom (usually carbon) that is bonded to four different groups.
- **Chlorohydrin:** A 1,2-chloroalcohol; obtained by addition of  $HOCl$  to an alkene.
- **Chromatography:** A technique for separating a mixture of compounds into pure components. Different compounds adsorb to a stationary support phase and are then carried along it at different rates by a mobile phase.
- **Cis–trans isomers:** Stereoisomers that differ in their stereochemistry about a ring or double bond.
- **Citric acid cycle:** The metabolic pathway by which acetyl CoA is degraded to  $CO_2$ .
- **Claisen condensation reaction:** The carbonyl condensation reaction of two ester molecules to give a  $\beta$ -keto ester product.
- **Claisen rearrangement:** The pericyclic conversion of an allyl phenyl ether to an *o*-allylphenol or an allyl vinyl ether to a  $\gamma,\delta$ -unsaturated ketone by heating.
- **Coding strand:** The sense strand of double-helical DNA that contains the gene.
- **Codon:** A three-base sequence on a messenger RNA chain that encodes the genetic information necessary to cause a specific amino acid to be incorporated into a protein. Codons on mRNA are read by complementary anticodons on tRNA.

- **Coenzyme:** A small organic molecule that acts as a cofactor in a biological reaction.
- **Cofactor:** A small nonprotein part of an enzyme that is necessary for biological activity.
- **Combinatorial chemistry:** A procedure in which anywhere from a few dozen to several hundred thousand substances are prepared simultaneously.
- **Complex carbohydrates:** Carbohydrates that are made of two or more simple sugars linked together by glycoside bonds.
- **Concerted reaction:** A reaction that takes place in a single step without intermediates. For example, the Diels–Alder cycloaddition reaction is a concerted process.
- **Condensed structures:** A shorthand way of writing structures in which carbon–hydrogen and carbon–carbon bonds are understood rather than shown explicitly. Propane, for example, has the condensed structure  $\text{CH}_3\text{CH}_2\text{CH}_3$ .
- **Configuration:** The three-dimensional arrangement of atoms bonded to a chirality center.
- **Conformations:** The three-dimensional shape of a molecule at any given instant, assuming that rotation around single bonds is frozen.
- **Conformational analysis:** A means of assessing the energy of a substituted cycloalkane by totaling the steric interactions present in the molecule.
- **Conformers:** Conformational isomers.
- **Conjugate acid:** The product that results from protonation of a Brønsted–Lowry base.
- **Conjugate addition:** Addition of a nucleophile to the  $\beta$  carbon atom of an  $\alpha,\beta$ -unsaturated carbonyl compound.
- **Conjugate base:** The product that results from deprotonation of a Brønsted–Lowry acid.
- **Conjugation:** A series of overlapping  $p$  orbitals, usually in alternating single and multiple bonds. For example, 1,3-butadiene is a conjugated diene, 3-buten-2-one is a conjugated enone, and benzene is a cyclic conjugated triene.
- **Conrotatory:** A term used to indicate that  $p$  orbitals must rotate in the same direction during electrocyclic ring-opening or ring-closure.
- **Constitutional isomers:** Isomers that have their atoms connected in a different order. For example, butane and 2-methylpropane are constitutional isomers.
- **Cope rearrangement:** The sigmatropic rearrangement of a 1,5-hexadiene.
- **Copolymers:** Polymers obtained when two or more different monomers are allowed to polymerize together.
- **Coupled reactions:** Two reactions that share a common intermediate so that the energy released in the favorable step allows the unfavorable step to occur.
- **Coupling constant,  $J$ :** The magnitude (expressed in hertz) of the interaction between nuclei whose spins are coupled.
- **Covalent bond:** A bond formed by sharing electrons between atoms.
- **Cracking:** A process used in petroleum refining in which large alkanes are thermally cracked into smaller fragments.
- **Crown ethers:** Large-ring polyethers; used as phase-transfer catalysts.
- **Crystallites:** Highly ordered crystal-like regions within a long polymer chain.
- **Curtius rearrangement:** The conversion of an acid chloride into an amine by reaction with azide ion, followed by heating with water.
- **Cyanohydrins:** A class of compounds with an  $-\text{OH}$  group and a  $-\text{CN}$  group bonded to the same carbon atom; formed by addition of  $\text{HCN}$  to an aldehyde or ketone.
- **Cycloaddition reaction:** A pericyclic reaction in which two reactants add together in a single step to yield a cyclic product. The Diels–Alder reaction between a diene and a dienophile to give a cyclohexene is an example.
- **Cycloalkane:** An alkane that contains a ring of carbons.
- **D Sugars:** Sugars whose hydroxyl group at the chirality center farthest from the carbonyl group has the same configuration as D-glyceraldehyde and points to the right when drawn in Fischer projection.
- **$d,l$  form:** The racemic mixture of a chiral compound.
- **Deactivating groups:** Electron-withdrawing substituents that decrease the reactivity of an aromatic ring toward electrophilic aromatic substitution.
- **Deamination:** The removal of an amino group from a molecule, as occurs with amino acids during metabolic degradation.
- **Debyes (D):** Units for measuring dipole moments;  $1 \text{ D} = 3.336 \times 10^{-30}$  coulomb meter ( $\text{C} \cdot \text{m}$ ).
- **Decarboxylation:** The loss of carbon dioxide from a molecule.  $\beta$ -Keto acids decarboxylate readily on heating.
- **Degenerate orbitals:** Two or more orbitals that have the same energy level.
- **Degree of unsaturation:** The number of rings and/or multiple bonds in a molecule.
- **Dehydration:** The loss of water from an alcohol to yield an alkene.



- **Dehydrohalogenation:** The loss of HX from an alkyl halide. Alkyl halides undergo dehydrohalogenation to yield alkenes on treatment with strong base.
- **Delocalization:** A spreading out of electron density over a conjugated  $\pi$  electron system. For example, allylic cations and allylic anions are delocalized because their charges are spread out over the entire  $\pi$  electron system. Aromatic compounds have  $4n + 2$   $\pi$  electrons delocalized over their ring.
- **Delta ( $\delta$ ) scale:** An arbitrary scale used to calibrate NMR charts. One delta unit ( $\delta$ ) is equal to 1 part per million (ppm) of the spectrometer operating frequency.
- **Denatured:** The physical changes that occur in a protein when secondary and tertiary structures are disrupted.
- **Deoxy sugar:** A sugar with one of its  $-OH$  groups replaced by an  $-H$ .
- **Deoxyribonucleic acid (DNA):** The biopolymer consisting of deoxyribonucleotide units linked together through phosphate-sugar bonds. Found in the nucleus of cells, DNA contains an organism's genetic information.
- **DEPT-NMR:** An NMR method for distinguishing among signals due to  $CH_3$ ,  $CH_2$ ,  $CH$ , and quaternary carbons. That is, the number of hydrogens attached to each carbon can be determined.
- **Deshielding:** An effect observed in NMR that causes a nucleus to absorb toward the left (downfield) side of the chart. Deshielding is caused by a withdrawal of electron density from the nucleus.
- **Dess–Martin periodinane:** An iodine-based reagent commonly used for the laboratory oxidation of a primary alcohol to an aldehyde or a secondary alcohol to a ketone.
- **Deuterium isotope effect:** A tool used in mechanistic investigations to establish whether a C–H bond is broken in the rate-limiting step of a reaction.
- **Dextrorotatory:** A word used to describe an optically active substance that rotates the plane of polarization of plane-polarized light in a right-handed (clockwise) direction.
- **Diastereomers:** Non-mirror-image stereoisomers; diastereomers have the same configuration at one or more chirality centers but differ at other chirality centers.
- **Diastereotopic:** Hydrogens in a molecule whose replacement by some other group leads to different diastereomers.
- **1,3-Diaxial interaction:** The strain energy caused by a steric interaction between axial groups three carbon atoms apart in chair cyclohexane.
- **Diazonium salts:** A type of compound with the general structure  $RN_2^+X^-$ .
- **Diazotization:** The conversion of a primary amine,  $RNH_2$ , into a diazonium ion,  $RN_2^+$ , by treatment with nitrous acid.
- **Dieckmann cyclization reaction:** An intramolecular Claisen condensation reaction of a diester to give a cyclic  $\beta$ -keto ester.
- **Diels–Alder reaction:** The cycloaddition reaction of a diene with a dienophile to yield a cyclohexene.
- **Dienophile:** A compound containing a double bond that can take part in the Diels–Alder cycloaddition reaction. The most reactive dienophiles are those that have electron-withdrawing groups on the double bond.
- **Digestion:** The first stage of catabolism, in which food is broken down by hydrolysis of ester, glycoside (acetal), and peptide (amide) bonds to yield fatty acids, simple sugars, and amino acids.
- **Dihedral angle:** The angle between two bonds on adjacent carbons as viewed along the C–C bond.
- **Dipole moment,  $\mu$ :** A measure of the net polarity of a molecule. A dipole moment arises when the centers of mass of positive and negative charges within a molecule do not coincide.
- **Dipole–dipole forces:** Noncovalent electrostatic interactions between dipolar molecules.
- **Disaccharide:** A carbohydrate formed by linking two simple sugars through an acetal bond.
- **Dispersion forces:** Noncovalent interactions between molecules that arise because of constantly changing electron distributions within the molecules.
- **Disrotatory:** A term used to indicate that  $p$  orbitals rotate in opposite directions during electrocyclic ring-opening or ring-closing reactions.
- **Disulfides ( $RSSR'$ ):** A class of compounds of the general structure  $RSSR'$ .
- **Deoxyribonucleic acid (DNA):** Chemical carriers of a cell's genetic information.
- **Double bond:** A covalent bond formed by sharing two electron pairs between atoms.
- **Double helix:** The structure of DNA in which two polynucleotide strands coil around each other.
- **Doublet:** A two-line NMR absorption caused by spin–spin splitting when the spin of the nucleus under observation couples with the spin of a neighboring magnetic nucleus.
- **Downfield:** Referring to the left-hand portion of the NMR chart.
- **E geometry:** A term used to describe the stereochemistry of a carbon–carbon double bond. The two groups on each carbon are ranked according to the Cahn–Ingold–Prelog sequence rules, and the two carbons are compared. If the higher-ranked groups on

each carbon are on opposite sides of the double bond, the bond has *E* geometry.

- **E1 reaction:** A unimolecular elimination reaction in which the substrate spontaneously dissociates to give a carbocation intermediate, which loses a proton in a separate step.
- **E1cB reaction:** A unimolecular elimination reaction in which a proton is first removed to give a carbanion intermediate, which then expels the leaving group in a separate step.
- **E2 reaction:** A bimolecular elimination reaction in which C–H and C–X bond cleavages are simultaneous.
- **Eclipsed conformation:** The geometric arrangement around a carbon–carbon single bond in which the bonds to substituents on one carbon are parallel to the bonds to substituents on the neighboring carbon as viewed in a Newman projection.
- **Eclipsing strain:** The strain energy in a molecule caused by electron repulsions between eclipsed bonds. Eclipsing strain is also called torsional strain.
- **Edman degradation:** A method for N-terminal sequencing of peptide chains by treatment with *N*-phenylisothiocyanate.
- **Eicosanoid:** A lipid derived biologically from 5,8,11,14-eicosatetraenoic acid, or arachidonic acid. Prostaglandins, thromboxanes, and leukotrienes are examples.
- **Elastomer:** An amorphous polymer that has the ability to stretch out and spring back to its original shape.
- **Electrocyclic reaction:** A unimolecular pericyclic reaction in which a ring is formed or broken by a concerted reorganization of electrons through a cyclic transition state. For example, the cyclization of 1,3,5-hexatriene to yield 1,3-cyclohexadiene is an electrocyclic reaction.
- **Electromagnetic spectrum:** The range of electromagnetic energy, including infrared, ultraviolet, and visible radiation.
- **Electron configuration:** A list of the orbitals occupied by electrons in an atom.
- **Electron-dot structure:** A representation of a molecule showing valence electrons as dots.
- **Electron shells:** A group of an atom's electrons with the same principal quantum number.
- **Electron-transport chain:** The final stage of catabolism in which ATP is produced.
- **Electronegativity (EN):** The ability of an atom to attract electrons in a covalent bond. Electronegativity increases across the periodic table from left to right and from bottom to top.
- **Electrophile:** An “electron-lover,” or substance that accepts an electron pair from a nucleophile in a polar bond-forming reaction.
- **Electrophilic addition reactions:** Addition of an electrophile to a carbon–carbon double bond to yield a saturated product.
- **Electrophilic aromatic substitution reaction:** A reaction in which an electrophile ( $E^+$ ) reacts with an aromatic ring and substitutes for one of the ring hydrogens.
- **Electrophoresis:** A technique used for separating charged organic molecules, particularly proteins and DNA fragments. The mixture to be separated is placed on a buffered gel or paper, and an electric potential is applied across the ends of the apparatus. Negatively charged molecules migrate toward the positive electrode, and positively charged molecules migrate toward the negative electrode.
- **Electrostatic potential maps:** Molecular representations that use color to indicate the charge distribution in molecules as derived from quantum-mechanical calculations.
- **Elimination reactions:** What occurs when a single reactant splits into two products.
- **Elution:** The passage of a substance from a chromatography column.
- **Embden–Meyerhof pathway:** An alternative name for glycolysis.
- **Enamines:** Compounds with the  $R_2N-CR=$  functional group.
- **Enantiomers:** Stereoisomers of a chiral substance that have a mirror-image relationship. Enantiomers have opposite configurations at all chirality centers.
- **Enantioselective synthesis:** A reaction method that yields only a single enantiomer of a chiral product starting from an achiral reactant.
- **Enantiotopic:** Hydrogens in a molecule whose replacement by some other group leads to different enantiomers.
- **3' End:** The end of a nucleic acid chain with a free hydroxyl group at C3'.
- **5' End:** The end of a nucleic acid chain with a free hydroxyl group at C5'.
- **Endergonic:** A reaction that has a positive free-energy change and is therefore nonspontaneous. In an energy diagram, the product of an endergonic reaction has a higher energy level than the reactants.
- **Endo:** A term indicating the stereochemistry of a substituent in a bridged bicycloalkane. An endo substituent is syn to the larger of the two bridges.
- **Endothermic:** A reaction that absorbs heat and therefore has a positive enthalpy change.

- **Energy diagram:** A representation of the course of a reaction, in which free energy is plotted as a function of reaction progress. Reactants, transition states, intermediates, and products are represented, and their appropriate energy levels are indicated.
- **Enol:** A vinylic alcohol that is in equilibrium with a carbonyl compound,  $C=C-OH$ .
- **Enolate ion:** The anion of an enol,  $C=C-O^-$ .
- **Enthalpy change ( $\Delta H$ ):** The heat of reaction. The enthalpy change that occurs during a reaction is a measure of the difference in total bond energy between reactants and products.
- **Entropy change ( $\Delta S$ ):** The change in amount of molecular randomness. The entropy change that occurs during a reaction is a measure of the difference in randomness between reactants and products.
- **Enzyme:** A biological catalyst. Enzymes are large proteins that catalyze specific biochemical reactions.
- **Epimers:** Diastereomers that differ in configuration at only one chirality center but are the same at all others.
- **Epoxide:** A three-membered-ring ether functional group.
- **Equatorial bonds:** Bonds or positions in chair cyclohexane that lie along the rough equator of the ring.
- **ESI:** Electrospray ionization; a “soft” ionization method used for mass spectrometry of biological samples of very high molecular weight.
- **Essential amino acid:** One of nine amino acids that are biosynthesized only in plants and microorganisms and must be obtained by humans in the diet.
- **Essential monosaccharide:** One of eight simple sugars that is best obtained in the diet rather than by biosynthesis.
- **Essential oil :** The volatile oil obtained by steam distillation of a plant extract.
- **Esters:** A class of compounds containing the  $-CO_2R$  functional group.
- **Estrogens:** Female steroid sex hormones.
- **Ethers:** A class of compounds that has two organic substituents bonded to the same oxygen atom,  $ROR'$ .
- **Exergonic:** A reaction that has a negative free-energy change and is therefore spontaneous. On an energy diagram, the product of an exergonic reaction has a lower energy level than that of the reactants.
- **Exo:** A term indicating the stereochemistry of a substituent in a bridged bicycloalkane. An exo substituent is anti to the larger of the two bridges.
- **Exon:** A section of DNA that contains genetic information.
- **Exothermic:** A reaction that releases heat and therefore has a negative enthalpy change.
- **Fats:** Solid triacylglycerols derived from an animal source.
- **Fatty acids:** A long, straight-chain carboxylic acid found in fats and oils.
- **Fiber:** A thin thread produced by extruding a molten polymer through small holes in a die.
- **Fibrous proteins:** A type of protein that consists of polypeptide chains arranged side by side in long threads. Such proteins are tough, insoluble in water, and used in nature for structural materials such as hair, hooves, and fingernails.
- **Fingerprint region:** The complex region of the infrared spectrum from  $1500-400\text{ cm}^{-1}$ .
- **First-order reaction:** Designates a reaction whose rate-limiting step is unimolecular and whose kinetics therefore depend on the concentration of only one reactant.
- **Fischer esterification reaction:** The acid-catalyzed nucleophilic acyl substitution reaction of a carboxylic acid with an alcohol to yield an ester.
- **Fischer projections:** A means of depicting the absolute configuration of a chiral molecule on a flat page. A Fischer projection uses a cross to represent the chirality center. The horizontal arms of the cross represent bonds coming out of the plane of the page, and the vertical arms of the cross represent bonds going back into the plane of the page.
- **Fmoc derivative:** A fluorenylmethyloxycarbonyl N-protected amino acid.
- **Formal charges:** The difference in the number of electrons owned by an atom in a molecule and by the same atom in its elemental state.
- **Formyl:** A  $-CHO$  group.
- **Frequency,  $\nu$ :** The number of electromagnetic wave cycles that travel past a fixed point in a given unit of time. Frequencies are expressed in units of cycles per second, or hertz.
- **Friedel-Crafts reaction:** An electrophilic aromatic substitution reaction to alkylate or acylate an aromatic ring.
- **Frontier orbitals:** The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.
- **FT-NMR:** Fourier-transform NMR; a rapid technique for recording NMR spectra in which all magnetic nuclei absorb at the same time.
- **Functional:** An atom or group of atoms that is part of a larger molecule and has a characteristic chemical reactivity.
- **Functional RNAs:** An alternative name for small RNAs.



- **Furanose:** The five-membered-ring form of a simple sugar.
- **Gabriel amine synthesis:** A method for preparing an amine by  $S_N2$  reaction of an alkyl halide with potassium phthalimide, followed by hydrolysis.
- **Gauche conformation:** The conformation of butane in which the two methyl groups lie  $60^\circ$  apart as viewed in a Newman projection. This conformation has 3.8 kJ/mol steric strain.
- **Geminal:** Referring to two groups attached to the same carbon atom. For example, the hydrate formed by nucleophilic addition of water to an aldehyde or ketone is a geminal diol.
- **Gibbs free-energy change ( $\Delta G$ ):** The free-energy change that occurs during a reaction, given by the equation  $\Delta G = \Delta H - T\Delta S$ . A reaction with a negative free-energy change is spontaneous, and a reaction with a positive free-energy change is nonspontaneous.
- **Gilman reagent ( $LiR_2Cu$ ):** A diorganocopper reagent.
- **Glass transition temperature,  $T_g$ :** The temperature at which a hard, amorphous polymer becomes soft and flexible.
- **Globular proteins:** A type of protein that is coiled into a compact, nearly spherical shape. Globular proteins, which are generally water-soluble and mobile within the cell, are the structural class to which enzymes belong.
- **Gluconeogenesis:** The anabolic pathway by which organisms make glucose from simple three-carbon precursors.
- **Glycal:** An unsaturated sugar with a C1–C2 double bond.
- **Glycal assembly method:** A method for linking monosaccharides together to synthesize polysaccharides.
- **Glycerophospholipids:** Lipids that contain a glycerol backbone linked to two fatty acids and a phosphoric acid.
- **Glycoconjugate:** A molecule in which a carbohydrate is linked through its anomeric center to another biological molecule such as a lipid or protein.
- **Glycol:** A diol, such as ethylene glycol,  $HOCH_2CH_2OH$ .
- **Glycolipid:** A biological molecule in which a carbohydrate is linked through a glycoside bond to a lipid.
- **Glycolysis:** A series of ten enzyme-catalyzed reactions that break down glucose into 2 equivalents of pyruvate,  $CH_3COCO_2^-$ .
- **Glycoprotein:** A biological molecule in which a carbohydrate is linked through a glycoside bond to a protein.
- **Glycoside:** A cyclic acetal formed by reaction of a sugar with another alcohol.
- **Graft copolymers:** Copolymers in which homopolymer branches of one monomer unit are “grafted” onto a homopolymer chain of another monomer unit.
- **Green chemistry:** The design and implementation of chemical products and processes that reduce waste and minimize or eliminate the generation of hazardous substances.
- **Grignard reagent ( $RMgX$ ):** An organomagnesium halide.
- **Ground-state electron configuration:** The most stable, lowest-energy electron configuration of a molecule or atom.
- **Haloform reaction:** The reaction of a methyl ketone with halogen and base to yield a haloform ( $CHX_3$ ) and a carboxylic acid.
- **Halogenation:** The reaction of halogen with an alkene to yield a 1,2-dihalide addition product or with an aromatic compound to yield a substitution product.
- **Halohydrin:** A 1,2-haloalcohol, such as that obtained on addition of  $HOBr$  to an alkene.
- **Halonium ion:** A species containing a positively charged, divalent halogen. Three-membered-ring bromonium ions are intermediates in the electrophilic addition of  $Br_2$  to alkenes.
- **Hammond postulate:** A postulate stating that we can get a picture of what a given transition state looks like by looking at the structure of the nearest stable species. Exergonic reactions have transition states that resemble reactant; endergonic reactions have transition states that resemble product.
- **Heat of combustion:** The amount of heat released when a compound burns completely in oxygen.
- **Heat of hydrogenation:** The amount of heat released when a carbon–carbon double bond is hydrogenated.
- **Heat of reaction:** An alternative name for the enthalpy change in a reaction,  $\Delta H$ .
- **Hell–Volhard–Zelinskii (HVZ) reaction:** The reaction of a carboxylic acid with  $Br_2$  and phosphorus to give an  $\alpha$ -bromo carboxylic acid.
- **Hemiacetal:** A functional group having one  $-OR$  and one  $-OH$  group bonded to the same carbon.
- **Henderson–Hasselbalch equation:** An equation for determining the extent of dissociation of a weak acid at various pH values.
- **Hertz, Hz:** A unit of measure of electromagnetic frequency, the number of waves that pass by a fixed point per second.
- **Heterocycle:** A cyclic molecule whose ring contains more than one kind of atom. For example, pyridine is a heterocycle that contains five carbon atoms and one nitrogen atom in its ring.
- **Heterolytic bond breakage:** The kind of bond-breaking that occurs in polar reactions when one fragment leaves with both of the bonding electrons:  $A : B \rightarrow A^+ + B:^-$ .

- **Hofmann elimination reaction:** The elimination reaction of an amine to yield an alkene by reaction with iodomethane followed by heating with  $\text{Ag}_2\text{O}$ .
- **Hofmann rearrangement:** The conversion of an amide into an amine by reaction with  $\text{Br}_2$  and base.
- **Highest occupied molecular orbital (HOMO):** The symmetries of the HOMO and LUMO are important in pericyclic reactions.
- **Homolytic bond breakage:** The kind of bond-breaking that occurs in radical reactions when each fragment leaves with one bonding electron:  $\text{A} : \text{B} \rightarrow \text{A}^\cdot + \text{B}^\cdot$ .
- **Homopolymers:** A polymer made up of identical repeating units.
- **Homotopic:** Hydrogens in a molecule that give the identical structure on replacement by X and thus show identical NMR absorptions.
- **Hormones:** Chemical messengers that are secreted by an endocrine gland and carried through the bloodstream to a target tissue.
- **HPLC:** High-pressure liquid chromatography; a variant of column chromatography using high pressure to force solvent through very small absorbent particles.
- **Hückel  $4n + 2$  rule:** A rule stating that monocyclic conjugated molecules having  $4n + 2 \pi$  electrons ( $n = \text{an integer}$ ) are aromatic.
- **Hund's rule:** If two or more empty orbitals of equal energy are available, one electron occupies each, with their spins parallel, until all are half-full.
- **Hybrid orbital:** An orbital derived from a combination of atomic orbitals. Hybrid orbitals, such as the  $sp^3$ ,  $sp^2$ , and  $sp$  hybrids of carbon, are strongly directed and form stronger bonds than atomic orbitals do.
- **Hydration:** Addition of water to a molecule, such as occurs when alkenes are treated with aqueous sulfuric acid to give alcohols.
- **Hydride shift:** The shift of a hydrogen atom and its electron pair to a nearby cationic center.
- **Hydroboration:** Addition of borane ( $\text{BH}_3$ ) or an alkylborane to an alkene. The resultant trialkylborane products can be oxidized to yield alcohols.
- **Hydrocarbons:** A class of compounds that contain only carbon and hydrogen.
- **Hydrogen bond:** A weak attraction between a hydrogen atom bonded to an electronegative atom and an electron lone pair on another electronegative atom.
- **Hydrogenated:** Addition of hydrogen to a double or triple bond to yield a saturated product.
- **Hydrogenolysis:** Cleavage of a bond by reaction with hydrogen. Benzylic ethers and esters, for instance, are cleaved by hydrogenolysis.
- **Hydrophilic:** Water-loving; attracted to water.
- **Hydrophobic:** Water-fearing; repelled by water.
- **Hydroquinones:** 1,4-dihydroxybenzene.
- **Hydroxylation:** Addition of two  $-\text{OH}$  groups to a double bond.
- **Hyperconjugation:** An electronic interaction that results from overlap of a vacant  $p$  orbital on one atom with a neighboring  $\text{C}-\text{H}$   $\sigma$  bond. Hyperconjugation is important in stabilizing carbocations and substituted alkenes.
- **Imide:** A compound with the  $-\text{CONHCO}-$  functional group.
- **Imines:** A class of compounds with the  $\text{R}_2\text{C}=\text{N}-$  functional group.
- **Inductive effect:** The electron-attracting or electron-withdrawing effect transmitted through  $\sigma$  bonds. Electronegative elements have an electron-withdrawing inductive effect.
- **Infrared (IR) spectroscopy:** A kind of optical spectroscopy that uses infrared energy. IR spectroscopy is particularly useful in organic chemistry for determining the kinds of functional groups present in molecules.
- **Initiator:** A substance that is used to initiate a radical chain reaction or polymerization. For example, radical chlorination of alkanes is initiated when light energy breaks the weak  $\text{Cl}-\text{Cl}$  bond to form  $\text{Cl}^\cdot$  radicals.
- **Integrating:** A technique for measuring the area under an NMR peak to determine the relative number of each kind of proton in a molecule.
- **Intermediate:** A species that is formed during the course of a multistep reaction but is not the final product. Intermediates are more stable than transition states but may or may not be stable enough to isolate.
- **Intramolecular, intermolecular:** A reaction that occurs within the same molecule is intramolecular; a reaction that occurs between two molecules is intermolecular.
- **Intron:** A section of DNA that does not contain genetic information.

- **Ion pairs:** A loose association between two ions in solution. Ion pairs are implicated as intermediates in  $S_N1$  reactions to account for the partial retention of stereochemistry that is often observed.
- **Ionic bond:** The electrostatic attraction between ions of unlike charge.
- **Isoelectric point (pI):** The pH at which the number of positive charges and the number of negative charges on a protein or an amino acid are equal.
- **Isomers:** Compounds that have the same molecular formula but different structures.
- **Isoprene rule:** An observation to the effect that terpenoids appear to be made up of isoprene (2-methyl-1,3-butadiene) units connected head-to-tail.
- **Isotactic:** A chain-growth polymer in which the stereochemistry of the substituents is oriented regularly along the backbone.
- **Isotopes:** Atoms of the same element that have different mass numbers.
- **IUPAC system of nomenclature:** Rules for naming compounds, devised by the International Union of Pure and Applied Chemistry.
- **Kekulé structure:** An alternative name for a line-bond structure, which represents a molecule by showing covalent bonds as lines between atoms.
- **Ketals:** An alternative name for acetals derived from a ketone rather than an aldehyde and consisting of two  $-OR$  groups bonded to the same carbon,  $R_2C(OR')_2$ . Ketals are often used as protecting groups for ketones.
- **Keto-enol tautomerism:** The equilibration between a carbonyl form and vinylic alcohol form of a molecule.
- **Ketones ( $R_2CO$ ):** A class of compounds with two organic substituents bonded to a carbonyl group,  $R_2C=$ .
- **Ketoses:** Carbohydrates with a ketone functional group.
- **Kiliani-Fischer synthesis:** A method for lengthening the chain of an aldose sugar.
- **Kinetic control:** A reaction that follows the lowest activation energy pathway is said to be kinetically controlled. The product is the most rapidly formed but is not necessarily the most stable.
- **Kinetics:** Referring to reaction rates. Kinetic measurements are useful for helping to determine reaction mechanisms.
- **Koenigs-Knorr reaction:** A method for the synthesis of glycosides by reaction of an alcohol with a pyranosyl bromide.
- **Krebs cycle:** An alternative name for the citric acid cycle, by which acetyl CoA is degraded to  $CO_2$ .
- **L Sugar:** A sugar whose hydroxyl group at the chirality center farthest from the carbonyl group points to the left when drawn in Fischer projection.
- **Lactams:** Cyclic amides.
- **Lactones:** Cyclic esters.
- **Lagging strand:** The complement of the original  $3' \rightarrow 5'$  DNA strand that is synthesized discontinuously in small pieces that are subsequently linked by DNA ligases.
- **LD50:** The amount of a substance per kilogram body weight that is lethal to 50% of test animals.
- **LDA:** Lithium diisopropylamide,  $LiN(i-C_3H_7)_2$ , a strong base commonly used to convert carbonyl compounds into their enolate ions.
- **Leading strand:** The complement of the original  $5' \rightarrow 3'$  DNA strand that is synthesized continuously in a single piece.
- **Leaving group:** The group that is replaced in a substitution reaction.
- **Levorotatory:** An optically active substance that rotates the plane of polarization of plane-polarized light in a left-handed (counterclockwise) direction.
- **Lewis acid:** A substance with a vacant low-energy orbital that can accept an electron pair from a base. All electrophiles are Lewis acids.
- **Lewis base:** A substance that donates an electron lone pair to an acid. All nucleophiles are Lewis bases.
- **Lewis structures:** Representations of molecules showing valence electrons as dots.
- **Lindlar catalyst:** A hydrogenation catalyst used to convert alkynes to cis alkenes.
- **Line-bond structure:** An alternative name for a Kekulé structure, which represents a molecule by showing covalent bonds as lines between atoms.
- **Lipids:** Naturally occurring substances isolated from cells and tissues by extraction with a nonpolar solvent. Lipids belong to many different structural classes, including fats, terpenoids, prostaglandins, and steroids.
- **Lipid bilayer:** The ordered lipid structure that forms a cell membrane.
- **Lipoprotein:** A complex molecule with both lipid and protein parts that transports lipids through the body.
- **Locant:** A number in a chemical name that locates the positions of the functional groups and substituents in the molecule.
- **Lone-pair electrons:** Nonbonding valence-shell electron pairs. Lone-pair electrons are used by nucleophiles in their reactions with electrophiles.

- **Lowest unoccupied molecular orbital (LUMO):** The symmetries of the LUMO and the HOMO are important in determining the stereochemistry of pericyclic reactions.
- **Magnetic resonance imaging, MRI:** A medical diagnostic technique based on nuclear magnetic resonance.
- **Magnetogyric ratio:** A ratio of the isotope's magnetic moment to its angular momentum.
- **MALDI:** Matrix-assisted laser desorption ionization; a soft ionization method used for mass spectrometry of biological samples of very high molecular weight.
- **Malonic ester synthesis:** The synthesis of a carboxylic acid by alkylation of an alkyl halide with diethyl malonate, followed by hydrolysis and decarboxylation.
- **Markovnikov's rule:** A guide for determining the regiochemistry (orientation) of electrophilic addition reactions. In the addition of HX to an alkene, the hydrogen atom bonds to the alkene carbon that has fewer alkyl substituents.
- **Mass number (A):** The total of protons plus neutrons in an atom.
- **Mass spectrometry (MS):** A technique for measuring the mass, and therefore the molecular weight (MW), of ions.
- **McLafferty rearrangement:** A mass-spectral fragmentation pathway for carbonyl compounds.
- **Mechanism:** A complete description of how a reaction occurs. A mechanism accounts for all starting materials and all products and describes the details of each individual step in the overall reaction process.
- **Meisenheimer complex:** An intermediate formed by addition of a nucleophile to a halo-substituted aromatic ring.
- **Melt transition temperature,  $T_m$ :** The temperature at which crystalline regions of a polymer melt to give an amorphous material.
- **Mercapto group:** An alternative name for the thiol group,  $-SH$ .
- **Meso compounds:** Compounds that contain chirality centers but are nevertheless achiral because they contain a symmetry plane.
- **Messenger RNA (mRNA):** A kind of RNA formed by transcription of DNA and used to carry genetic messages from DNA to ribosomes.
- **Meta (m):** A naming prefix used for 1,3-disubstituted benzenes.
- **Metabolism:** A collective name for the many reactions that go on in the cells of living organisms.
- **Metallacycle:** A cyclic compound that contains a metal atom in its ring.
- **Methylene group:** A  $-CH_2-$  or  $=CH_2$  group.
- **Micelles:** Spherical clusters of soaplike molecules that aggregate in aqueous solution. The ionic heads of the molecules lie on the outside, where they are solvated by water, and the organic tails bunch together on the inside of the micelle.
- **Michael reaction:** The conjugate addition reaction of an enolate ion to an unsaturated carbonyl compound.
- **Molar absorptivity ( $\epsilon$ ):** A quantitative measure of the amount of UV light absorbed by a sample.
- **Molecular ion:** The cation produced in a mass spectrometer by loss of an electron from the parent molecule. The mass of the molecular ion corresponds to the molecular weight of the sample.
- **Molecular mechanics:** A computer-based method for calculating the minimum-energy conformation of a molecule.
- **Molecular orbital (MO) theory:** A description of covalent bond formation as resulting from a mathematical combination of atomic orbitals (wave functions) to form molecular orbitals.
- **Molecule:** A neutral collection of atoms held together by covalent bonds.
- **Molozonide:** The initial addition product of ozone with an alkene.
- **Monomers:** The simple starting units from which polymers are made.
- **Monosaccharides:** Simple sugars.
- **Monoterpenoids:** Ten-carbon lipids.
- **Multiplet:** A pattern of peaks in an NMR spectrum that arises by spin-spin splitting of a single absorption because of coupling between neighboring magnetic nuclei.
- **Mutarotation:** The change in optical rotation observed when a pure anomer of a sugar is dissolved in water. Mutarotation is caused by the reversible opening and closing of the acetal linkage, which yields an equilibrium mixture of anomers.
- **$n + 1$  rule:** A hydrogen with  $n$  other hydrogens on neighboring carbons shows  $n + 1$  peaks in its  $^1H$  NMR spectrum.
- **N-terminal amino acid:** The amino acid with a free  $-NH_2$  group at the end of a protein chain.
- **Natural gas:** A naturally occurring hydrocarbon mixture consisting chiefly of methane, along with smaller amounts of ethane, propane, and butane.
- **Natural product:** A catchall term generally taken to mean a secondary metabolite found in bacteria, plants, and other living organisms.

- **New molecular entity, NME:** A new biologically active chemical substance approved for sale as a drug by the U.S. Food and Drug Administration.
- **Newman projection:** A means of indicating stereochemical relationships between substituent groups on neighboring carbons. The carbon–carbon bond is viewed end-on, and the carbons are indicated by a circle. Bonds radiating from the center of the circle are attached to the front carbon, and bonds radiating from the edge of the circle are attached to the rear carbon.
- **Nitration:** The substitution of a nitro group onto an aromatic ring.
- **Nitriles:** A class of compounds containing the  $\text{C}\equiv\text{N}$  functional group.
- **Nitrogen rule:** A compound with an odd number of nitrogen atoms has an odd-numbered molecular weight.
- **Node:** A surface of zero electron density within an orbital. For example, a  $p$  orbital has a nodal plane passing through the center of the nucleus, perpendicular to the axis of the orbital.
- **Nonbonding electrons:** Valence electrons that are not used in forming covalent bonds.
- **Noncoding strand:** An alternative name for the antisense strand of DNA.
- **Noncovalent interactions:** One of a variety of nonbonding interactions between molecules, such as dipole–dipole forces, dispersion forces, and hydrogen bonds.
- **Nonessential amino acid:** One of the eleven amino acids that are biosynthesized by humans.
- **Normal alkanes:** Straight-chain alkanes, as opposed to branched alkanes. Normal alkanes are denoted by the suffix  $n$ , as in  $n\text{-C}_4\text{H}_{10}$  ( $n$ -butane).
- **NSAID:** A nonsteroidal anti-inflammatory drug, such as aspirin or ibuprofen.
- **Nuclear magnetic resonance (NMR) spectroscopy:** A spectroscopic technique that provides information about the carbon–hydrogen framework of a molecule. NMR works by detecting the energy absorptions accompanying the transitions between nuclear spin states that occur when a molecule is placed in a strong magnetic field and irradiated with radiofrequency waves.
- **Nucleic acid:** Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA); biological polymers made of nucleotides joined together to form long chains.
- **Nucleophile:** An electron-rich species that donates an electron pair to an electrophile in a polar bond-forming reaction. Nucleophiles are also Lewis bases.
- **Nucleophilic acyl substitution reaction:** A reaction in which a nucleophile attacks a carbonyl compound and substitutes for a leaving group bonded to the carbonyl carbon.
- **Nucleophilic addition reaction:** A reaction in which a nucleophile adds to the electrophilic carbonyl group of a ketone or aldehyde to give an alcohol.
- **Nucleophilic aromatic substitution reactions:** The substitution reactions of an aryl halide by a nucleophile.
- **Nucleophilic substitution reactions:** Reactions in which one nucleophile replaces another attached to a saturated carbon atom.
- **Nucleophilicity:** The ability of a substance to act as a nucleophile in an  $\text{S}_{\text{N}}2$  reaction.
- **Nucleoside:** A nucleic acid constituent consisting of a sugar residue bonded to a heterocyclic purine or pyrimidine base.
- **Nucleotides:** Nucleic acid constituents consisting of a sugar residue bonded both to a heterocyclic purine or pyrimidine base and to a phosphoric acid. Nucleotides are the monomer units from which DNA and RNA are constructed.
- **Nylons:** Synthetic polyamide step-growth polymers.
- **Okazaki fragments:** Short segments of a DNA lagging strand that is biosynthesized discontinuously and then linked by DNA ligases.
- **Olefin:** An alternative name for an alkene.
- **Olefin metathesis polymerization:** A method of polymer synthesis based on using an olefin metathesis reaction.
- **Olefin metathesis reaction:** A reaction in which two olefins (alkenes) exchange substituents on their double bonds.
- **Oligonucleotides:** Short segments of DNA.
- **Optical isomers:** An alternative name for enantiomers. Optical isomers are isomers that have a mirror-image relationship.
- **Optically active:** A property of some organic molecules wherein the plane of polarization is rotated through an angle when a beam of plane-polarized light is passed through a solution of the molecules.
- **Orbital:** A wave function, which describes the volume of space around a nucleus in which an electron is most likely to be found.
- **Organic chemistry:** The study of carbon compounds.
- **Organohalides:** Compounds that contain one or more halogen atoms bonded to carbon.
- **Organometallic compound:** A compound that contains a carbon–metal bond. Grignard reagents,  $\text{RMgX}$ , are examples.
- **Organophosphate:** A compound that contains a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to carbon.



- **Ortho (o):** A naming prefix used for 1,2-disubstituted benzenes.
- **Oxidation:** A reaction that causes a decrease in electron ownership by carbon, either by bond formation between carbon and a more electronegative atom (usually oxygen, nitrogen, or a halogen) or by bond-breaking between carbon and a less electronegative atom (usually hydrogen).
- **Oximes:** Compounds with the  $R_2C=$  functional group.
- **Oxirane:** An alternative name for an epoxide.
- **Oxymercuration:** A method for double-bond hydration by reaction of an alkene with aqueous mercuric acetate followed by treatment with  $NaBH_4$ .
- **Ozonide:** The product initially formed by addition of ozone to a carbon-carbon double bond. Ozonides are usually treated with a reducing agent, such as zinc in acetic acid, to produce carbonyl compounds.
- **Para (p):** A naming prefix used for 1,4-disubstituted benzenes.
- **Paraffins:** A common name for alkanes.
- **Parent peak:** The peak in a mass spectrum corresponding to the molecular ion. The mass of the parent peak therefore represents the molecular weight of the compound.
- **Pauli exclusion principle:** No more than two electrons can occupy the same orbital, and those two must have spins of opposite sign.
- **Peptide bond:** An amide bond in a peptide chain.
- **Peptides:** A type of short amino acid polymer in which the individual amino acid residues are linked by amide bonds.
- **Pericyclic reaction:** A reaction that occurs in a single step by a reorganization of bonding electrons in a cyclic transition state.
- **Periplanar:** A conformation in which bonds to neighboring atoms have a parallel arrangement. In an eclipsed conformation, the neighboring bonds are syn periplanar; in a staggered conformation, the bonds are anti periplanar.
- **Peroxides:** Molecules containing an oxygen-oxygen bond functional group,  $ROOR'$  or  $ROOH$ .
- **Peroxyacid:** A compound with the  $-CO_3H$  functional group. Peroxyacids react with alkenes to give epoxides.
- **Phenols:** A class of compounds with an  $-OH$  group directly bonded to an aromatic ring,  $ArOH$ .
- **Phenoxide ion,  $ArO^-$ :** The anion of a phenol.
- **Phenyl:** The name for the  $-C_6H_5$  unit when the benzene ring is considered as a substituent. A phenyl group is abbreviated as  $-Ph$ .
- **Phosphine:** A trivalent phosphorus compound,  $R_3P$ .
- **Phosphite:** A compound with the structure  $P(OR)_3$ .
- **Phospholipids:** Lipids that contain a phosphate residue. For example, glycerophospholipids contain a glycerol backbone linked to two fatty acids and a phosphoric acid.
- **Phosphoramidite:** A compound with the structure  $R_2NP(OR)_2$ .
- **Phosphoric acid anhydride:** A substance that contains  $PO_2PO$  link, analogous to the  $CO_2CO$  link in carboxylic acid anhydrides.
- **Photochemical reactions:** A reaction carried out by irradiating the reactants with light.
- **Physiological pH:** The pH of 7.3 that exists inside cells.
- **Pi ( $\pi$ ) bond:** The covalent bond formed by sideways overlap of atomic orbitals. For example, carbon-carbon double bonds contain a  $\pi$  bond formed by sideways overlap of two  $p$  orbitals.
- **PITC:** Phenylisothiocyanate; used in the Edman degradation.
- **$pK_a$ :** The negative common logarithm of the  $K_a$ ; used to express acid strength.
- **Plane of symmetry:** A plane that bisects a molecule such that one half of the molecule is the mirror image of the other half. Molecules containing a plane of symmetry are achiral.
- **Plane-polarized light:** Light that has its electromagnetic waves oscillating in a single plane rather than in random planes. The plane of polarization is rotated when the light is passed through a solution of a chiral substance.
- **Plasticizers:** Small organic molecules added to polymers to act as a lubricant between polymer chains.
- **Polar aprotic solvents:** Polar solvents that can't function as hydrogen ion donors. Polar aprotic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) are particularly useful in  $S_N2$  reactions because of their ability to solvate cations.
- **Polar covalent bond:** A covalent bond in which the electron distribution between atoms is unsymmetrical.
- **Polar reactions:** Reactions in which bonds are made when a nucleophile donates two electrons to an electrophile and in which bonds are broken when one fragment leaves with both electrons from the bond.

- **Polarity:** The unsymmetrical distribution of electrons in a molecule that results when one atom attracts electrons more strongly than another.
- **Polarizability:** The measure of the change in a molecule's electron distribution in response to changing electrostatic interactions with solvents or ionic reagents.
- **Polycarbonates:** Polyesters in which the carbonyl groups are linked to two  $-OR$  groups,  $[O=C(OR)_2]$ .
- **Polycyclic:** Containing more than one ring.
- **Polycyclic aromatic compound:** A compound with two or more benzene-like aromatic rings fused together.
- **Polymer:** A large molecule made up of repeating smaller units. For example, polyethylene is a synthetic polymer made from repeating ethylene units, and DNA is a biopolymer made of repeating deoxyribonucleotide units.
- **Polymerase chain reaction (PCR):** A method for amplifying small amounts of DNA to produce larger amounts.
- **Polysaccharides:** A type of carbohydrate that is made of many simple sugars linked together by glycoside (acetal) bonds.
- **Polyunsaturated fatty acids:** Fatty acids that contain more than one double bond.
- **Polyurethane:** A step-growth polymer prepared by reaction between a diol and a diisocyanate.
- **Posttranslational modification:** A chemical modification of a protein that occurs after translation from DNA.
- **Primary, secondary, tertiary, and quaternary:** Terms used to describe the substitution pattern at a specific site. A primary site has one organic substituent attached to it, a secondary site has two organic substituents, a tertiary site has three, and a quaternary site has four.

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

- **Primary structure:** The amino acid sequence in a protein.
- **pro-R:** One of two identical atoms or groups of atoms in a compound whose replacement leads to an *R* chirality center.
- **pro-S:** One of two identical atoms or groups of atoms in a compound whose replacement leads to an *S* chirality center.
- **Prochiral:** A molecule that can be converted from achiral to chiral in a single chemical step.
- **Prochirality center:** An atom in a compound that can be converted into a chirality center by changing one of its attached substituents.
- **Promoter sequence:** A short sequence on DNA located upstream of the transcription start site and recognized by RNA polymerase.
- **Propagation step:** A step in a radical chain reaction that carries on the chain. The propagation steps must yield both product and a reactive intermediate.
- **Prostaglandins:** Lipids derived from arachidonic acid. Prostaglandins are present in nearly all body tissues and fluids, where they serve many important hormonal functions.
- **Protecting group:** A group that is introduced to protect a sensitive functional group toward reaction elsewhere in the molecule. After serving its protective function, the group is removed.
- **Proteins:** Large peptides containing 50 or more amino acid residues. Proteins serve both as structural materials and as enzymes that control an organism's chemistry.
- **Protein Data Bank:** A worldwide online repository of X-ray and NMR structural data for biological macromolecules. To access the Protein Data Bank, go to <https://www.rcsb.org>.
- **Protic solvents:** Solvents such as water or alcohol that can act as a proton donor.
- **Pyramidal inversion:** The rapid stereochemical inversion of a trivalent nitrogen compound.
- **Pyranose:** The six-membered, cyclic hemiacetal form of a simple sugar.
- **Quadrupole mass analyzer:** A type of mass spectrometer that uses four cylindrical rods to create an oscillating electrostatic field. Ion trajectories are determined by their  $m/z$  ratios. At a given field, only one  $m/z$  value will make it through the quadrupole region—the others will crash into the quadrupole rods or the walls of the instrument and never reach the detector.
- **Quartet:** A set of four peaks in an NMR spectrum, caused by spin-spin splitting of a signal by three adjacent nuclear spins.
- **Quaternary:** See **Primary**.

- **Quaternary ammonium salt:** An ionic compound containing a positively charged nitrogen atom with four attached groups,  $R_4N^+ X^-$ .
- **Quaternary structure:** The highest level of protein structure, involving an ordered aggregation of individual proteins into a larger cluster.
- **Quinone:** A 2,5-cyclohexadiene-1,4-dione.
- **R configuration:** The configuration at a chirality center as specified using the Cahn–Ingold–Prelog sequence rules.
- **R:** A generalized abbreviation for an organic partial structure.
- **Racemate:** A mixture consisting of equal parts (+) and (–) enantiomers of a chiral substance; also called a racemic mixture.
- **Radical:** A species that has an odd number of electrons, such as the chlorine radical,  $Cl\cdot$ .
- **Radical reactions:** Reactions in which bonds are made by donation of one electron from each of two reactants and in which bonds are broken when each fragment leaves with one electron.
- **Rate constant:** The constant  $k$  in a rate equation.
- **Rate equation:** An equation that expresses the dependence of a reaction's rate on the concentration of reactants.
- **Rate-limiting step:** The slowest step in a multistep reaction sequence; also called the rate-determining step. The rate-limiting step acts as a kind of bottleneck in multistep reactions.
- **Re face:** One of two faces of a planar,  $sp^2$ -hybridized atom.
- **Rearrangement reactions:** What occurs when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product.
- **Reducing sugars:** Sugars that reduce silver ion in the Tollens test or cupric ion in the Fehling or Benedict tests.
- **Reduction:** A reaction that causes an increase of electron ownership by carbon, either by bond-breaking between carbon and a more electronegative atom or by bond formation between carbon and a less electronegative atom.
- **Reductive amination:** A method for preparing an amine by reaction of an aldehyde or ketone with ammonia and a reducing agent.
- **Refining:** The process by which petroleum is converted into gasoline and other useful products.
- **Regiochemistry:** A term describing the orientation of a reaction that occurs on an unsymmetrical substrate.
- **Regiospecific:** A term describing a reaction that occurs with a specific regiochemistry to give a single product rather than a mixture of products.
- **Replication:** The process by which double-stranded DNA uncoils and is replicated to produce two new copies.
- **Replication forks:** The point of unraveling in a DNA chain where replication occurs.
- **Residues:** Amino acids in a protein chain.
- **Resolution:** The process by which a racemate is separated into its two pure enantiomers.
- **Resonance effect:** The donation or withdrawal of electrons through orbital overlap with neighboring  $\pi$  bonds. For example, an oxygen or nitrogen substituent donates electrons to an aromatic ring by overlap of the O or N orbital with the aromatic ring  $p$  orbitals.
- **Resonance forms:** Individual structural forms of a resonance hybrid.
- **Resonance hybrid:** A molecule, such as benzene, that can't be represented adequately by a single Kekulé structure but must instead be considered as an average of two or more resonance forms. The resonance forms themselves differ only in the positions of their electrons, not their nuclei.
- **Restriction endonucleases:** Enzymes that are able to cleave a DNA molecule at points in the chain where a specific base sequence occurs.
- **Retrosynthetic:** Planning an organic synthesis by working backward from the final product to the starting material.
- **Ribonucleic acid (RNA):** The biopolymer found in cells that serves to transcribe the genetic information found in DNA and uses that information to direct the synthesis of proteins.
- **Ribosomal RNA (rRNA):** A kind of RNA used in the physical makeup of ribosomes.
- **Ring-current:** The circulation of  $\pi$  electrons induced in aromatic rings by an external magnetic field. This effect accounts for the downfield shift of aromatic ring protons in the  $^1H$  NMR spectrum.
- **Ring-flip:** A molecular motion that interconverts two chair conformations of cyclohexane. The effect of a ring-flip is to convert an axial substituent into an equatorial substituent.
- **Ring-opening metathesis polymerization (ROMP):** A method of polymer synthesis that uses an olefin metathesis reaction of a cycloalkene.
- **RNA:** Ribonucleic acid.

- **Robinson annulation reaction:** A method for synthesis of cyclohexenones by sequential Michael reaction and intramolecular aldol reaction.
- **S configuration:** The configuration at a chirality center as specified using the Cahn–Ingold–Prelog sequence rules.
- **s-Cis conformation:** The conformation of a conjugated diene that is cis-like around the single bond.
- **Saccharide:** A sugar.
- **Salt bridge:** An ionic attraction between two oppositely charged groups in a protein chain.
- **Sandmeyer reaction:** The nucleophilic substitution reaction of an arenediazonium salt with a cuprous halide to yield an aryl halide.
- **Sanger dideoxy method:** A commonly used method of DNA sequencing.
- **Saponification:** An old term for the base-induced hydrolysis of an ester to yield a carboxylic acid salt.
- **Saturated:** A molecule that has only single bonds and thus can't undergo addition reactions. Alkanes are saturated, but alkenes are unsaturated.
- **Sawhorse representations:** A manner of representing stereochemistry that uses a stick drawing and gives a perspective view of the conformation around a single bond.
- **Schiff bases:** An alternative name for an imine,  $R_2C=NR'$ , used primarily in biochemistry.
- **Second-order reaction:** A reaction whose rate-limiting step is bimolecular and whose kinetics are therefore dependent on the concentration of two reactants.
- **Secondary:** See **Primary**.
- **Secondary metabolite:** A small naturally occurring molecule that is not essential to the growth and development of the producing organism and is not classified by structure.
- **Secondary structure:** The level of protein substructure that involves organization of chain sections into ordered arrangements such as  $\beta$ -pleated sheets or  $\alpha$  helices.
- **Semiconservative replication:** The process by which DNA molecules are made containing one strand of old DNA and one strand of new DNA.
- **Sense strand:** The coding strand of double-helical DNA that contains the gene.
- **Sequence rules:** A series of rules for assigning relative rankings to substituent groups on a double-bond carbon atom or on a chirality center.
- **Sesquiterpenoids:** 15-carbon lipids.
- **Sharpless epoxidation:** A method for enantioselective synthesis of a chiral epoxide by treatment of an allylic alcohol with *tert*-butyl hydroperoxide,  $(CH_3)_3C-OOH$ , in the presence of titanium tetrakisopropoxide and diethyl tartrate.
- **Shielding:** An effect observed in NMR that causes a nucleus to absorb toward the right (upfield) side of the chart. Shielding is caused by donation of electron density to the nucleus.
- **Si face:** One of two faces of a planar,  $sp^2$ -hybridized atom.
- **Sialic acid:** One of a group of more than 300 carbohydrates based on acetylneuramic acid.
- **Side chain:** The substituent attached to the  $\alpha$  carbon of an amino acid.
- **Sigma ( $\sigma$ ) bond:** A covalent bond formed by head-on overlap of atomic orbitals.
- **Sigmatropic reaction:** A pericyclic reaction that involves the migration of a group from one end of a  $\pi$  electron system to the other.
- **Silyl ether:** A substance with the structure  $R_3Si-O-R$ . The silyl ether acts as a protecting group for alcohols.
- **Simmons–Smith reaction:** The reaction of an alkene with  $CH_2I_2$  and  $Zn-Cu$  to yield a cyclopropane.
- **Simple sugars:** Carbohydrates that cannot be broken down into smaller sugars by hydrolysis.
- **Single bond:** A covalent bond formed by sharing one electron pair between atoms.
- **Skeletal structures:** A shorthand way of writing structures in which carbon atoms are assumed to be at each intersection of two lines (bonds) and at the end of each line.
- **Small RNAs:** A type of RNA that has a variety of functions within the cell, including silencing transcription and catalyzing chemical modifications of other RNA molecules.
- **$S_N1$  reaction:** A unimolecular nucleophilic substitution reaction.
- **$S_N2$  reaction:** A bimolecular nucleophilic substitution reaction.
- **Solid-phase synthesis:** A technique of synthesis whereby the starting material is covalently bound to a solid polymer bead and reactions are carried out on the bound substrate. After the desired transformations have been effected, the product is cleaved from the polymer.
- **Solvation:** The clustering of solvent molecules around a solute particle to stabilize it.

- **$sp$  hybrid orbitals:** Hybrid orbitals derived from the combination of an  $s$  and a  $p$  atomic orbital. The two  $sp$  orbitals that result from hybridization are oriented at an angle of  $180^\circ$  to each other.
- **$sp^2$  hybrid orbitals:** Hybrid orbitals derived by combination of an  $s$  atomic orbital with two  $p$  atomic orbitals. The three  $sp^2$  hybrid orbitals that result lie in a plane at angles of  $120^\circ$  to each other.
- **$sp^3$  hybrid orbitals:** Hybrid orbitals derived by combination of an  $s$  atomic orbital with three  $p$  atomic orbitals. The four  $sp^3$  hybrid orbitals that result are directed toward the corners of a regular tetrahedron at angles of  $109^\circ$  to each other.
- **Specific rotation,  $[\alpha]_D$ :** The optical rotation of a chiral compound under standard conditions.
- **Sphingomyelins:** Phospholipids that have sphingosine as the backbone rather than glycerol.
- **Spin–spin splitting:** The splitting of an NMR signal into a multiplet because of an interaction between nearby magnetic nuclei whose spins are coupled. The magnitude of spin–spin splitting is given by the coupling constant,  $J$ .
- **Staggered conformation:** The three-dimensional arrangement of atoms around a carbon–carbon single bond in which the bonds on one carbon bisect the bond angles on the second carbon as viewed end-on.
- **Statin:** A drug that controls cholesterol biosynthesis in the body by blocking the HMG-CoA reductase enzyme.
- **Step-growth polymers:** Polymers in which each bond is formed independently of the others. Polyesters and polyamides (nylons) are examples.
- **Stereocenter:** An alternative name for a chirality center.
- **Stereochemistry:** The branch of chemistry concerned with the three-dimensional arrangement of atoms in molecules.
- **Stereogenic center:** An alternative name for a chirality center.
- **Stereoisomers:** Isomers that have their atoms connected in the same order but have different three-dimensional arrangements. The term *stereoisomer* includes both enantiomers and diastereomers.
- **Stereospecific:** A term indicating that only a single stereoisomer is produced in a given reaction rather than a mixture.
- **Steric strain:** The strain imposed on a molecule when two groups are too close together and try to occupy the same space. Steric strain is responsible both for the greater stability of trans versus cis alkenes and for the greater stability of equatorially substituted versus axially substituted cyclohexanes.
- **Steroids:** Lipids whose structure is based on a tetracyclic carbon skeleton with three 6-membered and one 5-membered ring. Steroids occur in both plants and animals and have a variety of important hormonal functions.
- **Stork enamine reaction:** The conjugate addition of an enamine to an  $\alpha,\beta$ -unsaturated carbonyl compound, followed by hydrolysis to yield a 1,5-dicarbonyl product.
- **STR loci:** Short tandem repeat sequences of noncoding DNA that are unique to every individual and allow DNA fingerprinting.
- **Straight-chain alkanes:** Alkanes whose carbon atoms are connected without branching.
- **Substitution reactions:** What occurs when two reactants exchange parts to give two new products.  $S_N1$  and  $S_N2$  reactions are examples.
- **Sulfides:** A class of compounds that has two organic substituents bonded to the same sulfur atom,  $RSR'$ .
- **Sulfonation:** The substitution of a sulfonic acid group ( $-SO_3H$ ) onto an aromatic ring.
- **Sulfone:** A compound of the general structure  $RSO_2R'$ .
- **Sulfonium ions:** A species containing a positively charged, trivalent sulfur atom,  $R_3S^+$ .
- **Sulfoxide:** A compound of the general structure  $RSOR'$ .
- **Suprafacial:** A word used to describe the geometry of pericyclic reactions. Suprafacial reactions take place on the same side of the two ends of a  $\pi$  electron system.
- **Suzuki–Miyaura reaction:** The palladium-catalyzed coupling reaction of an aromatic or vinylic halide with an aromatic or vinylic boronic acid.
- **Symmetry-allowed, symmetry-disallowed:** A symmetry-allowed reaction is a pericyclic process that has a favorable orbital symmetry for reaction through a concerted pathway. A symmetry-disallowed reaction is one that does not have favorable orbital symmetry for reaction through a concerted pathway.
- **Symmetry plane:** A plane that bisects a molecule such that one half of the molecule is the mirror image of the other half. Molecules containing a plane of symmetry are achiral.
- **Syn periplanar:** Describing a stereochemical relationship in which two bonds on adjacent carbons lie in the same plane and are eclipsed.
- **Syn stereochemistry:** The opposite of anti. A syn addition reaction is one in which the two ends of the double bond react from the same side. A syn elimination is one in which the two groups leave from the same side of the molecule.
- **Syndiotactic:** A chain-growth polymer in which the stereochemistry of the substituents alternates regularly on opposite sides of the backbone.



- **Tautomers:** Isomers that interconvert spontaneously, usually with the change in position of a hydrogen.
- **Terpenoids:** Lipids that are formally derived by head-to-tail polymerization of isoprene units.
- **Tertiary:** See **Primary**.
- **Tertiary structure:** The level of protein structure that involves the manner in which the entire protein chain is folded into a specific three-dimensional arrangement.
- **Thermodynamic control:** An equilibrium reaction that yields the lowest-energy, most stable product is said to be thermodynamically controlled.
- **Thermoplastics:** Polymers that have a high  $T_g$  and are hard at room temperature but become soft and viscous when heated.
- **Thermosetting resins:** Polymers that become highly cross-linked and solidify into a hard, insoluble mass when heated.
- **Thioesters:** A class of compounds with the  $\text{RCOSR'}$  functional group.
- **Thiols:** A class of compounds containing the  $-\text{SH}$  functional group.
- **Thiolate ion:** The anion of a thiol,  $\text{RS}^-$ .
- **TMS:** Tetramethylsilane; used as an NMR calibration standard.
- **TOF:** Time-of-flight mass spectrometry; a sensitive method of mass detection accurate to about 3 ppm.
- **Tollens' reagent:** A solution of  $\text{Ag}_2\text{O}$  in aqueous ammonia; used to oxidize aldehydes to carboxylic acids.
- **Torsional strain:** The strain in a molecule caused by electron repulsion between eclipsed bonds. Torsional strain is also called eclipsing strain.
- **Tosylate:** A *p*-toluenesulfonate ester; useful as a leaving group in nucleophilic substitution reactions.
- **Transamination:** The exchange of an amino group and a keto group between reactants.
- **Transcription:** The process by which the genetic information encoded in DNA is read and used to synthesize RNA in the nucleus of the cell. A small portion of double-stranded DNA uncoils, and complementary ribonucleotides line up in the correct sequence for RNA synthesis.
- **Transfer RNA (tRNA):** A kind of RNA that transports amino acids to the ribosomes, where they are joined together to make proteins.
- **Transimination:** The exchange of an amino group and an imine group between reactants.
- **Transition state:** An activated complex between reactants, representing the highest energy point on a reaction curve. Transition states are unstable complexes that can't be isolated.
- **Translation:** The process by which the genetic information transcribed from DNA onto mRNA is read by tRNA and used to direct protein synthesis.
- **Tree diagram:** A diagram used in NMR to sort out the complicated splitting patterns that can arise from multiple couplings.
- **Triacylglycerols:** Lipids, such as those found in animal fat and vegetable oil, that are a triester of glycerol with long-chain fatty acids.
- **Tricarboxylic acid cycle:** An alternative name for the citric acid cycle by which acetyl CoA is degraded to  $\text{CO}_2$ .
- **Triple bonds:** A type of covalent bond formed by sharing three electron pairs between atoms.
- **Triplet:** A symmetrical three-line splitting pattern observed in the  $^1\text{H}$  NMR spectrum when a proton has two equivalent neighbor protons.
- **Turnover number:** The number of substrate molecules acted on by an enzyme molecule per unit time.
- **Twist-boat conformation:** A conformation of cyclohexane that is somewhat more stable than a pure boat conformation.
- **Ultraviolet (UV) spectroscopy:** An optical spectroscopy employing ultraviolet irradiation. UV spectroscopy provides structural information about the extent of  $\pi$  electron conjugation in organic molecules.
- **Unimolecular reaction:** A reaction that occurs by spontaneous transformation of the starting material without the intervention of other reactants. For example, the dissociation of a tertiary alkyl halide in the  $\text{S}_{\text{N}}1$  reaction is a unimolecular process.
- **Unsaturated:** A molecule that has one or more multiple bonds.
- **Upfield:** The right-hand portion of the NMR chart.
- **Urethane:** A functional group in which a carbonyl group is bonded to both an  $-\text{OR}$  and an  $-\text{NR}_2$ .
- **Uronic acid:** A monocarboxylic acid formed by oxidizing the  $-\text{CH}_2\text{OH}$  end of an aldose without affecting the  $-\text{CHO}$  end.
- **Valence bond theory:** A bonding theory that describes a covalent bond as resulting from the overlap of two atomic orbitals.
- **Valence shell:** The outermost electron shell of an atom.
- **van der Waals forces:** Intermolecular forces that are responsible for holding molecules together in the liquid and solid states.
- **Vegetable oils:** Liquid triacylglycerols derived from a plant source.
- **Vicinal:** A term used to refer to a 1,2-disubstitution pattern. For example, 1,2-dibromoethane is a vicinal dibromide.
- **Vinyl group:** A  $\text{H}_2\text{C}=\text{CH}-$  substituent.

- **Vinyl monomer:** A substituted alkene monomer used to make a chain-growth polymer.
- **Vinylic:** A term that refers to a substituent at a double-bond carbon atom. For example, chloroethylene is a vinylic chloride, and enols are vinylic alcohols.
- **Vitamin:** A small organic molecule that must be obtained in the diet and is required in trace amounts for proper growth and function.
- **Vulcanization:** A technique for cross-linking and hardening a diene polymer by heating with a few percent by weight of sulfur.
- **Walden inversion:** The inversion of configuration at a chirality center that accompanies an  $S_N2$  reaction.
- **Wave equation:** A mathematical expression that defines the behavior of an electron in an atom.
- **Wave function:** A solution to the wave equation for defining the behavior of an electron in an atom. The square of the wave function defines the shape of an orbital.
- **Wavelength,  $\lambda$ :** The length of a wave from peak to peak. The wavelength of electromagnetic radiation is inversely proportional to frequency and inversely proportional to energy.
- **Wavenumber,** Unexpected text node: 'Section 12.6): The reciprocal of the wavelength in centimeters.'
- **Waxes:** A mixture of esters of long-chain carboxylic acids with long-chain alcohols.
- **Williamson ether synthesis:** A method for synthesizing ethers by  $S_N2$  reaction of an alkyl halide with an alkoxide ion.
- **Wittig reaction:** The reaction of a phosphorus ylide with a ketone or aldehyde to yield an alkene.
- **Wohl degradation:** A method for shortening the chain of an aldose sugar by one carbon.
- **Wolff–Kishner reaction:** The conversion of an aldehyde or ketone into an alkane by reaction with hydrazine and base.
- **X-ray crystallography:** A technique that uses X rays to determine the structure of molecules.
- **Ylide:** A neutral species with adjacent + and – charges, such as the phosphoranes used in Wittig reactions.
- **Z geometry:** A term used to describe the stereochemistry of a carbon–carbon double bond. The two groups on each carbon are ranked according to the Cahn–Ingold–Prelog sequence rules, and the two carbons are compared. If the higher ranked groups on each carbon are on the same side of the double bond, the bond has Z geometry.
- **Zaitsev's rule:** A rule stating that E2 elimination reactions normally yield the more highly substituted alkene as major product.
- **Ziegler–Natta catalysts:** Catalysts of an alkylaluminum and a titanium compound used for preparing alkene polymers.
- **Zwitterion:** A neutral dipolar molecule in which the positive and negative charges are not adjacent. For example, amino acids exist as zwitterions,  $H_3C-N^+H_2-CH(R)-CO_2^-$

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