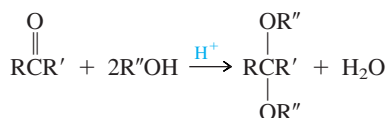


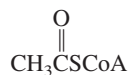
GLOSSARY

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

Acetal (Section 11.8): Product of the reaction of an aldehyde or a ketone with 2 moles of an alcohol according to the equation



Acetyl coenzyme A (Section 16.11): A thiol ester abbreviated as



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

Acetylene (Sections 1.15 and 4.12): The simplest alkyne, $\text{HC}\equiv\text{CH}$.

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

Acid (Section 3.5): 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 13.1): Compound of the type



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

Acid dissociation constant K_a (Section 3.5): Equilibrium constant for dissociation of an acid:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Activating substituent (Sections 6.9 and 6.10): 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 17.13): The region of an enzyme at which the substrate is bound.

Acylation (Section 6.6 and Chapter 13): 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 13.1): Compound of the type



R may be alkyl or aryl.

Acyl group (Sections 6.8 and 13.1): The group



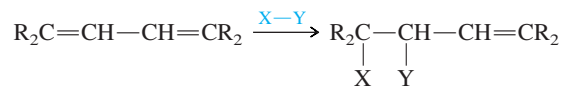
R may be alkyl or aryl.

Acylium ion (Section 6.8): The cation $\text{R}-\text{C}\equiv\text{O}^+$.

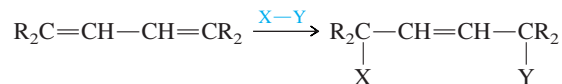
Acyl transfer (Section 13.3): A nucleophilic acyl substitution. A reaction in which one type of carboxylic acid derivative is converted to another.

Addition (Section 5.1): 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 5.8): Addition of reagents of the type X–Y to conjugated dienes in which X and Y add to adjacent doubly bonded carbons:



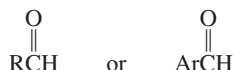
1,4 Addition (Section 5.8): Addition of reagents of the type X–Y to conjugated dienes in which X and Y add to the termini of the diene system:



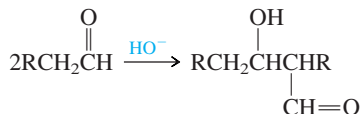
Alcohol (Section 3.1): Compound of the type ROH.

Alcohol dehydrogenase (Section 10.5): Enzyme in the liver that catalyzes the oxidation of alcohols to aldehydes and ketones.

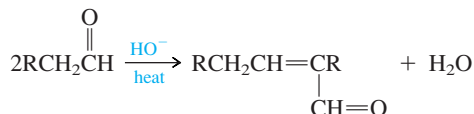
Aldehyde (Sections 2.3 and 11.1): Compound of the type



Aldol addition (Section 11.18): 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.



Aldol condensation (Section 11.18): 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.



Aldose (Section 15.1): 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 4.1): Hydrocarbon that contains two carbon-carbon double bonds; commonly referred to as a *diene*.

Alkaloid (Section 14.3): 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. Alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$.

Alkene (Section 2.1): Hydrocarbon that contains a carbon-carbon double bond ($\text{C}=\text{C}$); also known by the older name *olefin*.

Alkoxide ion (Section 10.10): Conjugate base of an alcohol; a species of the type $\text{R}-\ddot{\text{O}}:^-$.

Alkylamine (Section 14.1): Amine in which the organic groups attached to nitrogen are alkyl groups.

Alkylation (Section 5.10): Reaction in which an alkyl group is attached to some structural unit in a molecule.

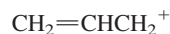
Alkyl group (Section 2.10): Structural unit related to an alkane by replacing one of the hydrogens by a potential point of attachment to some other atom or group. The general symbol for an alkyl group is $\text{R}-$.

Alkyl halide (Section 3.1): Compound of the type RX , in which X is a halogen substituent (F, Cl, Br, I).

Alkyloxonium ion (Section 3.5): Positive ion of the type ROH_2^+ .

Alkyne (Section 2.1): Hydrocarbon that contains a carbon-carbon triple bond.

Allyl cation (Section 5.8): The carbocation

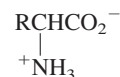


The carbocation is stabilized by delocalization of the π electrons of the double bond, and the positive charge is shared by the two CH_2 groups. Substituted analogs of allyl cation are called *allylic carbocations*.

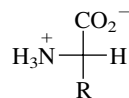
Amide (Sections 2.3 and 13.1): Compound of the type RCNR'_2

Amine (Chapter 14): Molecule in which a nitrogen-containing group of the type $-\text{NH}_2$, $-\text{NHR}$, or $-\text{NR}_2$ is attached to an alkyl or aryl group.

α -Amino acid (Section 17.1): A carboxylic acid that contains an amino group at the α -carbon atom. α -Amino acids are the building blocks of peptides and proteins. An α -amino acid normally exists as a *zwitterion*.



L-Amino acid (Section 17.2): A description of the stereochemistry at the α -carbon atom of a chiral amino acid. The Fischer projection of an α -amino acid has the amino group on the left when the carbon chain is vertical with the carboxyl group at the top.



Amino acid residues (Section 17.5): Individual amino acid components of a peptide or protein.

Amino sugar (Section 15.9): Carbohydrate in which one of the hydroxyl groups has been replaced by an amino group.

Amylopectin (Section 15.12): 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 15.12): The water-dispersible component of starch. It is a polymer of $\alpha(1,4)$ -linked glucose units.

Anabolic steroid (Section 16.9): A steroid that promotes muscle growth.

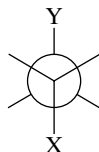
Androgen (Section 16.9): A male sex hormone.

Angle strain (Section 2.13): The strain a molecule possesses because its bond angles are distorted from their normal values.

Anion (Section 1.2): Negatively charged ion.

Anomeric carbon (Section 15.5): 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.

Anti (Section 2.6): 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 5.1): Addition reaction in which the two portions of the attacking reagent X—Y add to opposite faces of the double bond.

Anticodon (Section 18.6): Sequence of three bases in a molecule of tRNA that is complementary to the codon of mRNA for a particular amino acid.

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

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

Arenium ion (Section 6.7): The carbocation intermediate formed by attack of an electrophile on an aromatic substrate in electrophilic aromatic substitution. See *cyclohexadienyl cation*.

Aromatic compound (Section 6.1): 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.

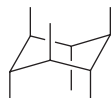
Aromaticity (Section 6.1): Special stability associated with aromatic compounds.

Arylamine (Section 14.1): An amine that has an aryl group attached to the amine nitrogen.

Asymmetric center (Section 7.2): Obsolete name for a *stereogenic center*.

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 2.14): 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 14.11): Formation of a compound of the type $\text{ArN}=\text{NAr}'$ 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 $-\text{OH}$ or $-\text{NR}_2$.

Ball-and-stick model (Section 1.10): Type of molecular model in which balls representing atoms are connected by sticks representing bonds.

Base (Section 3.5): 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 18.5): 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 19.13): 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.

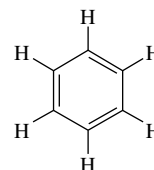
Basicity constant K_b (Section 14.4): A measure of base strength, especially of amines.

$$K_b = \frac{[\text{R}_3\text{NH}^+][\text{HO}^-]}{[\text{R}_3\text{N}]}$$

Bending vibration (Section 19.10): 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 15.13): A solution containing the citrate complex of CuSO_4 . It is used to test for the presence of reducing sugars.

Benzene (Section 6.1): The most typical aromatic hydrocarbon:

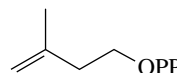


Benzylic carbon (Section 6.5): A carbon directly attached to a benzene ring. A hydrogen attached to a benzylic carbon is a benzylic hydrogen. A carbocation in which the benzylic carbon is positively charged is a benzylic carbocation. A free radical in which the benzylic carbon bears the unpaired electron is a benzylic radical.

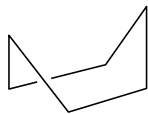
Bile acids (Section 16.7): Steroid derivatives biosynthesized in the liver that aid digestion by emulsifying fats.

Bimolecular (Section 3.6): A process in which two particles react in the same elementary step.

Biological isoprene unit (Section 16.13): Isopentenyl pyrophosphate, the biological precursor to terpenes and steroids:



Boat conformation (Section 2.14): An unstable conformation of cyclohexane, depicted as

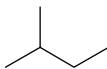


π bond (Section 1.14): In alkenes, a bond formed by overlap of p orbitals in a side-by-side manner. A π bond is weaker than a σ bond. The carbon-carbon double bond in alkenes consists of two sp^2 -hybridized carbons joined by a σ bond and a π bond.

σ bond (Section 1.12): 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 9.2): 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 9.1 gives bond dissociation energies for some representative compounds.

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 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.

Branched-chain carbohydrate (Section 15.9): Carbohydrate in which the main carbon chain bears a carbon substituent in place of a hydrogen or hydroxyl group.

Bromohydrin (Section 5.6): A halohydrin in which the halogen is bromine (see *halohydrin*).

Bromonium ion (Section 5.6): A halonium ion in which the halogen is bromine (see *halonium ion*).

Brønsted acid: See *acid*.

Brønsted base: See *base*.

***n*-Butane** (Section 2.6): Common name for butane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.

***n*-Butyl group** (Section 2.10): The group $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$.

***sec*-Butyl group** (Section 2.10): The group

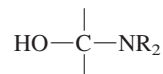


***tert*-Butyl group** (Section 2.10): The group $(\text{CH}_3)_3\text{C}-$.

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.

Carbanion (Section 5.9): Anion in which the negative charge is borne by carbon. An example is acetylide ion.

Carbinolamine (Section 11.9): Compound of the type

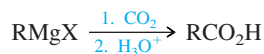


Carbinolamines are formed by nucleophilic addition of an amine to a carbonyl group and are intermediates in the formation of imines.

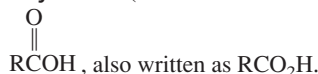
Carbocation (Section 3.8): Positive ion in which the charge resides on carbon. An example is *tert*-butyl cation, $(\text{CH}_3)_3\text{C}^+$. Carbocations are unstable species that, though they cannot normally be isolated, are believed to be intermediates in certain reactions.

Carboxylate ion (Section 12.7): The conjugate base of a carboxylic acid, an ion of the type RCO_2^- .

Carboxylation (Section 12.9): In the preparation of a carboxylic acid, the reaction of a carbanion with carbon dioxide. Typically, the carbanion source is a Grignard reagent.



Carboxylic acid (Sections 2.3 and 12.1): Compound of the type



Carboxylic acid derivative (Chapter 13): Compound that yields a carboxylic acid on hydrolysis. Carboxylic acid derivatives include acyl chlorides, anhydrides, esters, and amides.

Carotenoids (Section 16.10): Naturally occurring tetraterpenoid plant pigments.

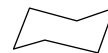
Cation (Section 1.2): Positively charged ion.

Cellobiose (Section 15.11): 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 15.12): A polysaccharide in which thousands of glucose units are joined by $\beta(1,4)$ linkages.

Chain reaction (Section 9.4): 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 2.14): The most stable conformation of cyclohexane:



Chemical shift (Section 19.3): 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 superimposable 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 5.6): A halohydrin in which the halogen is chlorine (see *halohydrin*).

Chloronium ion (Section 5.6): A halonium ion in which the halogen is chlorine (see *halonium ion*).

Cholesterol (Section 16.5): 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 19.13): 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 19.11): The structural unit of a molecule principally responsible for absorption of radiation of a particular frequency; a term usually applied to ultraviolet-visible spectroscopy.

Chymotrypsin (Section 17.8): 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- (Sections 2.17 and 4.3): Stereochemical prefix indicating that two substituents are on the same side of a ring or double bond. (Contrast with the prefix *trans-*.)

Closed-shell electron configuration (Section 1.1): 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^+), or a molecule (e.g., benzene) are filled.

^{13}C NMR (Section 19.8): Nuclear magnetic resonance spectroscopy in which the environments of individual carbon atoms are examined via their mass 13 isotope.

Codon (Section 18.6): 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 17.14): Molecule that acts in combination with an enzyme to bring about a reaction.

Coenzyme Q (Section 10.17): Naturally occurring group of related quinones involved in the chemistry of cellular respiration. Also known as ubiquinone.

Combustion (Section 2.20): 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 3.6): Reaction that occurs in a single elementary step.

Condensation polymer (Section 13.12): Polymer in which the bonds that connect the monomers are formed by condensation reactions. Typical condensation polymers include polyesters and polyamides.

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 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.

Conformational analysis (Section 2.5): 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 2.5): Nonidentical representations of a molecule generated by rotation about single bonds.

Conformers (Section 2.5): Different conformations of a single molecule.

Conjugate acid (Section 3.5): The species formed from a Brønsted base after it has accepted a proton.

Conjugate addition (Section 5.8): 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.

Conjugate base (Section 3.5): The species formed from a Brønsted acid after it has donated a proton.

Conjugated diene (Section 4.1): System of the type $\text{C}=\text{C}-\text{C}=\text{C}$, in which two pairs of doubly bonded carbons are joined by a single bond. The π electrons are delocalized over the unit of four consecutive sp^2 -hybridized carbons.

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.

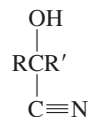
Constitutional isomers (Section 1.8): Isomers that differ in respect to the order in which the atoms are connected. Butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$) and isobutane [$(\text{CH}_3)_3\text{CH}$] are constitutional isomers.

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

C terminus (Section 17.5): 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 4.1): Diene of the type $\text{C}=\text{C}=\text{C}$, in which a single carbon atom participates in double bonds with two others.

Cyanohydrin (Section 11.7): Compound of the type

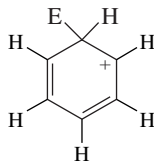


Cyanohydrins are formed by nucleophilic addition of HCN to the carbonyl group of an aldehyde or a ketone.

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

Cycloalkene (Section 4.1): A cyclic hydrocarbon characterized by a double bond between two of the ring carbons.

Cyclohexadienyl cation (Section 6.7): 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 6.9 and 6.11): 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.

Dehydration (Section 4.7): 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 4.1): Removal of the elements of H₂ 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 4.9): 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 π electron systems, where an electron may be associated with several carbon atoms.

Deoxy sugar (Section 15.9): A carbohydrate in which one of the hydroxyl groups has been replaced by a hydrogen.

Detergents (Section 12.7): Substances that clean by micellar action. Although the term usually refers to a synthetic detergent, soaps are also detergents.

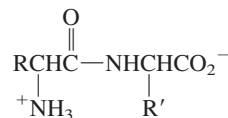
Diastereomers (Section 7.10): Stereoisomers that are not enantiomers—stereoisomers that are not mirror images of each other.

1,3-Diaxial repulsion (Section 2.16): Repulsive forces between axial substituents on the same side of a cyclohexane ring.

Diazonium ion (Section 14.9): 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, and aryl cyanides.

Dimer (Section 12.3): Molecule formed by the combination of two identical molecules.

Dipeptide (Section 17.5): A compound in which two α -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 3.4): A force of attraction between oppositely polarized atoms.

Dipole/induced-dipole attraction (Section 3.4): 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.

Disaccharide (Section 15.11): A carbohydrate that yields two monosaccharide units (which may be the same or different) on hydrolysis.

Disubstituted alkene (Section 4.5): Alkene of the type R₂C=CH₂ 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 two carbons are *directly* bonded to the carbons of the double bond.

Disulfide bridge (Section 17.5): An S—S bond between the sulfur atoms of two cysteine residues in a peptide or protein.

DNA (deoxyribonucleic acid) (Section 18.5): A polynucleotide of 2'-deoxyribose present in the nuclei of cells that serves to store and replicate genetic information. Genes are DNA.

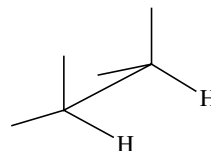
Double bond (Section 1.4): Bond formed by the sharing of four electrons between two atoms.

Double dehydrohalogenation (Section 4.14): 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 18.5) 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 19.3): 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 2.5): 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 17.9): Method for determining the N-terminal amino acid of a peptide or protein. It involves treating the material with phenyl isothiocyanate ($C_6H_5N=C=S$), cleaving with acid, and then identifying the phenylthiohydantoin (PTH derivative) produced.

Electromagnetic radiation (Section 19.1): 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.

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 4.5): 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 19.13): Method for producing positive ions in mass spectrometry whereby a molecule is bombarded by high-energy electrons.

Electrophile (Section 3.10): 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 5.2): Mechanism of addition in which the species that first attacks the multiple bond is an electrophile ("electron seeker").

Electrophilic aromatic substitution (Section 6.6): Fundamental reaction type exhibited by aromatic compounds. An electrophilic species (E^+) attacks an aromatic ring and replaces one of the hydrogens.



Electrophoresis (Section 17.3): Method for separating substances on the basis of their tendency to migrate to a positively or negatively charged electrode at a particular pH.

Elementary step (Section 3.6): 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*.

Elimination (Section 4.6): 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 bimolecular (E2) mechanism (Section 4.10): 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.

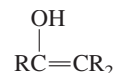
Elimination unimolecular (E1) mechanism (Section 4.11): Mechanism for elimination characterized by the slow formation of a carbocation intermediate followed by rapid loss of a proton from the carbocation to form the alkene.

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

Eneidyne antibiotics (Section 4.13): A family of tumor-inhibiting substances that is characterized by the presence of a $C\equiv C-C=C-C\equiv C$ unit as part of a nine- or ten-membered ring.

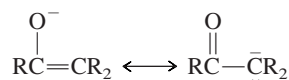
Energy of activation (Section 3.6): Minimum energy that a reacting system must possess above its most stable state in order to undergo a chemical or structural change.

Enol (Section 11.16): Compound of the type



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

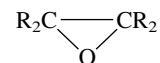
Enolate ion (Section 11.17): The conjugate base of an enol. Enolate ions are stabilized by electron delocalization.



Enzyme (Section 17.13): A protein that catalyzes a chemical reaction in a living system.

Epoxidation (Section 10.11): Conversion of an alkene to an epoxide by treatment with a peroxy acid.

Epoxide (Section 10.9): Compound of the type



Equatorial bond (Section 2.14): A bond to a carbon in the chair conformation of cyclohexane oriented approximately along the equator of the molecule.



Essential amino acids (Section 17.1): Amino acids that must be present in the diet for normal growth and good health.

Essential oils (Section 16.12): Pleasant-smelling oils of plants, consisting of mixtures of terpenes, esters, alcohols, and other volatile organic substances.

Ester (Sections 2.3 and 13.1): Compound of the type



Estrogen (Section 16.9): A female sex hormone.

Ethene (Section 4.1): IUPAC name for $CH_2=CH_2$. The common name *ethylene*, however, is used far more often, and the IUPAC rules permit its use.

Ether (Sections 2.3 and 10.8): 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 4.1): $\text{CH}_2=\text{CH}_2$, the simplest alkene and the most important industrial organic chemical.

Ethyl group (Section 2.10): The group CH_3CH_2- .

Exothermic (Section 5.1): Term describing a reaction or process that gives off heat.

Extinction coefficient: See *molar absorptivity*.

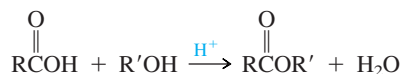
E-Z notation for alkenes (Section 4.4): System for specifying double-bond configuration that is an alternative to cis-trans notation. When higher ranked substituents are on the same side of the double bond, the configuration is *Z*. When higher ranked substituents are on opposite sides, the configuration is *E*. Rank is determined by the Cahn-Ingold-Prelog system.

Fats and oils (Section 16.2): Triesters of glycerol. Fats are solids at room temperature, oils are liquids.

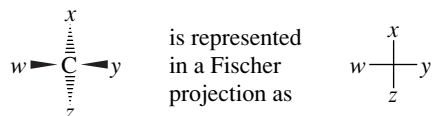
Fatty acids (Section 16.2): Carboxylic acids obtained by hydrolysis of fats and oils. Fatty acids typically have unbranched chains and contain an even number of carbon atoms in the range of 12–20 carbons. They may include one or more double bonds.

Fingerprint region (Section 19.10): The region $1400\text{--}625\text{ cm}^{-1}$ 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 (Section 13.5): Acid-catalyzed ester formation between an alcohol and a carboxylic acid:



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.



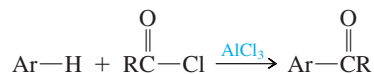
Formal charge (Section 1.6): The charge, either positive or negative, on an atom calculated by subtracting from the number of valence electrons in the neutral atom a number equal to the sum of its unshared electrons plus half the electrons in its covalent bonds.

Fragmentation pattern (Section 19.13): In mass spectrometry, the ions produced by dissociation of the molecular ion.

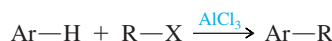
Free radical (Section 9.1): Neutral species in which one of the electrons in the valence shell of carbon is unpaired. An example is methyl radical, $\cdot\text{CH}_3$.

Frequency (Section 19.1): Number of waves per unit time. Although often expressed in hertz (Hz), or cycles per second, the SI unit for frequency is s^{-1} .

Friedel-Crafts acylation (Section 6.6): 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.



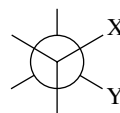
Friedel-Crafts alkylation (Section 6.6): An electrophilic aromatic substitution in which an aromatic compound reacts with an alkyl halide in the presence of aluminum chloride. An alkyl group becomes bonded to the ring.



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 15.5): Five-membered ring arising via cyclic hemiacetal formation between the carbonyl group and a hydroxyl group of a carbohydrate.

Gauche (Section 2.6): 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° . Atoms X and Y in the structure shown are gauche to each other.



Geminal dihalide (Section 4.14): A dihalide of the form R_2CX_2 , in which the two halogen substituents are located on the same carbon.

Geminal diol (Section 11.6): The hydrate $\text{R}_2\text{C(OH)}_2$ of an aldehyde or a ketone.

Genome (Section 18.4): The aggregate of all the genes that determine what an organism becomes.

Globular protein (Section 17.13): An approximately spherically shaped protein that forms a colloidal dispersion in water. Most enzymes are globular proteins.

Glycogen (Section 15.12): A polysaccharide present in animals that is derived from glucose. Similar in structure to amylopectin.

Glycoside (Section 15.10): 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 3.1): A common name for ethanol ($\text{CH}_3\text{CH}_2\text{OH}$).

Grignard reagent (Section 11.11): An organomagnesium compound of the type RMgX formed by the reaction of magnesium with an alkyl or aryl halide.

Halogenation (Sections 6.6 and 9.3): 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.

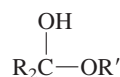
Halohydrin (Section 5.6): A compound that contains both a halogen atom and a hydroxyl group. The term is most often used for compounds in which the halogen and the hydroxyl group are on adjacent atoms (vicinal halohydrins). The most commonly encountered halohydrins are *chlorohydrins* and *bromohydrins*.

Halonium ion (Section 5.6): 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.

Haworth formulas (Section 15.5): Planar representations of furanose and pyranose forms of carbohydrates.

α -Helix (Section 17.12): 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.

Hemiacetal (Section 11.8): Product of nucleophilic addition of one molecule of an alcohol to an aldehyde or a ketone. Hemiacetals are compounds of the type



Hemiketal (Section 11.8): An old name for a hemiacetal derived from a ketone.

Heteroatom (Section 1.7): An atom in an organic molecule that is neither carbon nor hydrogen.

Heterocyclic compound (Section 6.15): 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.

Heterolytic cleavage (Section 9.2): Dissociation of a two-electron covalent bond in such a way that both electrons are retained by one of the initially bonded atoms.

Hexose (Section 15.1): A carbohydrate with six carbon atoms.

High-density lipoprotein (HDL) (Section 16.5): A protein that carries cholesterol from the tissues to the liver where it is metabolized. HDL is often called “good cholesterol.”

Homolytic cleavage (Section 9.2): Dissociation of a two-electron covalent bond in such a way that one electron is retained by each of the initially bonded atoms.

Hückel's rule (Section 6.14): Completely conjugated planar monocyclic hydrocarbons possess special stability when the number of their π 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 1.12): An atomic orbital represented as a mixture of various contributions of that atom's s , p , d , etc. orbitals.

Hydration (Section 5.5): Addition of the elements of water (H, OH) to a multiple bond.

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

Hydrogenation (Section 5.1): Addition of H_2 to a multiple bond.

Hydrogen bonding (Section 3.4): 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 (Sections 8.5 and 13.7): Water-induced cleavage of a bond.

Hydronium ion (Section 3.5): The species H_3O^+ .

Hydrophilic (Section 12.7): 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 12.7): Literally, “water-hating”; a term applied to substances that are not soluble in water, but are soluble in nonpolar, hydrocarbon-like media.

Imine (Section 11.9): Compound of the type $\text{R}_2\text{C}=\text{NR}'$ formed by the reaction of an aldehyde or a ketone with a primary amine ($\text{R}'\text{NH}_2$). Imines are sometimes called *Schiff's bases*.

Index of hydrogen deficiency (Section 19.14): 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:

$$\text{Index of hydrogen deficiency} = \frac{1}{2}(\text{C}_n\text{H}_{2n+2} - \text{C}_n\text{H}_x)$$

Induced-dipole/induced-dipole attraction (Section 2.19): Force of attraction resulting from a mutual and complementary polarization of one molecule by another.

Inductive effect (Section 3.9): An electronic effect transmitted by successive polarization of the σ bonds within a molecule or an ion.

Infrared (IR) spectroscopy (Section 19.10): 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.

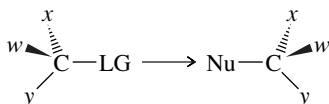
Initiation step (Section 9.4): A process that causes a reaction, usually a free-radical reaction, to begin but that by itself is not the principal source of products. The initiation step in the halogenation of an alkane is the dissociation of a halogen molecule to two halogen atoms.

Integrated area (Section 19.5): 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 3.8): 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 2.19): Forces, either attractive or repulsive, between two atoms or groups in *separate* molecules.

Inversion of configuration (Section 8.3): 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.



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

Isobutane (Section 2.6): The common name for 2-methylpropane, $(CH_3)_3CH$.

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

Isoelectric point (Section 17.3): 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.

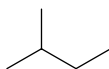
Isolated diene (Section 4.1): Diene of the type



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.

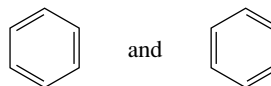
Isoprene unit (Section 16.13): The characteristic five-carbon structural unit found in terpenes:



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

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.

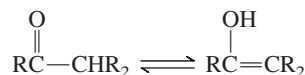
Kekulé structure (Section 6.1): Structural formula for an aromatic compound that satisfies the customary rules of bonding and is usually characterized by a pattern of alternating single and double bonds. There are two Kekulé formulations for benzene:



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

Ketal (Section 11.8): An old name for an acetal derived from a ketone.

Keto-enol tautomerism (Section 11.16): Process by which an aldehyde or a ketone and its enol equilibrate:



Ketone (Sections 2.3 and 11.1): A member of the family of compounds in which both atoms attached to a carbonyl group ($C=O$) are carbon, as in



Ketose (Section 15.8): A carbohydrate that contains a ketone carbonyl group in its open-chain form.

Lactose (Section 15.11): Milk sugar; a disaccharide formed by a β -glycosidic linkage between C-4 of glucose and C-1 of galactose.

Leaving group (Sections 4.10 and 8.1): The group, normally a halide ion, that is lost from carbon in a nucleophilic substitution or elimination.

Le Châtelier's principle (Section 5.5): 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 5.11): 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 16.3): 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 hydrophobic hydrocarbon tails cluster on the inside.

Lipids (Section 16.1): Biologically important natural products characterized by high solubility in nonpolar organic solvents.

Lipophilic (Section 12.7): 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.

Low-density lipoprotein (LDL) (Section 16.5): A protein that 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.”

Magnetic resonance imaging (MRI) (Section 19.9): A diagnostic method in medicine in which tissues are examined by NMR.

Maltose (Section 15.11): A disaccharide obtained from starch in which two glucose units are joined by an $\alpha(1,4)$ -glycosidic link.

Markovnikov's rule (Section 5.3): 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 19.13): 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 3.6): 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 10.6): 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 18.6): 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 6.3): Term describing a 1,3 relationship between substituents on a benzene ring.

Meta director (Section 6.9): A group that when present on a benzene ring directs an incoming electrophile to a position meta to itself.

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

Methine group (Section 2.6): The group CH.

Methylene group (Section 2.6): The group $-\text{CH}_2-$.

Methyl group (Section 1.13): The group CH_3- .

Mevalonic acid (Section 16.13): An intermediate in the biosynthesis of steroids from acetyl coenzyme A.

Micelle (Section 12.7): A spherical aggregate of species such as carboxylate salts of fatty acids that contain a hydrophobic end and a hydrophilic end. Micelles containing 50–100 carboxylate salts of fatty acids are soaps.

Molar absorptivity (Section 19.11): A measure of the intensity of a peak, usually in UV-Vis spectroscopy.

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 19.13): In mass spectrometry, the species formed by loss of an electron from a molecule.

Monomer (Section 9.8): The simplest stable molecule from which a particular polymer may be prepared.

Monosaccharide (Section 15.1): A carbohydrate that cannot be hydrolyzed further to yield a simpler carbohydrate.

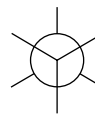
Monosubstituted alkene (Section 4.5): An alkene of the type $\text{RCH}=\text{CH}_2$, in which only one carbon is *directly* bonded to the carbons of the double bond.

Multiplicity (Section 19.6): 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.

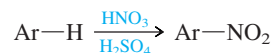
Mutarotation (Section 15.7): The change in optical rotation that occurs when a single form of a carbohydrate is allowed to equilibrate to a mixture of isomeric hemiacetals.

Neurotransmitter (Section 14.3): Substance, usually a naturally occurring amine, that mediates the transmission of nerve impulses.

Newman projection (Section 2.5): Method for depicting conformations in which one sights down a carbon–carbon bond and represents the front carbon by a point and the back carbon by a circle.



Nitration (Section 6.6): Replacement of a hydrogen by an $-\text{NO}_2$ group. The term is usually used in connection with electrophilic aromatic substitution.



Nitrile (Section 12.10): A compound of the type $\text{RC}\equiv\text{N}$. R may be alkyl or aryl. Also known as alkyl or aryl cyanides.

Nitrosamine See *N-nitroso amine*.

N-Nitroso amine (Section 14.9): A compound of the type $\text{R}_2\text{N}-\text{N}=\text{O}$. 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 14.9): 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.

N terminus (Section 17.5): The amino acid at the end of a peptide or protein chain that has its α -amino group intact; that is, the α -amino group is not part of a peptide bond.

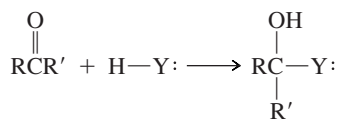
Nuclear magnetic resonance (NMR) spectroscopy (Section 19.2): A method for structure determination based on the effect of molecular environment on the energy required to promote a given nucleus from a lower energy spin state to a higher energy state.

Nucleic acid (Section 18.4): A polynucleotide present in the nuclei of cells.

Nucleophile (Section 3.10): 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 13.3): Nucleophilic substitution at the carbon atom of an acyl group.

Nucleophilic addition (Section 11.6): 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.



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

Nucleoside (Section 18.2): The combination of a purine or pyrimidine base and a carbohydrate, usually ribose or 2-deoxyribose.

Nucleotide (Section 18.3): The phosphate ester of a nucleoside.

Octane rating (Section 2.20): 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.

Oligosaccharide (Section 15.1): 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.

Orbital (Section 1.1): The region in space where the probability of finding an electron is high.

σ Orbital (Section 1.12): A bonding orbital characterized by rotational symmetry.

Organometallic compound (Section 11.10): A compound that contains a carbon-to-metal bond.

Ortho (Section 6.3): Term describing a 1,2 relationship between substituents on a benzene ring.

Ortho, para director (Section 6.9): A group that when present on a benzene ring directs an incoming electrophile to the positions ortho and para to itself.

Oxidation (Section 10.2): 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.

Oxonium ion (Section 3.5): Specific name for the species H_3O^+ (also called *hydronium ion*). General name for species such as alkyloxonium ions ROH_2^+ analogous to H_3O^+ .

Para (Section 6.3): Term describing a 1,4 relationship between substituents on a benzene ring.

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 10.5): Abbreviation for pyridinium chlorochromate $\text{C}_5\text{H}_5\text{NH}^+ \text{ClCrO}_3^-$. When used in an anhydrous medium, PCC oxidizes primary alcohols to aldehydes and secondary alcohols to ketones.

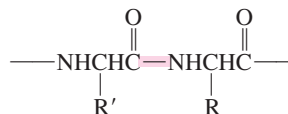
PDC (Section 10.5): Abbreviation for pyridinium dichromate $(\text{C}_5\text{H}_5\text{NH})_2^{2+} \text{Cr}_2\text{O}_7^{2-}$. Used in same manner and for same purposes as PCC (see preceding entry).

***n*-Pentane** (Section 2.7): The common name for pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

Pentose (Section 15.4): A carbohydrate with five carbon atoms.

Peptide (Section 17.5): Structurally, a molecule composed of two or more α -amino acids joined by peptide bonds.

Peptide bond (Section 17.5): An amide bond between the carboxyl group of one α -amino acid and the amino group of another.



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

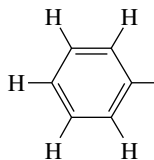
Period (Section 1.1): A horizontal row of the periodic table.

Peroxide (Section 9.7): A compound of the type ROOR.

Phenols (Section 10.13): Family of compounds characterized by a hydroxyl substituent on an aromatic ring as in ArOH.

Phenol is also the name of the parent compound, C₆H₅OH.

Phenyl group (Section 6.3): The group



It is often abbreviated C₆H₅—.

Phospholipid (Section 16.3): A diacylglycerol bearing a choline-phosphate “head group.” Also known as phosphatidylcholine.

Photon (Section 19.1): Term for an individual “bundle” of energy, or particle, of electromagnetic radiation.

pK_a (Section 3.5): 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 19.1): Constant of proportionality (*h*) in the equation $E = h\nu$, which relates the energy (*E*) to the frequency (ν) 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 17.12): 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.

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

Polycyclic aromatic hydrocarbon (Section 6.4): An aromatic hydrocarbon characterized by the presence of two or more benzene-like rings.

Polycyclic hydrocarbon (Section 2.18): A hydrocarbon in which two carbons are common to two or more rings.

Polyester (Section 13.12): A polymer in which individual structural units are joined by ester bonds.

Polyether (Section 10.9): A molecule that contains many ether linkages. Polyethers occur naturally in a number of antibiotic substances.

Polyethylene (Section 9.8): A polymer of ethylene.

Polymer (Section 9.8): Large molecule formed by the repetitive combination of many smaller molecules (monomers).

Polymerization (Section 9.8): Process by which a polymer is prepared. The principal processes include *free-radical*, *cationic*, coordination, and *condensation polymerization*.

Polypeptide (Section 17.5): A polymer made up of “many” (more than eight to ten) amino acid residues.

Polypropylene (Section 9.8): A polymer of propene.

Polysaccharide (Section 15.12): A carbohydrate that yields “many” monosaccharide units on hydrolysis.

Potential energy (Section 3.6): The energy a system has exclusive of its kinetic energy.

Potential energy diagram (Section 3.6): 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 RCH₂—, in which the point of attachment is to a primary carbon.

Primary amine (Section 14.1): An amine with a single alkyl or aryl substituent and two hydrogens: an amine of the type RNH₂ (primary alkylamine) or ArNH₂ (primary arylamine).

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

Primary structure (Section 17.6): 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 9.4): 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.

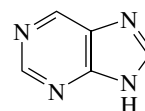
Protecting group (Section 17.11): A temporary alteration in the nature of a functional group so that it is rendered inert under the conditions in which reaction occurs somewhere else in the molecule. To be synthetically useful, a protecting group must be stable under a prescribed set of reaction conditions, yet be easily introduced and removed.

Protein (Chapter 17): A naturally occurring polymer that typically contains 100–300 amino acid residues.

Protein Data Bank (Section 17.15): 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 8.5): A solvent that has easily exchangeable protons, especially protons bonded to oxygen as in hydroxyl groups, as in water and alcohols.

Purine (Section 18.1): The heterocyclic aromatic compound.



Pyranose form (Section 15.6): Six-membered ring arising via cyclic hemiacetal formation between the carbonyl group and a hydroxyl group of a carbohydrate.

Pyrimidine (Section 18.1): The heterocyclic aromatic compound.



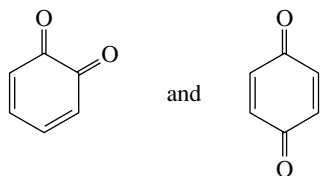
Quantum (Section 19.1): The energy associated with a photon.

Quaternary ammonium salt (Section 14.1): 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 17.15): Description of the way in which two or more protein chains, not connected by chemical bonds, are organized in a larger protein.

Quinone (Section 10.17): 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 4.10): Slowest step of a multi-step reaction mechanism. The overall rate of a reaction can be no faster than its slowest step.

Reducing sugar (Section 15.13): 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 10.2): 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 that is more electronegative than carbon is replaced by a bond to an atom that is less electronegative than carbon.

Refining (Section 2.20): Conversion of crude oil to useful materials, especially gasoline.

Reforming (Section 2.20): 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 4.7): 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, α , and β describe relative configuration.

Resolution (Section 7.13): 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 6.1): 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.

Retention of configuration (Section 8.7): Stereochemical pathway observed when a new bond is made that has the same spatial orientation as the bond that was broken.

Retrosynthetic analysis (Section 11.13): Technique for synthetic planning based on reasoning backward from the target molecule to appropriate starting materials. An arrow of the type  designates a retrosynthetic step.

Ring inversion (Section 2.15): 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.

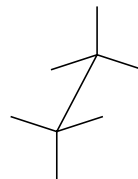
RNA (ribonucleic acid) (Section 8.6): A polynucleotide of ribose.

Sandmeyer reaction (Section 14.10): Reaction of an aryl diazonium ion with CuCl, CuBr, or CuCN to give, respectively, an aryl chloride, aryl bromide, or aryl cyanide (nitrile).

Saponification (Section 13.7): 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 5.1): A hydrocarbon in which no multiple bonds occur.

Sawhorse formula (Section 2.5): A representation of the three-dimensional arrangement of bonds in a molecule by a drawing of the type shown.



Schiff's base (Section 11.9): Another name for an imine; a compound of the type $R_2C=NR'$.

Secondary alkyl group (Section 2.10): Structural unit of the type R_2CH- , in which the point of attachment is to a secondary carbon.

Secondary amine (Section 14.1): An amine with any combination of two alkyl or aryl substituents and one hydrogen on nitrogen; an amine of the type



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

Secondary structure (Section 17.12): The conformation with respect to nearest neighbor amino acids in a peptide or protein. The α helix and the β 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 19.3): Effect of a molecule's electrons that decreases the strength of an external magnetic field felt by a proton or another nucleus.

Soaps (Section 12.7): Cleansing substances obtained by the hydrolysis of fats in aqueous base. Soaps are sodium or potassium salts of unbranched carboxylic acids having 12–18 carbon atoms.

Solid-phase peptide synthesis (Section 17.11): 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 8.5): Nucleophilic substitution in a medium in which the only nucleophiles present are the solvent and its conjugate base.

Space-filling model (Section 1.10): 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 α is the observed rotation in degrees, c is the concentration in g/100 mL, and l is the path length in decimeters.

Spectrometer (Section 19.1): Device designed to measure absorption of electromagnetic radiation by a sample.

Spectrum (Section 19.1): Output, usually in chart form, of a spectrometer. Analysis of a spectrum provides information about molecular structure.

sp Hybridization (Section 1.15): 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 1.14): 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.

sp^3 Hybridization (Section 1.13): 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.

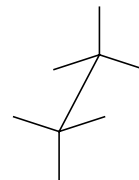
Spin quantum number (Section 1.1): One of the four quantum numbers that describe an electron. An electron may have either of two different spin quantum numbers, $+\frac{1}{2}$ or $-\frac{1}{2}$.

Spin–spin coupling (Section 19.6): The communication of nuclear spin information between two nuclei.

Spin–spin splitting (Section 19.6): 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.

Squalene (Section 16.12): A naturally occurring triterpene from which steroids are biosynthesized.

Staggered conformation (Section 2.5): 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.

Stereogenic center (Section 7.2): An atom that has four non-equivalent atoms or groups attached to it. At various times stereogenic centers have been called *asymmetrical centers* or *chiral centers*.

Stereoisomers (Section 2.17): Isomers that have the same constitution but that differ in respect to the arrangement of their atoms in space. Stereoisomers may be either *enantiomers* or *diastereomers*.

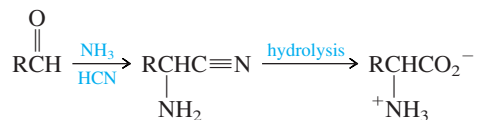
Stereoselective reaction (Section 4.7): Reaction in which a single starting material has the capacity to form two or more stereoisomeric products but forms one of them in greater amounts than any of its stereoisomers. Terms such as “addition to the less hindered side” describe stereoselectivity.

Steric hindrance (Section 8.4): An effect on structure or reactivity that depends on van der Waals repulsive forces.

Steric strain (Section 2.6): Destabilization of a molecule as a result of van der Waals repulsion, distorted bond distances, bond angles, or torsion angles.

Steroid (Section 16.5): 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 17.4): 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.



Stretching vibration (Section 19.10): A regular, repetitive motion of two atoms or groups along the bond that connects them.

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

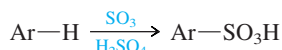
Substitution nucleophilic bimolecular (S_N2) mechanism (Section 8.2): Concerted mechanism for nucleophilic substitution in which the nucleophile attacks carbon from the side opposite the bond to the leaving group and assists the departure of the leaving group.

Substitution nucleophilic unimolecular (S_N1) mechanism (Section 8.5): 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 3.8): Chemical reaction in which an atom or a group of a molecule is replaced by a different atom or group.

Sucrose (Section 15.11): A disaccharide of glucose and fructose in which the two monosaccharides are joined at their anomeric positions.

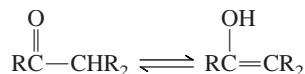
Sulfonation (Section 6.6): Replacement of a hydrogen by an $-\text{SO}_3\text{H}$ group. The term is usually used in connection with electrophilic aromatic substitution.



Syn addition (Section 5.1): Addition reaction in which the two portions of the reagent that add to a multiple bond add from the same side.

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 (Section 11.16): Process by which two isomers are interconverted by movement of an atom or a group. Enolization is a form of tautomerism.



Terminal alkyne (Section 4.12): Alkyne of the type $\text{RC}\equiv\text{CH}$, in which the triple bond appears at the end of the chain.

Termination steps (Section 9.4): 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 16.12): 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 $\text{R}_3\text{C}-$, in which the point of attachment is to a tertiary carbon.

Tertiary amine (Section 14.1): Amine of the type R_3N 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 17.13): A description of how a protein chain is folded.

Tesla (Section 19.2): SI unit for magnetic field strength.

Tetrahedral intermediate (Section 13.3): The key intermediate in nucleophilic acyl substitution. Formed by nucleophilic addition to the carbonyl group of a carboxylic acid derivative.

Tetramethylsilane (TMS) (Section 19.3): The molecule $(\text{CH}_3)_4\text{Si}$, used as a standard to calibrate proton and carbon-13 NMR spectra.

Tetrasubstituted alkene (Section 4.5): Alkene of the type $\text{R}_2\text{C}=\text{CR}_2$, in which four carbons are *directly* bonded to the carbons of the double bond. (The R groups may be the same or different.)

Tetrose (Section 15.3): A carbohydrate with four carbon atoms.

Thiol (Section 10.6): Compound of the type RSH or ArSH .

Torsional strain (Section 2.5): Decreased stability of a molecule that results from the eclipsing of bonds.

trans- (Section 2.17): Stereochemical prefix indicating that two substituents are on opposite sides of a ring or a double bond. (Contrast with the prefix *cis-*.)

Transcription (Section 18.6): Construction of a strand of mRNA complementary to a DNA template.

Transfer RNA (tRNA) (Section 18.6): 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 3.6): The point of maximum energy in an elementary step of a reaction mechanism.

Translation (Section 18.6): The “reading” of mRNA by various tRNAs, each one of which is unique for a particular amino acid.

Triacylglycerol (Section 16.2): A derivative of glycerol (1,2,3-propanetriol) in which the three oxygens bear acyl groups derived from fatty acids.

Tripeptide (Section 17.5): A compound in which three α -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 4.5): Alkene of the type $\text{R}_2\text{C}=\text{CHR}$, in which three carbons are *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 17.8): 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.

Ultraviolet-visible (UV-Vis) spectroscopy (Section 19.11): An 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.

Unsaturated hydrocarbon (Section 5.1): A hydrocarbon that can undergo addition reactions; that is, one that contains multiple bonds.

Upfield (Section 19.3): The high-field region of an NMR spectrum. A signal that is upfield with respect to another lies to its right on the spectrum.

Valence bond theory (Section 1.12): 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 each other. 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 2.19): Intermolecular forces that do not involve ions (dipole–dipole, dipole/induced-dipole, and induced-dipole/induced-dipole forces).

Van der Waals strain (Section 2.6): Destabilization that results when two atoms or groups approach each other too closely. Also known as van der Waals repulsion.

Vicinal (Section 4.14): Describing two substituents that are located on adjacent atoms.

Vicinal coupling (Section 19.6): 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 ^1H NMR spectroscopy.

Walden inversion (Section 8.3): 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.

Wavelength (Section 19.1): Distance between two successive maxima (peaks) or two successive minima (troughs) of a wave.

Wave numbers (Section 19.10): Conventional units in infrared spectroscopy that are proportional to frequency. Wave numbers are in reciprocal centimeters (cm^{-1}).

Wax (Section 16.4): 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 10.10): Method for the preparation of ethers involving an $\text{S}_{\text{N}}2$ reaction between an alkoxide ion and a primary alkyl halide:



Wood alcohol (Section 3.1): A common name for methanol, CH_3OH .

Zaitsev's rule (Section 4.7): 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 17.3): 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

