CHAPTER 19: ORGANIC CHEMISTRY

Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry

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In this chapter, you will learn about:

- Hydrocarbons
- Alkanes, Alkenes, Alkynes and Aromatic Hydrocarbons
- Alcohols and Ethers
- Aldehydes, Ketones, Carboxylic Acids, and Esters
- Amines and Amides
- Classifying Functional Groups

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The elements hydrogen and carbon.
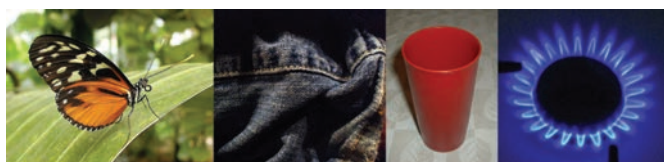
Figure 19.0a. All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credits left: modification of work by Jon Sullivan, PDM; left middle: modification of work by Deb Tremper, PDM; right middle: modification of work by annszyp, CC BY 2.0; right: modification of work by George Shuklin, PDM)

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet "carbon-based" life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*. The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms. The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of

vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials. Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon. Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO_2. Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems.

The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon. Refer to Appendix A: Key Element Information for more details about carbon and other elements.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 19.0a.

Table 19.0a: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Table source: "12.1: Organic Chemistry" In *Basics of GOB (Ball et al.)*, CC BY-NC-SA 4.0.

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 19a also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 19a.
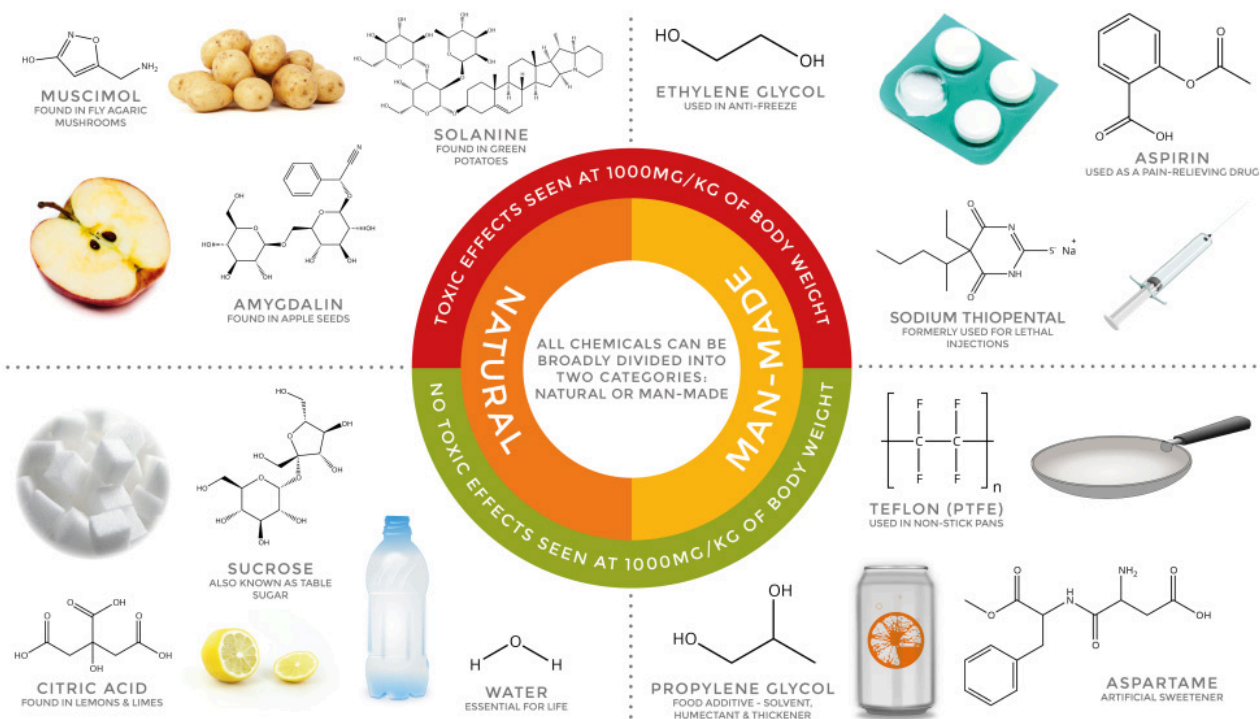
The largest database[1] of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated[2] at 10^{60}—an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest **organic compounds** contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

As mentioned above, hydrocarbons can be man-made (in the laboratory) or naturally present. How do we know which is better for us overall? Well, it depends on the organic compound in question. Both man-made and natural products can be good or bad for us. Infographic 19.0a looks at some common misconceptions about man-made and natural chemicals.

NATURAL & MAN-MADE CHEMICALS

A COMMON MISCONCEPTION IS THAT ALL MAN-MADE CHEMICALS ARE HARMFUL, AND ALL NATURAL CHEMICALS ARE GOOD FOR US. HOWEVER, MANY NATURAL CHEMICALS ARE JUST AS HARMFUL TO HUMAN HEALTH, IF NOT MORE SO, THAN MAN-MADE CHEMICALS.

ALL CHEMICALS CAN BE BROADLY DIVIDED INTO TWO CATEGORIES: NATURAL OR MAN-MADE

TOXIC EFFECTS SEEN AT 1000MG/KG OF BODY WEIGHT
NO TOXIC EFFECTS SEEN AT 1000MG/KG OF BODY WEIGHT

MUSCIMOL — FOUND IN FLY AGARIC MUSHROOMS
SOLANINE — FOUND IN GREEN POTATOES
AMYGDALIN — FOUND IN APPLE SEEDS
SUCROSE — ALSO KNOWN AS TABLE SUGAR
CITRIC ACID — FOUND IN LEMONS & LIMES
WATER — ESSENTIAL FOR LIFE

ETHYLENE GLYCOL — USED IN ANTI-FREEZE
ASPIRIN — USED AS A PAIN-RELIEVING DRUG
SODIUM THIOPENTAL — FORMERLY USED FOR LETHAL INJECTIONS
TEFLON (PTFE) — USED IN NON-STICK PANS
PROPYLENE GLYCOL — FOOD ADDITIVE - SOLVENT, HUMECTANT & THICKENER
ASPARTAME — ARTIFICIAL SWEETENER

"EVERYTHING IS POISON, THERE IS POISON IN EVERYTHING. ONLY THE DOSE MAKES A THING NOT A POISON."
PARACELSUS, 1493-1541, 'THE FATHER OF TOXICOLOGY'

ANY SUBSTANCE, IF GIVEN IN LARGE ENOUGH AMOUNTS, CAN CAUSE DEATH. SOME ARE LETHAL AFTER ONLY A FEW NANOGRAMS, WHILST OTHERS REQUIRE KILOGRAMS TO ACHIEVE A LETHAL DOSE.

CHEMICAL TOXICITY IS A SLIDING SCALE, NOT BLACK AND WHITE - AND WHETHER A CHEMICAL IS NATURALLY OCCURING OR MAN-MADE TELLS US **NOTHING** ABOUT ITS TOXICITY.

Infographic 19.0a: Read more about "Natural vs. Man-Made Chemicals – Dispelling Misconceptions (https://www.compoundchem.com/2014/05/19/natural-vs-man-made-chemicals-dispelling-misconceptions/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.0a [New tab].

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter,

we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings. Infographic 19.0b looks at one of the roles organic compounds play in our everyday lives such as the beautiful aromas from various flowers.

Spotlight on Everyday Chemistry: The Scent of Flowers

The infographic 19.0b below demonstrates one of the many interesting characteristics of organic compounds. The specific aroma of some common flowers is due to the organic compound that makes up the flower.
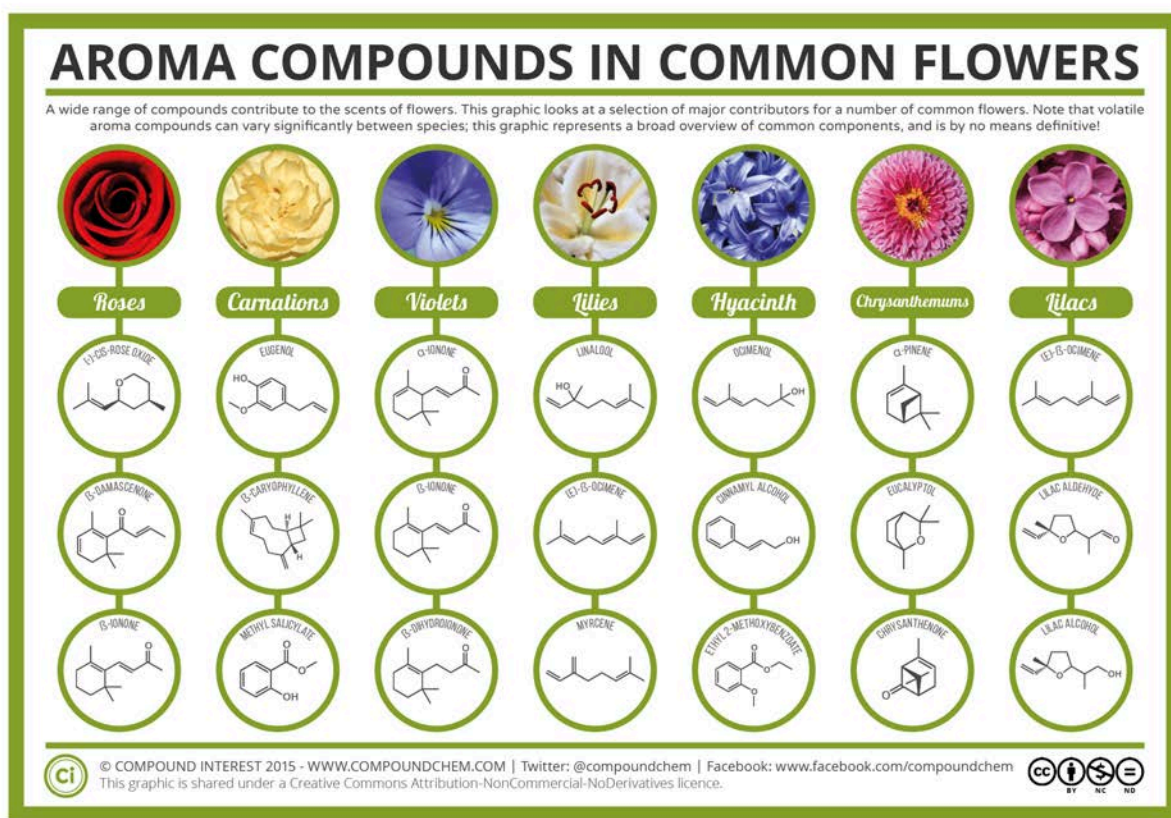
Infographic 19.0b: Read more about "The Chemical Compounds Behind the Smell of Flowers (https://www.compoundchem.com/2015/02/12/flowers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.0b [New tab].

The video below gives a summary of organic chemistry and the upcoming topics that will be described in this textbook.

Watch Crash Course Organic Chemistry Preview (3 mins) on YouTube (https://youtu.be/bSMx0NS0XfY)

Attribution & References

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- "Chapter 18 Introduction (https://boisestate.pressbooks.pub/chemistry/chapter/intro-21/)", "18.1 Hydrocarbons (https://boisestate.pressbooks.pub/chemistry/chapter/21-1-hydrocarbons/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* and
- "12.1: Organic Chemistry" In *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, licensed under CC BY-NC-SA 4.0. / A derivative of *Introduction to Chemistry: GOB (v. 1.0),* CC BY-NC 3.0.

Notes

1. This is the Beilstein database, now available through the Reaxys site (https://www.elsevier.com/solutions/reaxys) .
2. Peplow, Mark. "Organic Synthesis: The Robo-Chemist," *Nature* 512 (2014): 20–2.

19.1 ALKANES, ALKENES, ALKYNES AND AROMATIC HYDROCARBONS

Alkanes

Alkanes, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp^3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in Figure 19.1a. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the sp^3 hybridization, the bond angles in carbon chains are close to 109.5°, giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a molecular structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of Figure 19.1a.
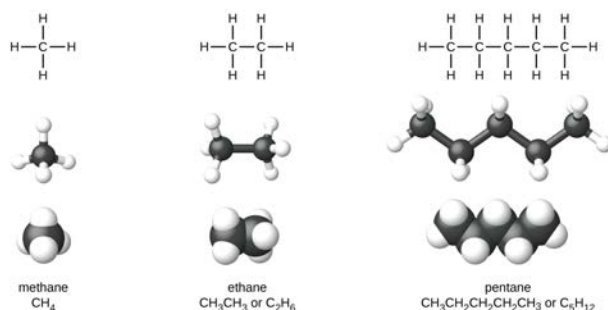
Figure 19.1a Pictured are the expanded structural formulas, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane. Below the chemical names methane, ethane and pentane represent the condensed structural formulas. (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-1-hydrocarbons)*, CC BY 4.0).

Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 19.1b); the butene structures follow in the series.
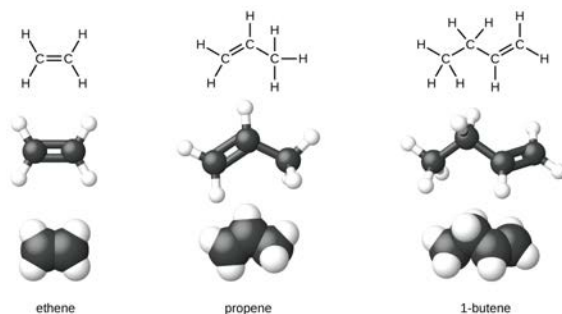
Figure 19.1b. The expanded molecular structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-1-hydrocarbons)*, CC BY 4.0).

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene

and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape. The molecular structure for ethyne, a linear molecule, is:

$$H-C\equiv C-H$$
ethyne (acetylene)
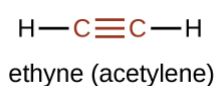
Figure 19.1c. The expanded structural formula of ethyne (acetylene) (credit: *Chemistry (OpenStax)* (https://openstax.org/books/chemistry/pages/20-1-hydrocarbons), CC BY 4.0).

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene is represented in Figure 19.1c.

Aromatic Hydrocarbons
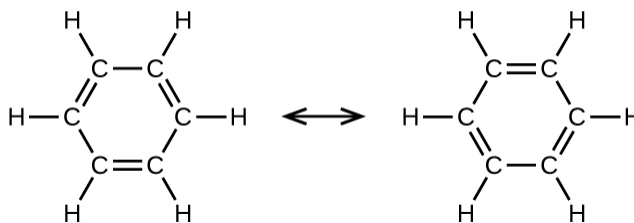
Figure 19.1d. The ring structure of benzene, the simplest aromatic compound. (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-1-hydrocarbons)*, CC BY 4.0).

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**. Benzene is represented in Figure 19.1d. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:

Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as

hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a $C = C$ double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 19.1e.
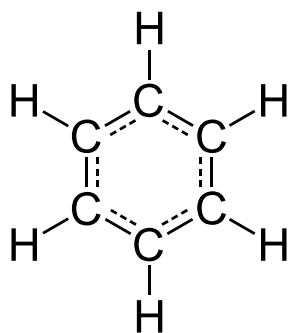
Figure 19.1e. This condensed formula shows the unique bonding structure of benzene (credit: Image by Jynto, PDM).

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different **substituents**. Aromatic compounds more readily undergo **substitution reactions** than **addition reactions**; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene. These molecules are shown in Figure 19.1f.
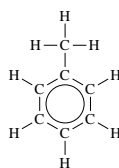
Figure 19.1f. Toluene represents a typical example of substituted benzene derivative (credit: Image by Jarozwj, PDM)

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19.2 ALCOHOLS AND ETHERS

Alcohols

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or **ether**.

Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH⁻ ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

$$C_6H_{12}O_6(aq) \xrightarrow{\text{Yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$$

glucose   ethanol
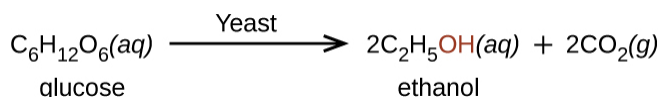
Figure 19.2a. The formation of ethanol derived by the fermentation of yeast and sugars (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers)*, CC BY 4.0).

Ethanol, CH_3CH_2OH, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars as illustrated in Figure 19.2a.
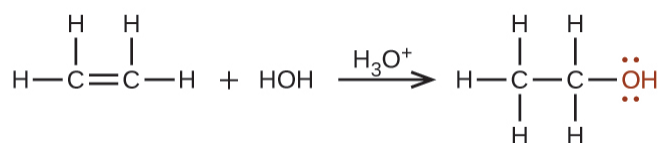
Figure 19.2b. Ethanol produced by the addition of water with ethylene in the presence of an acid (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers)*, CC BY 4.0).

Alternatively, large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst as shown in Figure 19.2b.


1,2-ethanediol   1,2,3-propanetriol
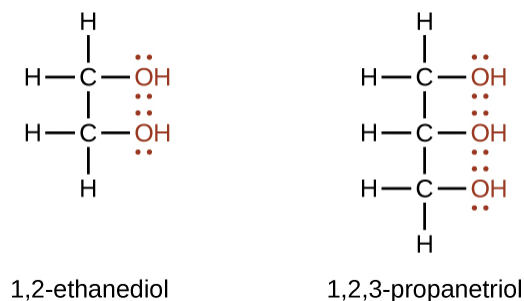
Figure 19.2c. Alcohols containing more than one hydroxyl group such as 1,2-ethanediol and 1,2,3-propanetriol (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers)*, CC BY 4.0).

Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines) as shown in Figure 19.2c.

The name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

Ethers
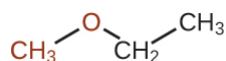
Figure 19.2d. An example of an ether, ethylmethyl ether (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers)*, CC BY 4.0).

Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the

other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named "methoxy." The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by "ether." The common name for the compound shown in Figure 19.2d is ethylmethyl ether:
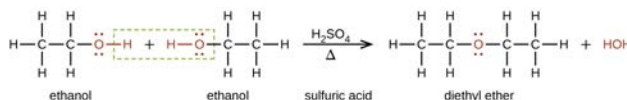
Figure 19.2e. The production of diethyl ether from two molecules of ethanol (credit: *Chemistry (OpenStax)* (https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers), CC BY 4.0).

Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol as illustrated in Figure 19.2e. For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed as demonstrated in Figure 19.2e.

In the general formula for ethers, R—**O**—R, the hydrocarbon groups (R) may be the same or different. Diethyl ether, the most widely used compound of this class, is a colourless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

Attribution & References

19.3 ALDEHYDES, KETONES, CARBOXYLIC ACIDS, AND ESTERS

The Carbonyl Group

Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a **carbonyl group** as shown in Figure 19.3a. The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.
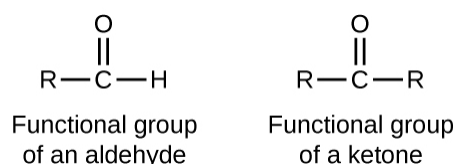
$$-\overset{\overset{\textstyle O}{\|}}{C}-$$

Figure 19.3a. The carbonyl group (credit: *Chemistry (OpenStax) (https://openstax.org/books/ chemistry/pages/ 20-3-aldehydes-ketones-carboxylic-acids-and-ester s)*, CC BY 4.0).

Aldehydes and Ketones

Both **aldehydes** and **ketones** contain a **carbonyl group**, a functional group with a carbon-oxygen double bond as shown in Figure 19.3a. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes *-al* and *-one*, respectively.

$$\begin{array}{c} \quad\;\; O \\ \quad\;\; \parallel \\ R-C-H \end{array} \qquad \begin{array}{c} \quad\;\; O \\ \quad\;\; \parallel \\ R-C-R \end{array}$$

Functional group
of an aldehyde

Functional group
of a ketone

Figure 19.3b. The carbonyl group represented in an aldehyde and a ketone (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms as shown in Figure 19.3b.

CH_3CHO
An aldehyde
ethanal (acetaldehyde)

$CH_3COCH_2CH_3$
A ketone
butanone
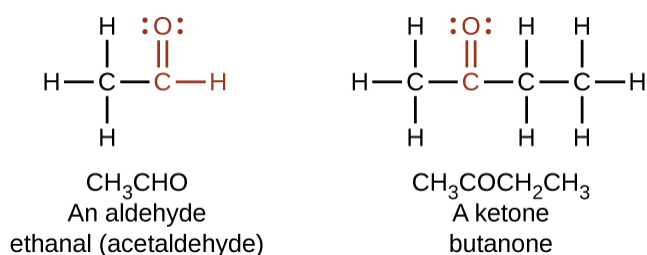
Figure 19.3c. The aldehyde is represented as –CHO whereas a ketone is represented as –C(O)– or –CO– (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

As text, an aldehyde group is represented as –CHO; a ketone is represented as –C(O)– or –CO– as shown in the examples within Figure 19.3c.

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization. Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule. The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom. The unhybridized p orbital on the carbon atom in the carbonyl group overlaps a p orbital on the oxygen atom to form the π bond in the double bond.

Like the $C = O$ bond in carbon dioxide, the $C = O$ bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar $C = O$ bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (Figure 19.3d).
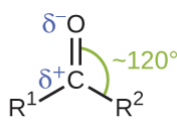
Figure 19.3d. The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones. We can prepare a carbonyl group by oxidation of an alcohol—for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond as shown in Figure 19.3e.
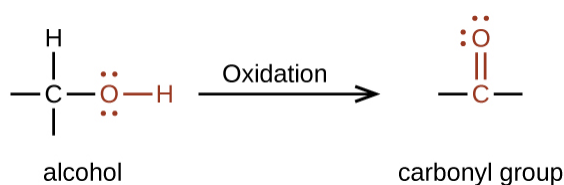
Figure 19.3e. The formation of the carbonyl group (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

Formation of Aldehydes and Ketones

Aldehydes are commonly prepared by the oxidation of alcohols (Figure 19.3f), whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:
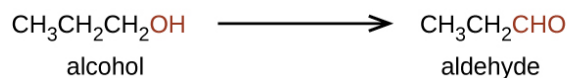
Figure 19.3f. The formation of an aldehyde from the oxidation of an alcohol (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone (Figure 19.3g), which requires the carbonyl group to be bonded to two other carbon atoms:

$$CH_3CH(OH)CH_3 \longrightarrow CH_3COCH_3$$
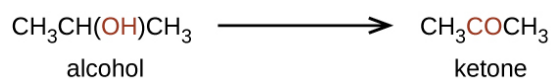
alcohol   ketone

Figure 19.3g. The formation of a ketone from the oxidation of an alcohol (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

An alcohol with its –OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its –OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the –OH, the molecule will not have a C–H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO, is a colourless gas with a pungent and irritating odour. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol. Acetone is a colourless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.
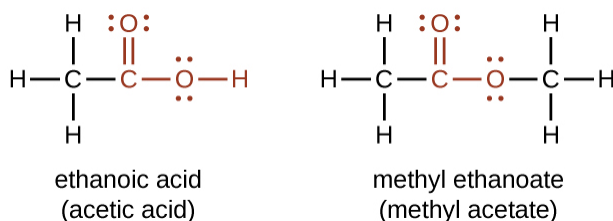
Carboxylic Acids and Esters

The odour of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odour of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived (see Figure 19.3h).
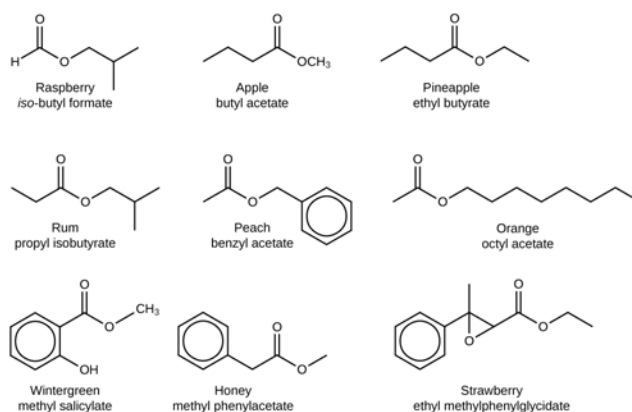
Figure 19.3h. Esters are responsible for the odours associated with various plants and their fruits (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

Both **carboxylic acids** and **esters** contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond (Figure 19.3i). In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see Figure 19.3i).

Figure 19.3i. The functional groups for an acid and for an ester are shown in red in these formulas (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-3-aldehydes-ketones-carboxylic-acids-and-esters)*, CC BY 4.0).

Carboxylic acids are weak acids, meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

The simplest carboxylic acid is formic acid, HCO_2H, known since 1670. Its name comes from the Latin word *formicus*, which means "ant"; it was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odour of ants that can be sometimes detected in their nests.

Acetic acid, CH_3CO_2H, constitutes 3–6% vinegar. Cider vinegar is produced by allowing apple juice to ferment without oxygen present. Yeast cells present in the juice carry out the fermentation reactions. The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid. Pure acetic acid

has a penetrating odour and produces painful burns. It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

The distinctive and attractive odours and flavours of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters. Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$. Oleic acid is an unsaturated acid; it contains a C=C double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

Attribution & References

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19.4 AMINES AND AMIDES

> ## Learning Objectives
>
> By the end of this section, you will be able to:
>
> - Classify amines and amides

Amines

Amines are molecules that contain carbon-nitrogen bonds. The nitrogen atom in an amine has a lone pair of electrons and three bonds to other atoms, either carbon or hydrogen. Various nomenclatures are used to derive names for amines, but all involve the class-identifying suffix *–ine* as illustrated here for a few simple examples in Figure 19.4a.
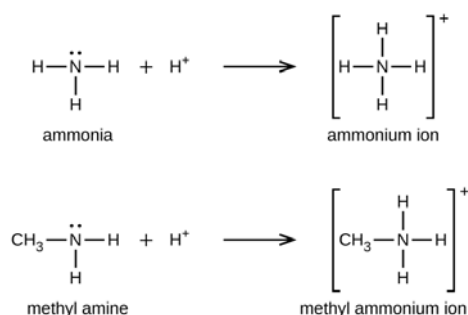

methyl amine   dimethyl amine   trimethyl amine
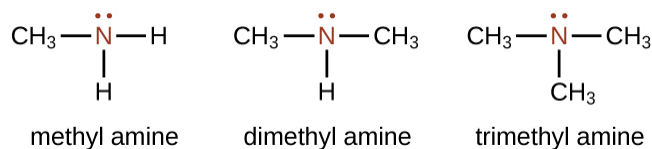
Figure 19.4a. The simplest amines: methyl amine, dimethyl amine and trimethyl amine (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

In some amines, the nitrogen atom replaces a carbon atom in an aromatic hydrocarbon. Pyridine (Figure 19.4b) is one such heterocyclic amine. A heterocyclic compound contains atoms of two or more different elements in its ring structure.
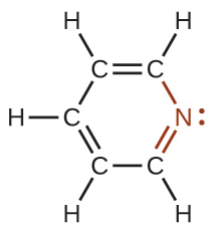
Figure 19.4b. The illustration shows one of the resonance structures of pyridine (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

Like ammonia, amines are weak bases (Figure 19.4c), due to the lone pair of electrons on their nitrogen atoms:

**Figure 19.4c.** Methyl amine, an example, to demonstrate how amines are weak bases similar to ammonia (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

The basicity of an amine's nitrogen atom plays an important role in much of the compound's chemistry. Amine functional groups are found in a wide variety of compounds, including natural and synthetic dyes, polymers, vitamins, and medications such as penicillin and codeine. They are also found in many molecules essential to life, such as amino acids, hormones, neurotransmitters, and DNA.

Spotlight on Everyday Chemistry: Addictive Alkaloids

Since ancient times, plants have been used for medicinal purposes. One class of substances, called *alkaloids*, found in many of these plants has been isolated and found to contain cyclic molecules with an amine functional group. These amines are bases. They can react with H_3O^+ in a dilute acid to form an ammonium salt, and this property is used to extract them from the plant:

$$R_3N \;+\; H_3O^+ \;+\; Cl^- \;\longrightarrow\; [R_3NH^+]\,Cl^- \;+\; H_2O$$

The name alkaloid means "like an alkali." Thus, an alkaloid reacts with acid. The free compound can be recovered after extraction by reaction with a base:

$$[R_3NH^+]\,Cl^- \;+\; OH^- \;\longrightarrow\; R_3N \;+\; H_2O \;+\; Cl^-$$
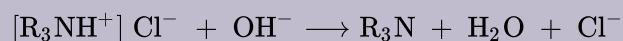
The structures of many naturally occurring alkaloids have profound physiological and psychotropic effects in humans. Examples of these drugs include nicotine, morphine, codeine, and heroin (Figure 19.4d). The plant produces these substances, collectively called secondary plant compounds, as chemical defenses against the numerous pests that attempt to feed on the plant:
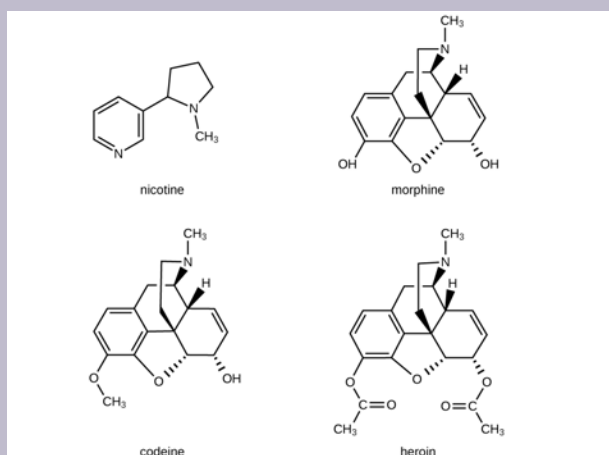
Figure 19.4d. The structural images of drugs include nicotine, morphine, codeine, and heroin (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

In these diagrams, as is common in representing structures of large organic compounds, carbon atoms in the rings and the hydrogen atoms bonded to them have been omitted for clarity. The solid wedges indicate bonds that extend out of the page. The dashed wedges indicate bonds that extend into the page. Notice that small changes to a part of the molecule change the properties of morphine, codeine, and heroin. Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (Figure 19.4e).

Figure 19.4e. Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized (credit: Karen Roe, *Chemistry (Open Stax)*, CC BY 4.0).

Read more about the colours of poppies in Compound Interest: The chemistry of poppies: colours and opium (compoundchem.com) (https://www.compoundchem.com/2020/11/11/poppies/).

Furthermore, in some foods that contain poppy seeds, trace amounts of codeine and morphine are present up to 48 hours in urine. In Hungary, there is a sweet roll filled with poppy seeds along with a walnut or chestnut paste, known as Bejgli often served at Christmas. For more information on the Bejgli dessert, see Compound Chemistry Advent 2023 (https://www.compoundchem.com/2023advent/#day9).

Amides

Amides are molecules that contain nitrogen atoms connected to the carbon atom of a carbonyl group (Figure 19.4f). Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:
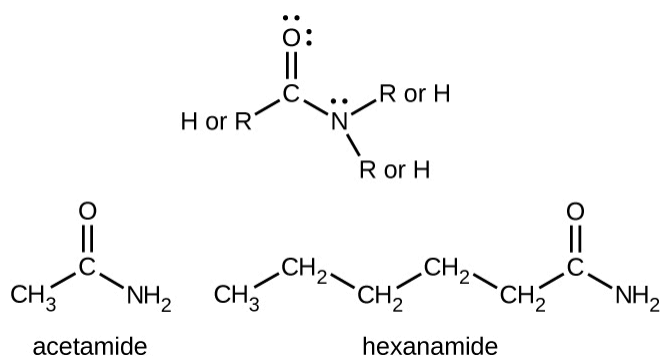
Figure 19.4f. Examples of amides acetamide (bottom left) and hexanamide (bottom right) with the top structure representing the amide functional group (credit: *Chemistry (Open Stax)*, CC BY 4.0).

Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation (Figure 19.4g). A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine.
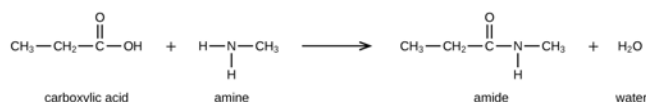
Figure 19.4g. The reaction between a carboxylic acid and an amine produces an amide and water (credit: *Chemistry (Open Stax)*, CC BY 4.0).

Attribution & References

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19.5 FAMILIES OF ORGANIC MOLECULES - FUNCTIONAL GROUPS

Learning Objectives

By the end of this section, you will be able to:

- Identify and describe functional groups in organic molecules.

Organic molecules can be classified into *families* based on structural similarities. Within a family, molecules have similar physical behavior and often have predictable chemical reactivity. The structural components differentiating different organic families involve specific arrangements of atoms or bonds, called **functional groups**. If you understand the behavior of a particular functional group, you can describe the general properties of that class of compounds.

The simplest organic compounds are in the alkane family and contain only carbon–carbon and carbon–hydrogen *single* bonds but do not have any specific functional group. Hydrocarbons containing at least one carbon–carbon double bond, (denoted C=C), are in the alkene family. Alkynes have at least one carbon–carbon triple bond (C≡C). Both carbon–carbon double bonds and triple bonds chemically react in specific ways that differ from reactions of alkanes and each other, making these specific functional groups.

In the next few chapters, we will learn more about additional functional groups that are made up of atoms or groups of atoms attached to hydrocarbons. Being able to recognize different functional groups will help to understand and describe common medications and biomolecules such as amino acids, carbohydrates, and fats. Table 19.5a. below list several of the functional groups to become familiar with as you learn about organic chemistry.

The table here summarizes the structures discussed in this chapter:

Table 19.5a. Summary of the Classification of Organic Compounds.

Compound Name	Structure of Compound and Functional Group (red)	Example		
		Formula		Name
alkene	C=C	C_2H_4		ethene
alkyne	C≡C	C_2H_2		ethyne
alcohol	R—Ö—H	CH_3CH_2OH		ethanol
ether	R—Ö—R'	$(C_2H_5)_2O$		diethyl ether
aldehyde	:O: ‖ R—C—H	CH_3CHO		ethanal
ketone	:O: ‖ R—C—R'	$CH_3COCH_2CH_3$		methyl ethyl ketone
carboxylic acid	:O: ‖ R—C—Ö—H	CH_3COOH		acetic acid
ester	:O: ‖ R—C—Ö—R'	$CH_3CO_2CH_2CH_3$		ethyl acetate
amine	R—N—H R—N—H R—N—R" $\quad$ H $\qquad$ R' $\qquad$ R'	$C_2H_5NH_2$		ethylamine
amide	:O: ‖ R—C—N—R' $\quad$ H	CH_3CONH_2		acetamide

Source: Summary of the Classification of Organic Compounds. (credit: *Chemistry (OpenStax)* *(https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

Exercise 19.5a

Exercise 19.5a (text version)

Organic Functional Groups: Match the organic structure (1-10) with its functional group.

Structures:

1. CH_3CH_3
2. $CH_2=CH_2$
3. $CH≡CH$
4. CH_3OH
5. CH_3COCH_3
6. CH_3CHO
7. CH_3COOH
8. CH_3COOCH_3
9. CH_3CONH_2
10. CH_3NH_2

Functional Group List:

amide, alkane, carboxylic acid, alkene, alcohol, ketone, alkyne, amine, aldehyde, ester

Check Your Answers:[1]

Source: Exercise 19.5a by Samantha Sullivan Sauer is licensed under CC BY-NC 4.0

Exercise 19.5b

Exercise 19.5b (text version)

Organic Functional Group Naming: Match the organic structure (1-10) with its functional group name.

Structures:

1. CH_3CH_3
2. $CH_2=CH_2$
3. $CH\equiv CH$
4. CH_3OH
5. CH_3COCH_3
6. CH_3CHO
7. CH_3COOH
8. CH_3COOCH_3
9. CH_3CONH_2
10. CH_3NH_2

Functional Group Names List:

-amide, -ane, -oic acid, -ene, -ol, -one, -yne, -amine, -al, -oate

Check Your Answers:[2]

Source: Exercise 19.5b by Samantha Sullivan Sauer is licensed under CC BY-NC 4.0

Spotlight on Everyday Chemistry: Doping in Sports

Doping in sports continues to make headlines as some athletes have turned to various drugs to enhance their performance against their opponents. Regulating bodies of professional sports monitor doping closely. The infographic looks at the major drugs used in doping.
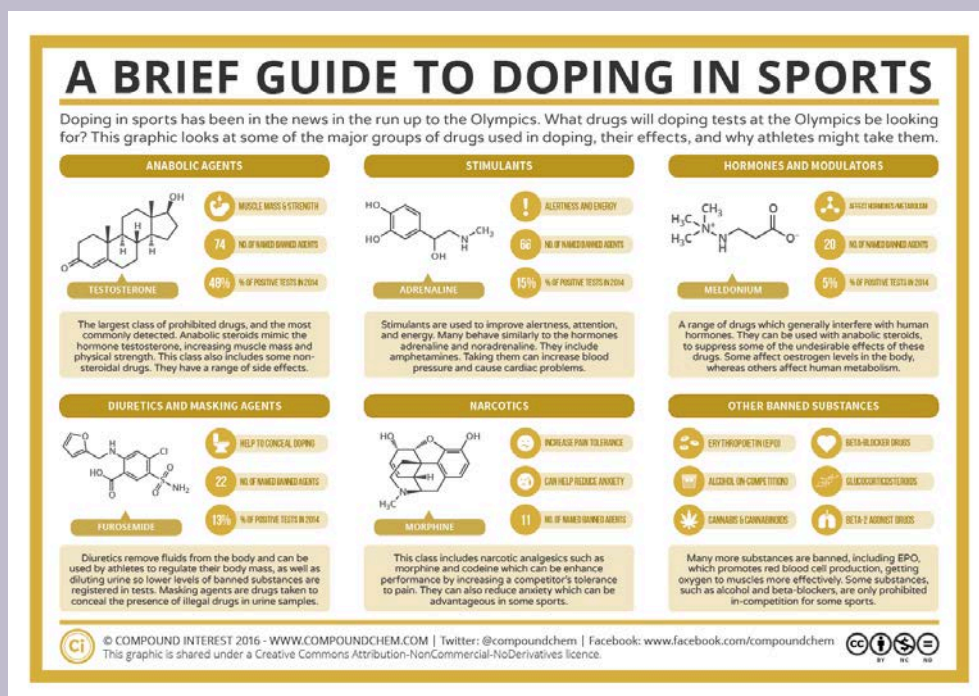
Infographic 19.5a: Read more about "A Brief Guide to Doping in Sports (https://www.compoundchem.com/2016/08/09/doping/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.5a [New tab].

Links to Enhanced Learning

Explore two infographics Functional Groups in Organic Chemistry (https://www.compoundchem.com/2020/02/21/functional-groups/) (first infographic) and Functional Groups in Organic Chemistry (https://www.compoundchem.com/2014/01/24/functional-groups-in-organic-compounds/) (second infographic) by Compound Interest for an extensive summary of functional groups.

Complex molecules have multiple functional groups within them. Explore the infographics from Compound Interest for a comprehensive look at:

- Intravenous anesthetics drug molecules through A Brief Summary to Intravenous Anesthetics [New tab] (https://www.compoundchem.com/2015/09/08/iv-anaesthetics/)
- General inhalant anesthetic drug molecules through A Brief Summary of Inhalation Anesthetics [New tab] (https://www.compoundchem.com/2014/11/10/anaesthetics-pt1/)
- Antidepressant drug molecules through Major Classes of Antidepressant Drugs [New tab] (https://www.compoundchem.com/2015/01/20/antidepressants/)
- Common painkiller molecules such as aspirin, ibuprofen and tramadol through A Brief Guide to Selected Common Painkillers [New tab]
- Antibiotic molecules through Different Classes of Antibiotics – An Overview [New tab] (https://www.compoundchem.com/2014/09/08/antibiotics/)

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Notes

1. 1. alkane 2. alkene 3. alkyne 4. alcohol 5. ketone 6. aldehyde 7. carboxylic acid 8. ester 9. amide 10. amine
2. 1. -ane 2. -ene 3. -yne 4. -ol 5. -one 6. -al 7. -oic acid 8. -oate 9. -amide 10. -amine

19.6 GENERAL REACTIONS OF CARBON

Common Chemical Reactions in Organic Chemistry

There are multiple types of organic chemical reactions. Some of the general organic reactions are additions, eliminations, substitutions, rearrangements and oxidation-reduction.
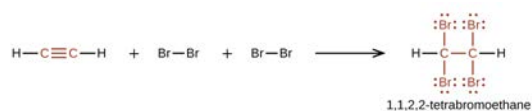
Addition reactions

Addition reactions occur when two reactants add together to form a single product with no atoms "left over." An example that we'll be studying soon is the reaction of an alkene, such as ethylene, with HBr to yield an alkyl bromide as shown in Figure 19.6a.

The two reactants ethylene (an alkene) and hydrogen bromide react to form one product: bromoethane (an alkyl halide).

Figure 19.6a. Addition reaction of ethylene with HBr. (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).

Chemically, the alkynes are similar to the alkenes. Since the $C \equiv C$ functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example that is demonstrated in Figure 19.6b.

Figure 19.6b. Addition reaction of acetylene with bromine. (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).

Elimination reactions

- **Elimination reactions** are, in a sense, the opposite of addition reactions. They occur when a single reactant splits into two products, often with the formation of a small molecule such as water or HBr. An example is the acid-catalyzed reaction of an alcohol to yield water and an alkene as shown in Figure 19.6c.

A reversible reaction shows the single reactant ethanol (an alcohol) in the presence of acid catalyst forming two products: ethylene (an alkene) and water.

Figure 19.6c. Elimination reaction of ethanol to yield ethylene and water. (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).
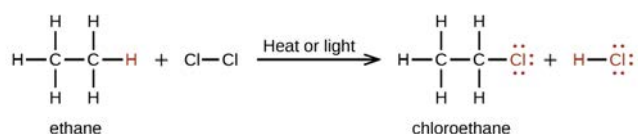
Substitution reactions

Substitution reactions occur when two reactants exchange parts to give two new products. An example is the reaction of an ester such as methyl acetate with water to yield a carboxylic acid plus an alcohol as shown in Figure 19.6d. Similar reactions occur in many biological pathways, including the metabolism of dietary fats.

The two reactants methyl acetate (ester) and water in the presence of acid catalyst form two products: acetic acid (a carboxylic acid) and methanol (an alcohol).

Figure 19.6d. Substitution reaction of methyl acetate and water yielding acetic acid and methanol. (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).

Another typical substitution reaction is one that involves alkanes, where one or more of the alkane's hydrogen

atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted in Figure 19.6e. is a substitution reaction:

Figure 19.6e. Substitution reaction between ethane and chlorine to yield chloroethane and HCl. (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-1-hydrocarbons)*, CC BY 4.0).

Rearrangement reactions

Rearrangement reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product. An example as demonstrated in Figure 19.6f. is the conversion of dihydroxyacetone phosphate into its constitutional isomer glyceraldehyde 3-phosphate, a step in the glycolysis pathway by which carbohydrates are metabolized.

The single reactant dihydroxyacetone phosphate reacts to form a single isomeric product, glyceraldehyde 3-phosphate.

Figure 19.6f. Rearrangement reaction where dihydroxyacetone phosphate is converted to its constitutional isomer glyceraldehyde 3-phosphate (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).
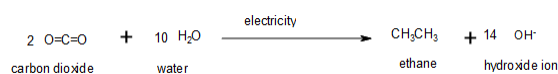
Oxidation-reduction reactions

Oxidation–reduction reactions, which are common in organic chemistry, can often be identified by changes in the number of oxygen atoms at a particular position in the hydrocarbon skeleton or in the number of bonds between carbon and oxygen at that position (Figure 19.6g.). An increase in either corresponds to an oxidation, whereas a decrease corresponds to a reduction (Figure 19.6h.). Conversely, an increase in the number of hydrogen atoms in a hydrocarbon is often an indication of a reduction. In Figure 19.6g, ethane is oxidized to carbon dioxide. The number of oxygen atoms and this the number of bonds between carbon and oxygen increase through the reaction so it is an oxidation of carbon reaction. In Figure 19.6h., carbon dioxide

is reduced to ethane. The number of carbon-oxygen bonds is decreased; more carbon-hydrogen bonds are formed so it is a reduction of carbon reaction.
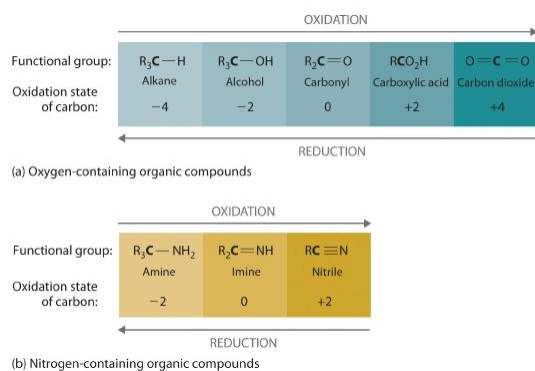
$$2 \ CH_3CH_3 \ + \ 7 \ O_2 \longrightarrow 4 \ O=C=O \ + \ 6 \ H_2O$$

ethane   oxygen   carbon dioxide   water
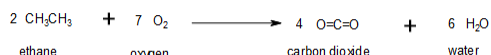
Figure 19.6g: Oxidation of ethane to carbon dioxide. (credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC-SA 4.0)

$$2 \ O=C=O \ + \ 10 \ H_2O \xrightarrow{\text{electricity}} CH_3CH_3 \ + 14 \ OH^-$$

carbon dioxide   water   ethane   hydroxide ion

Figure 19.6h. Reduction of carbon dioxide to ethane (Chen et al, 2015). (Image credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC-SA 4.0.

We can illustrate these points by considering how the oxidation state of the carbon atom changes in the series of compounds, which is shown in part (a) in Figure 19.6i. The number of oxygen atoms or the number of bonds to oxygen changes throughout the series. Hence the conversion of methane to formic acid is an oxidation, whereas the conversion of carbon dioxide to methanol is a reduction. Also, the number of hydrogen atoms increases in going from the most oxidized to least oxidized compound. As expected, as the oxidation state of carbon increases, the carbon becomes a more potent electrophile. Thus the carbon of CO_2 is a stronger electrophile (i.e., more susceptible to nucleophilic attack) than the carbon of an alkane such as methane.

OXIDATION →

Functional group:	R_3C-H	R_3C-OH	$R_2C=O$	RCO_2H	$O=C=O$
	Alkane	Alcohol	Carbonyl	Carboxylic acid	Carbon dioxide
Oxidation state of carbon:	−4	−2	0	+2	+4

← REDUCTION

(a) Oxygen-containing organic compounds

OXIDATION →

Functional group:	R_3C-NH_2	$R_2C=NH$	$RC\equiv N$
	Amine	Imine	Nitrile
Oxidation state of carbon:	−2	0	+2

← REDUCTION

(b) Nitrogen-containing organic compounds

Figure 19.6i. The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups (a) In a hydrocarbon, oxidation is indicated by an increase in the number of oxygen atoms or carbon–oxygen bonds or a decrease in the number of hydrogen atoms. (b) In nitrogen-containing compounds, the number of carbon–nitrogen bonds changes with the oxidation state of carbon. (credit: *General Chem: Principles, Patterns, and Applications (Averill)*, CC BY-NC-SA 3.0).

Similarly, in compounds with a carbon–nitrogen bond, the number of bonds between the C and N atoms increases as the oxidation state of the carbon increases (part (b) in Figure 19.6i. In a nitrile, which contains the

$-C\equiv N$ group, the carbon has the same oxidation state (+2) as in a carboxylic acid, characterized by the $-CO_2H$ group. We therefore expect the carbon of a nitrile to be a rather strong electrophile.

An example of an oxidation reaction is a **combustion reaction** involving hydrocarbons such as alkanes. Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$CH_4(g) \; + \; 2O_2(g) \; \longrightarrow \; CO_2(g) \; + \; 2H_2O(g)$$
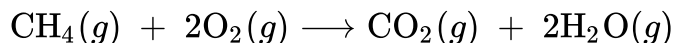
Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture. You may recall that boiling point is a function of intermolecular interactions. Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

Smudging is an example of a combustion reaction. Learn more about this by looking at the Indigenous Perspective below.

Indigenous Perspectives: Smudging

Combustion reactions occur within indigenous smudging ceremonies through the burning of natural plants such as sage, sweetgrass, cedar and tobacco.

Watch Smudging Ceremony Explained by Stephen Augustine on YouTube (5 mins) (https://youtu.be/KVsJGkSa8YU?)

Example 19.6a

Write an equation to describe each reaction.

1. the substitution reaction of potassium cyanide with 1-chloropropane to give $CH_3CH_2CH_2CN$

(butyronitrile)

2. the addition reaction of HBr with *cis*-2-butene

Solution

Given: reactants, products, and reaction mechanism

Asked for: equation

Strategy: Use the mechanisms described to show how the indicated products are formed from the reactants.

1. The CN¯ ion of KCN can displace the chlorine atom of 1-chloropropane, releasing a chloride ion. Substitution results in the formation of a new C–C bond:

   $$CN^{-}+\underset{1\text{-chloropropane}}{CH_{3}CH_{2}CH_{2}Cl}\rightarrow \underset{butylnitrile}{CH_{3}CH_{2}CH_{2}CN} + Cl^{-}$$
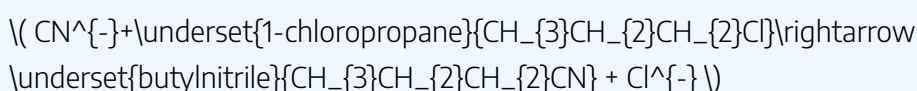
2. In the addition of a hydrogen halide to an alkene, the reaction is shown in Figure 19.6j.
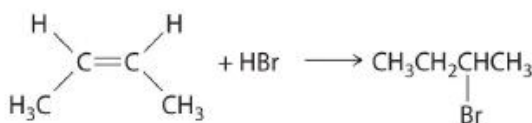
Figure 19.6j. The electrophilic addition of a HBr to 2-butene. (credit: *General Chem: Principles, Patterns, and Applications (Averill)*, CC BY-NC-SA 3.0).

Source: Example 19.6a is adapted by Adrienne Richards from *General Chemistry: Principles, Patterns, and Applications (Averill)*, CC BY-NC-SA 3.0

Exercise 19.6a

Write an equation to describe each reaction.

1. the substitution reaction of sodium methoxide ($NaOCH_3$) with benzyl bromide ($C_6H_5CH_2Br$)
2. the acid-catalyzed addition reaction of water with cyclopentene

Check Your Answer[1]

Source: Exercise 19.6a is adapted by Adrienne Richards from *Map: General Chemistry: Principles, Patterns, and Applications (Averill)*, CC BY-NC-SA 3.0

The reactions described above only cover the common reactions seen in organic chemistry, however, there are plenty more! Infographic 19.6a. provides an overview of the various types of organic chemistry reactions that can occur.
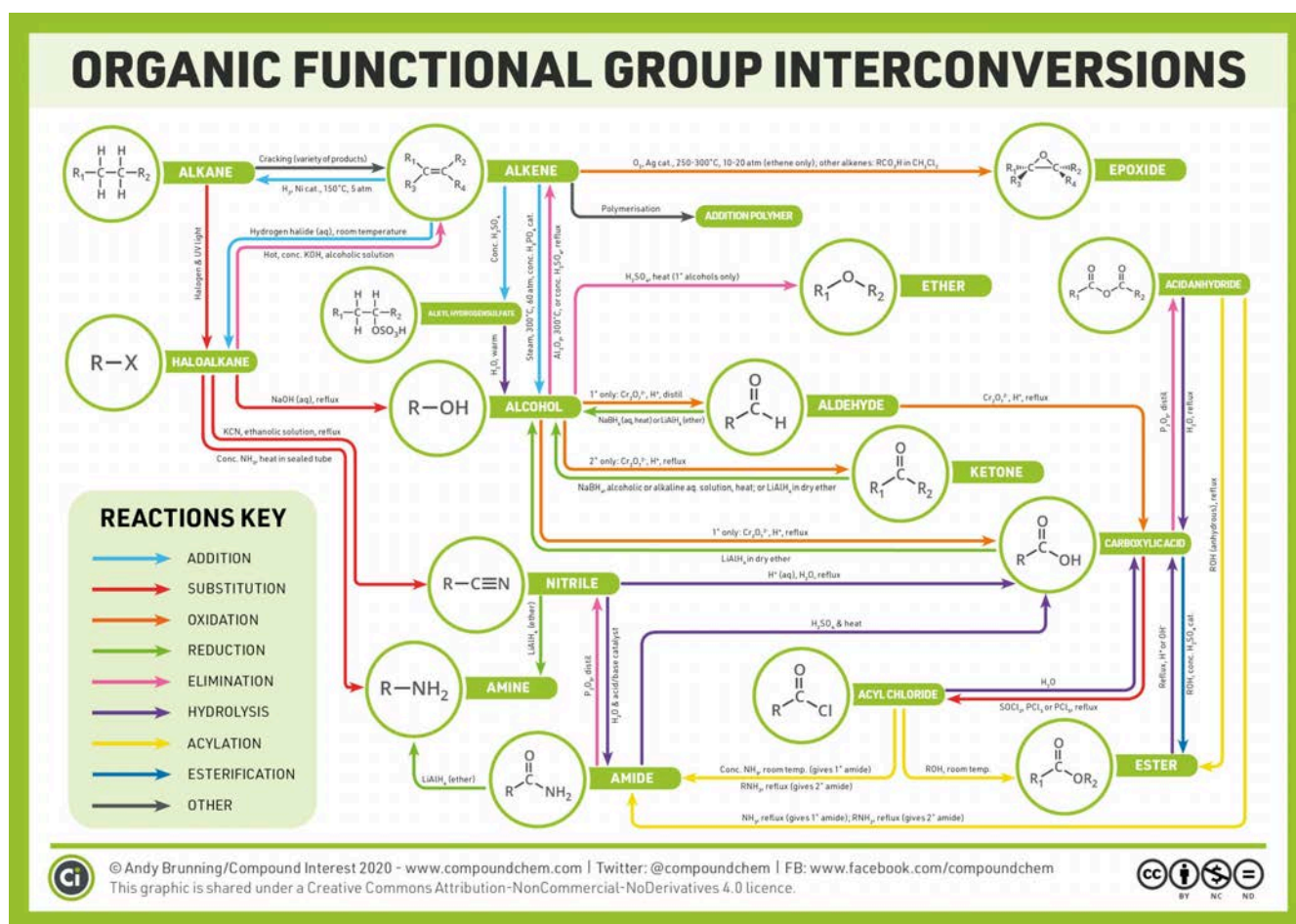
Infographic 19.6a. Summary of organic functional group interconversions. Read more about "Organic Chemistry Re (https://www.compoundchem.com/2014/02/17/organic-chemistry-reaction-map/)action Map" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.6a [New tab]
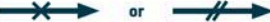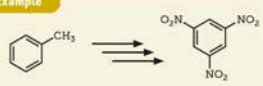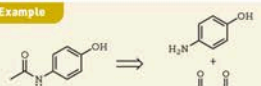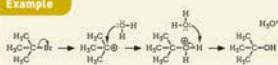
Reaction Mechanisms

Having looked at the kinds of reactions that take place, let's now see how they occur. An overall description of how a reaction occurs is called a reaction mechanism. A mechanism describes in detail exactly what takes place at each stage of a chemical transformation—which bonds are broken and in what order, which bonds are formed and in what order, and what the relative rates are for each step. A complete mechanism must also account for all reactants used and all products formed.

Arrows in organic chemistry reactions are important to understand as they differ depending on the type of reaction taking place. Infographic 19.6b. summarizes the various arrows used in organic chemistry reactions.

Infographic 19.6b. Summary of arrows in chemistry. Read more about "A short guide to different arrows in chemistry (https://www.compoundchem.com/2022/12/12/arrows/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.6b [New tab].

All chemical reactions involve bond-breaking and bond-making. When two molecules come together, react, and yield products, specific bonds in the reactant molecules are broken and specific bonds in the product molecules are formed. Fundamentally, there are two ways in which a covalent two-electron bond can break. A bond can break in an electronically unsymmetrical way so that both bonding electrons remain with one product fragment, leaving the other with a vacant orbital, or a bond can break in an electronically symmetrical way so that one electron remains with each product fragment. The unsymmetrical cleavage is said to be *heterolytic*, and the symmetrical cleavage is said to be *homolytic*.

Generally, the movement of *two* electrons in the unsymmetrical process is indicated using a full-headed A full-headed curved arrow originating from left to curved arrow (right.), whereas the movement of *one* electron in the symmetrical process is indicated using a half-headed, or "fishhook," arrow (A fish hook (single-headed curved) arrow that denotes the movement of one electron.) as demonstrated in Figure 19.6k.

Two reactions of A B with a shared pair of electrons
show unsymmetrical bond-breaking (full arrow) and
symmetrical bond-breaking (fish hook arrows),
respectively.

Figure 19.6k. The unsymmetrical and symmetrical bond breaking showing the full headed and half-headed arrows respectively. (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).

Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form. A bond can form in an electronically unsymmetrical way if both bonding electrons are donated to the new bond by one reactant, or in a symmetrical way if one electron is donated by each reactant as demonstrated in Figure 19.6l.

Two reactions for the formation of A B with a shared
pair of electrons show unsymmetrical bond-making
(full arrow) and symmetrical bond-making (fish hook
arrows), respectively.

Figure 19.6l. The unsymmetrical and symmetrical bond formations (credit: *Organic Chemistry (OpenStax)*, CC BY NC SA 4.0).

Processes that involve unsymmetrical bond-breaking and bond-making are called polar reactions. Polar reactions involve species that have an even number of electrons and thus have only electron pairs in their orbitals. Polar processes are by far the more common reaction type in both organic and biological chemistry, and a large part of this book is devoted to their description.

Processes that involve symmetrical bond-breaking and bond-making are called radical reactions. A radical, often called a **free radical**, is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals.

In addition to polar and radical reactions, there is a third, less commonly encountered process called a *pericyclic reaction*.

For a visual explanation of reaction mechanism refer to the video below called Intro to Reaction Mechanisms.

Watch Intro to Reaction Mechanisms: Crash Course Organic Chemistry #13 – YouTube (13 min)

Video Source: Crash Course. (2020, September 30). *Intro to Reaction Mechanisms: Crash Course Organic Chemistry #13 (youtube.com)*[Video]. YouTube.

Attribution & References

Except where otherwise noted, this page is adapted by Adrienne Richards from

- "18.1 Hydrocarbons (https://boisestate.pressbooks.pub/chemistry/chapter/21-1-hydrocarbons/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*
- "6.1 Kinds of Organic Reactions" and "6.2 How Organic Reactions Occur: Mechanisms" In *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0. Access for free at *Organic Chemistry (OpenStax)* (https://openstax.org/books/organic-chemistry/)
- Oxidation- Reduction Reaction section is adapted from "23.5: Common Classes of Organic Reactions" In *Map: General Chemistry: Principles, Patterns, and Applications (Averill)* was authored, remixed, and/or curated by Joshua B. Halpern / LibreTexts / Anonymous, CC BY-NC-SA 3.0
- "23.5: Common Classes of Organic Reactions" In *Map: General Chemistry: Principles, Patterns, and Applications (Averill)*, CC BY-NC-SA 3.0

References cited in-text

Chen, C. S., Wan, J. H., & Yeo, B. S. (2015). Electrochemical reduction of Carbon Dioxide to Ethane using nanostructured Cu_2O-Derived Copper Catalyst and Palladium(II) Chloride. *The Journal of Physical Chemistry, 119*(48), 26875-26882. DOI: 10.1021/acs.jpcc.5b09144

Notes

1. 1. OCH_3^- (methoxide ion) + $C_6H_5CH_2Br$ (benzyl bromide) → $C_6H_5CH_2OCH_3$ (benzylmethyl ether) + Br 2. The addition reaction is shown below. Water and acid become the hydronium ion.

Cyclopentene   Hydronium ion   + H_3O^+ →   Cyclopentanol   + H^+
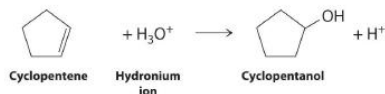
19.7 INTRODUCTION TO GREEN CHEMISTRY

Learning Objectives

By the end of this section, you will be able to:

- Describe the principles of green chemistry
- Outline the general strategy of greening a reaction

Organic chemistry reactions are essential to supporting the world's economic progress. As a result, the chemical industry is a large user of energy and greenhouse gas emissions. Ethylene, propylene, methanol, and aromatics production account for much of the demands and production. See Compound Interest: The environmental impact of industrial reactions – in C&EN (https://www.compoundchem.com/2019/06/19/impact-reactions/) for more details.

What is Green Chemistry?

Green chemistry involves inventing new chemicals, new chemical processes and commercial products that reduce chemical hazards and minimize hazardous effects on human health and the environment. The philosophy is based on 12 principles and are summarized by four key ideas:

1. Prevent the formation of waste in the first place.
2. Employ safer reagents or solvents.
3. Implement selective and efficient transformations (reactions).
4. Avoid unnecessary transformations.

For more details on the 12 principles, view Infographic 19.7a.

The 12 Principles of
GREEN CHEMISTRY

Green chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and the environment. While no reaction can be perfectly 'green', the overall negative impact of chemistry research and the chemical industry can be reduced by implementing the 12 Principles of Green Chemistry wherever possible.

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

Infographic 19.7a: The 12 Principles of Green Chemistry. Read more about "The Twelve Principles of Green Chemistry: What it is, & Why it Matters (https://www.compoundchem.com/2015/09/24/green-chemistry/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.7a [New tab].

General Strategy

The process of greening a chemical reaction involves a cyclic process that is outlined in Figure 19.7a. It starts by assessing the existing procedure including the reagents, products, by-products, solvents, reaction conditions, and efficacy. Essentially any components that are used to start, run or are produced in a reaction need to be examined.
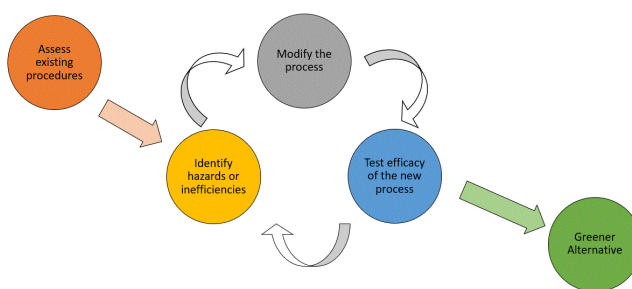
Figure 19.7a: The process of greening a chemical process.

Examples of Green Chemistry

A search of the internet produces many examples of green chemistry. Much of today's current research in chemistry is focused on green chemistry.

One example is shown in Infographic 19.7b, finding a new source for the production of rubber in tires.

DANDELIONS: DIURETICS AND CAR TYRES

DANDELIONS' MEDICINAL USES

The French name for dandelion is pissenlit ('wet the bed') from their supposed ability to act as a diuretic, increasing production of urine. Research attributes this to several diuretic compounds, but evidence for the effect is mixed. Dandelions' high potassium content helps replace potassium lost through urine.

Potassium content of dandelion leaves versus bananas

Dandelion leaves
397 mg per 100g

Bananas
358 mg per 100g

Source: US Department of Agriculture – FoodData Central

Studies show dandelion extracts or compounds have anti-inflammatory, anti-carcinogenic and anti-oxidative actions. These effects are mostly due to polyphenols and sesquiterpenes, also responsible for the bitter flavour of the leaves.
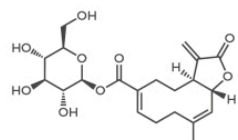
Taraxinic acid β-D-glucopyranoside

*A sesquiterpene lactone in dandelion, also thought to be a contact allergen.*

RUBBER FROM DANDELIONS

The sticky white liquid that seeps out from dandelion stems when they're picked contains natural latex, which can be turned into rubber. The roots of Russian dandelions (*Taraxacum koksaghyz*) contain a particularly high percentage of latex, making them ideal for rubber production.

1941   30%

Percentage of the USSR's rubber provided by the Russian dandelion during rubber shortages in World War II.
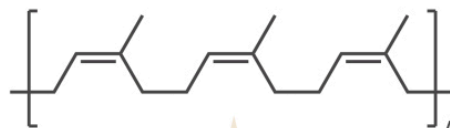
cis-1,4-polyisoprene (main constituent of rubber)

In the past decade, tyre manufacturers have been developing dandelion rubber tyres. Currently bike tyres made from dandelion rubber are commercially available and tyres for cars and trucks will be available within ten years.

Infographic 19.7b: Dandelions used to make rubber for car tires. Read more about "Dandelion chemistry: Diuretics and the tyres of the future (https://www.compoundchem.com/2022/05/26/dandelion/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 19.7b [New tab].

Links to Enhanced Learning

For additional examples, view:

- Examples of Green Chemistry & Sustainable Chemistry – American Chemical Society [New tab] (https://www.acs.org/greenchemistry/what-is-green-chemistry/examples.html)
- Where curiosity and scientific rigor lead to greener chemistry: UNLP-case-study-document-ad-1.pdf [New tab] (https://elsevier.widen.net/s/dxrwznwh7s/unlp-case-study-document-ad-1)

- Green Chemistry | US EPA [New tab] (https://www.epa.gov/greenchemistry)

Attribution & References

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References

American Chemical Society. (2024). *What is green chemistry? (https://www.acs.org/greenchemistry/what-is-green-chemistry.html)*

American Chemical Society. (2024). *Explore the design principles of green & sustainable chemistry & engineering (https://www.acs.org/greenchemistry/principles.html).*

Doxsee, K. M. & Hutchinson, J. E. (2004). *Green Organic Chemistry*. Thomson: Brooks-Cole.

CHAPTER 19 - SUMMARY

19.1 Alkanes, Alkenes, Alkynes and Aromatic Hydrocarbons

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings. The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized π electron systems.

19.2 Alcohols and Ethers

Many organic compounds that are not hydrocarbons can be thought of as derivatives of hydrocarbons. A hydrocarbon derivative can be formed by replacing one or more hydrogen atoms of a hydrocarbon by a functional group, which contains at least one atom of an element other than carbon or hydrogen. The properties of hydrocarbon derivatives are determined largely by the functional group. The –OH group is the functional group of an alcohol. The –R–O–R– group is the functional group of an ether.

19.3 Aldehydes, Ethers, Carboxylic Acids and Esters

Functional groups related to the carbonyl group include the –CHO group of an aldehyde, the –CO– group of a ketone, the $-CO_2H$ group of a carboxylic acid, and the $-CO_2R$ group of an ester. The carbonyl group, a carbon-oxygen double bond, is the key structure in these classes of organic molecules: Aldehydes contain at least one hydrogen atom attached to the carbonyl carbon atom, ketones contain two carbon groups attached to the carbonyl carbon atom, carboxylic acids contain a hydroxyl group attached to the carbonyl carbon atom, and esters contain an oxygen atom attached to another carbon group connected to the carbonyl carbon atom. All of these compounds contain oxidized carbon atoms relative to the carbon atom of an alcohol group.

19.4 Amines and Amides

The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that

have a nitrogen atom bonded to one side of a carbonyl group are classified as amides. Amines are a basic functional group. Amines and carboxylic acids can combine in a condensation reaction to form amides.

19.5 Families of Organic Molecules – Functional Groups

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	C=C	C_2H_4	ethene
alkyne	C≡C	C_2H_2	ethyne
alcohol	R—Ö—H	CH_3CH_2OH	ethanol
ether	R—Ö—R'	$(C_2H_5)_2O$	diethyl ether
aldehyde	R—C(=O)—H	CH_3CHO	ethanal
ketone	R—C(=O)—R'	$CH_3COCH_2CH_3$	methyl ethyl ketone
carboxylic acid	R—C(=O)—Ö—H	CH_3COOH	acetic acid
ester	R—C(=O)—Ö—R'	$CH_3CO_2CH_2CH_3$	ethyl acetate
amine	R—N̈—H R—N̈—H R—N̈—R" (H, R', R')	$C_2H_5NH_2$	ethylamine
amide	R—C(=O)—N̈—R' (H)	CH_3CONH_2	acetamide

Summary of the Classification of Organic Compounds. (credit: *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/20-4-amines-and-amides)*, CC BY 4.0).

19.6 General Reactions of Carbon

All chemical reactions, whether in the laboratory or in living organisms, follow the same chemical rules. To understand both organic and biological chemistry, it's necessary to know not just *what* occurs but also *why* and *how* chemical reactions take place. In this chapter, we've taken a brief look at the fundamental kinds of organic reactions, we've seen why reactions occur, and we've seen how reactions can be described.

There are four common kinds of reactions: addition reactions take place when two reactants add together to give a single product; elimination reactions take place when one reactant splits apart to give two products; substitution reactions take place when two reactants exchange parts to give two new products; and rearrangement reactions take place when one reactant undergoes a reorganization of bonds and atoms to give an isomeric product.

Additionally, there are oxidation reactions that occur. Oxidation reactions are those that involve a reaction between hydrocarbons and oxygen producing carbon dioxide and water. An example of an oxidation reaction is combustion.

Lastly, oxidation–reduction reactions in organic chemistry are identified by the change in the number of

oxygens in the hydrocarbon skeleton or the number of bonds between carbon and oxygen or carbon and nitrogen.

19.7 Introduction to Green Chemistry

Green chemistry involves inventing new chemicals, new chemical processes and commercial products that reduce chemical hazards and minimize hazardous effects on human health and the environment. The philosophy is based on 12 principles and are summarized by four key ideas: prevent the formation of waste in the first place, employ safer reagents or solvents, implement selective and efficient transformations (reactions), and avoid unnecessary transformations. Current research has many examples of green chemistry in action.

Attribution & References

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- "18.1 Hydrocarbons (https://boisestate.pressbooks.pub/chemistry/chapter/21-1-hydrocarbons/)," "18.2 Alcohols and Ethers (https://boisestate.pressbooks.pub/chemistry/chapter/21-2-alcohols-and-ethers/)," "18.3 Aldehydes, Ketones, Carboxylic Acids, and Esters "and "18.4 Amines and Amides" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*
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CHAPTER 19 - REVIEW

19.1 – 19.5 Alkanes, Alkenes, Alkynes and Aromatic Hydrocarbons; Alcohols and Ethers; Aldehydes, Ketones, Carboxylic Acids and Esters; Amines and Amides; and Families of Organic Molecules – Functional Groups

1. Classify each compound as organic or inorganic. **Check answers**[1]
   a. C_3H_8O
   b. $CaCl_2$
   c. $Cr(NH_3)_3Cl_3$
   d. $C_{30}H_{48}O_3N$

2. Which compound is likely organic and which is likely inorganic? **Check answers**[2]
   a. a flammable compound that boils at 80°C and is insoluble in water
   b. a compound that does not burn, melts at 630°C, and is soluble in water

3. Classify each compound as organic or inorganic. **Check answers**[3]
   a. C_6H_{10}
   b. $CoCl_2$
   c. $C_{12}H_{22}O_{11}$

4. Classify each compound as organic or inorganic.
   a. CH_3NH_2
   b. $NaNH_2$
   c. $Cu(NH_3)_6Cl_2$

5. Which member of each pair has a higher melting point? **Check answers**[4]
   a. CH_3OH and $NaOH$
   b. CH_3Cl and KCl

6. Which member of each pair has a higher melting point?
   a. C_2H_6 and $CoCl_2$
   b. CH_4 and LiH

7. Locate and identify the functional groups in the following molecules.

A benzene ring with CH_2OH group on the C_1 and $NHCH_3$ group on the C_2 carbon is represented.

(b)

A six membered ring with a double bond and a carbonyl group is represented.

(c)

A benzene ring linked to an NH group linked to a $COCH_3$ group is represented.

(d)

A CH_3 group linked to a CH connected to an amine group is shown. The CH is connected to a $COOH$ group.

(e)

Two six membered rings fused together is shown. Both the rings have double bond, carbonyl group and a CH_3 group.

(f)

Two C H 3 groups linked to a triple bond linked to a carbonyl linked to a chlorine group.

(Credit: *Organic Chemistry* (OpenStax), CC BY-NC-SA 4.0).

19.6 General Reactions of Carbon

1. Classify each of the following reactions as an addition, elimination, substitution, or rearrangement: **Check answers**[5]
   a. 1. $CH_3Br + KOH \diamond">\diamond$
   b. 2. $CH_3CH_2Br \diamond">\diamond$
   c. 3. $H_2C=CH_2 + H_2 \diamond">\diamond \diamond">$

2. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 2-bromobutane with KCN. **Check answer** [6]

3. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 1-chloropentane with sodium methoxide.

4. Do you expect an elimination reaction to be favoured by a strong or a weak base? Why?

5. Why do molecules with π bonds behave as nucleophiles when mixed with strong electrophiles?

6. Sketch the mechanism for the nucleophilic substitution reaction of potassium cyanide with iodoethane.

7. Sketch the mechanism for the nucleophilic substitution reaction of NaSH with 1-bromopropane.

8. Sketch the mechanism for the elimination reaction of cyclohexylchloride with potassium ethoxide. Identify the electrophile and the nucleophile in this reaction.

9. What is the product of the elimination reaction of 1-bromo-2-methylpropane with sodium ethoxide?

10. Write the structure of the product expected from the electrophilic addition of HBr to *cis*-3-hexene.

11. Write the structure of the product expected from the electrophilic addition of 1-methylcyclopentene to HBr. Identify the electrophile and the nucleophile, and then write a mechanism for this reaction.

12. Write a synthetic scheme for making propene from propane. After synthesizing propene, how would you make 2-bromopropane?

13. Write a synthetic scheme for making ethylene from ethane. After synthesizing ethylene, how would you make iodoethane?

14. From the high-temperature reaction of Br_2 with 3-methylpentane, how many monobrominated isomers would you expect to be produced? Which isomer is produced from the most stable radical? **Check answer** [7]

15. For the photochemical reaction of Cl_2 with 2,4-dimethylpentane, how many different monochlorinated isomers would you expect to be produced? Which isomer is produced from the most stable precursor radical?

16. How many different radicals can be formed from the photochemical reaction of Cl_2 with

3,3,4-trimethylhexane? **Check answer** [8]

17. How many monobrominated isomers would you expect from the photochemical reaction of Br_2 with
    a. isobutene?
    b. 2,2,3-trimethylpentane?
18. Arrange acetone, ethane, carbon dioxide, acetaldehyde, and ethanol in order of increasing oxidation state of carbon.
19. What product(s) do you expect from the reduction of a ketone? the oxidation of an aldehyde?
20. What product(s) do you expect from the reduction of formaldehyde? the oxidation of ethanol? **Check answer** [9]

Links to Enhanced Learning

Samantha Sullivan-Sauer's H5P Matching Organic Chemistry Functional Groups (https://h5pstudio.ecampusontario.ca/content/2381).

Khan Academy reviews Identifying Functional Groups [New tab] (https://www.khanacademy.org/science/in-in-class-10-chemistry-india/x87dd2847d57ee419:in-in-carbon-and-its-compounds-coming-soon/x87dd2847d57ee419:in-in-functional-groups/e/identify-functional-groups-).

Science Geek reviews Organic Functional Groups [New tab] (https://www.sciencegeek.net/APchemistry/organic/functional.htm)

Create your own organic nomenclature quiz to identify functional groups using Organic Nomenclature [New tab] (https://orgchem101.com/nom/en/index.php). You can customize the types of questions you receive and get instant feedback.

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- "12.E: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Exercises)" In *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott, CC

Notes

1. a) organic b) inorganic c) inorganic d) organic
2. a) organic b) inorganic
3. a) organic b) inorganic c) organic
4. a) NaOH b) KCl
5. a) CH_3OH + KBr b) $H_2C{=}CH_2$ + KBr c) CH_3CH_3
6. CN^- is the nucleophile, and $C_2H_5C^{\delta+}HBrCH_3$ is the electrophile.
7. four; 3-bromo-3-methylpentane
8. seven
9. methanol; acetaldehyde, followed by acetic acid and finally CO_2

CHAPTER 19 - INFOGRAPHIC DESCRIPTIONS

Infographics used in Chapter 19

- 19.0a Natural and Man-made Chemicals
- 19.0b The chemical compounds behind the smell of flowers
- 19.5a A brief guide to doping in sports
- 19.6a Organic Chemistry Reaction Map
- 19.6b A Short Guide to Arrows in Chemistry
- 19.7a The 12 Principles of Green Chemistry
- 19.7b Dandelions: Diuretics and Car Tyres

19.0a Natural and Man-made Chemicals

Infographic about natural and man-made chemicals. A common misconception is that all man-made chemicals are harmful and all natural chemicals are good for us. However, many natural chemicals are just as harmful to human health, if not more so, than man-made chemicals.

Toxic effects seen at 1000mg/kg of body weight:

Natural:

- Muscimol: found in fly agaric mushrooms
- Solanine: found in green potatoes
- Amygdalin: found in apple seeds

Man-made:

- Ethylene glycol: Used in anti-freeze.
- Aspirin: used as a pain-reliving drug.
- Sodium thiopental: formerly used for lethal injections.

No toxic effects seen at 1000mg/kg of body weight:

Natural:

- Sucrose: also known as table sugar.
- Water: essential for life.
- Citric acid: found in lemons and limes.

Man-made:

- Teflon (PTFE): used in non-stick pans.
- Propylene glycol: food additive-solvent, humectant and thickener.
- Aspartame: artificial sweetener.

"Everything is poison, there is poison in everything. Only the dose makes a thing not a poison." Paracelsus, 1493-1541, "The father of toxicology".

Any substance, if given in large enough amounts, can cause death. Some are lethal after only a few nanograms, whilst others require kilograms to achieve a lethal dose.

Chemical toxicology is a sliding scale, not black and white – and whether a chemical is naturally occurring or man-made tells us nothing about its toxicity.

Read more about "Natural vs. Man-Made Chemicals – Dispelling Misconceptions [New tab] (https://www.compoundchem.com/2014/05/19/natural-vs-man-made-chemicals-dispelling-misconceptions/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

19.0b The chemical compounds behind the smell of flowers

Infographic on aroma compounds in common flowers. A wide range of compounds contribute to the scent of flowers. The following is a majority of the common flowers and a broad overview of their components, with chemical structure images. Note that the volatile aroma compounds can vary significantly between species.

- Roses: (-)-cis-rose oxide, beta-damascenone, beta-ionone.
- Carnations: eugenol, beta-carayophyllene, methyl salicylate.
- Violets: alpha-ionone, beta-ionone, beta-dihyroionone.
- Lilies: linalool, (E)-beta-ocimene, myrcene.
- Hyacinth: ocimenol, cinnamyl alcohol, ethyl 2-methoxybenzoate.
- Chrysanthemums: alpha-pinene, eucalyptol, chrysanthenone.
- Lilacs: (E)-beta-ocimene, lilac aldehyde, lilac alcohol.

Read more about "The Chemical Compounds Behind the Smell of Flowers [New tab] (https://www.compoundchem.com/2015/02/12/flowers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND.

19.5a A brief guide to doping in sports

Doping in sports has been in the news in the run up to the Olympics. What drugs will doping tests at the Olympics be looking for? See below some of the major groups of drugs used in doping, their effects, and why athletes might take them.

Anabolic agents: The largest class of prohibited drugs, and the most commonly detected. Anabolic steroids mimic the hormone testosterone, increasing muscle mass and physical strength. This class also includes some non-steroidal drugs. They have a range of side effects. 74 named banned agents. 48% of positive tests in 2014.

Stimulants: Stimulants are used to improve alertness, attention and energy. Many behave similarly to the hormones adrenaline and noradrenaline. They include amphetamines. Taking them can increase blood pressure and cause cardiac problems. 66 named banned agents. 15% of positive tests in 2014.

Hormones and modulators: A range of drugs which generally interfere with human hormones, including meldonium. They can be used with anabolic steroids, to suppress some of the undesirable effects of these drugs. Some affect oestrogen levels in the body, whereas others affect human metabolism. 20 named banned agents. 5% of positive tests in 2014.

Diuretics and masking agents: This includes furosemide. Diuretics remove fluids from the body and can be used by athletes to regular their body mass, as well as diluting urine so lower levels of banned substances are registered in tests. Masking agents are drugs taken to conceal the presence of illegal drugs in urine samples. 22 named banned agents. 13% positive tests in 2014.

Read more about "A Brief Guide to Doping in Sports [New tab] (https://www.compoundchem.com/2016/08/09/doping/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

19.6a Organic Chemistry Reaction Map

Organic Functional Group Interconversions

Starting Functional Group	Type of Reaction	Reaction Conditions	Resulting Functional Group
Acid anhydride	Acylation	ROH (anhydrous), reflux	Ester
Acid anhydride	Acylation	NH_3, reflux (gives primary amide); RNH_2, reflux (gives secondary amide)	Amide
Acid anhydride	Hydrolysis	H_2O, reflux	Carboxylic acid
Acyl chloride	Hydrolysis	H_2O	Carboxylic acid
Acyl chloride	Acylation	ROH, room temperature	Ester
Acyl chloride	Acylation	Conc. NH_3, room temperature (gives primary amide)	Amide
Alcohol	Elimination	Al_2O_3, 300 degree Celsius, or conc. H_2SO_4, reflux	Alkene
Alcohol	Elimination	H_4SO_4, (primary alcohols only)	Ether
Alcohol	Oxidation	Secondary only: $Cr_2O_7{}^{2-}$, H^+, reflux	Ketone
Alcohol	Oxidation	Primary only: $Cr_2O_7{}^{2-}$, H^+, distil	Aldehyde
Alcohol	Oxidation	Primary only: $Cr_2O_7{}^{2-}$, H^+, reflux	Carboxylic acid
Aldehyde	Reduction	$NaBH_6$ (aq, heat) or $LiAlH_6 (ether)$	Alcohol
Aldehyde	Oxidation	Primary only: $Cr_2O_7{}^{2-}$, H^+, distil	Carboxylic acid
Alkane	Other	Cracking (variety of products)	Alkene
Alkane	Substitution	Halogen and UV light	Haloalkane

Alkene	Addition	H_2, Ni cat., 150 degree Celsius , 5 atm	Alkane
Alkene	Addition	Hydrogen halide (aq), room temperature	Haloalkane
Alkene	Addition	Conc. H_2SO_4	Alkyl hydrogen sulfate
Alkene	Oxidation	O_2, Ag cat., 250-300 degree Celsius, 10-20 atm (ethene only); other alkenes: RCO_3H in CH_2Cl_2	Epoxide
Alkene	Other	Polymerization	Addition polymer
Alkene	Addition	Steam, 300 degree Celsius, 60 atm, conc. H_3PO_4 cat.	Alcohol
Alkyl hydrogen sulfate	Hydrolysis	H_2O, warm	Alcohol
Amide	Hydrolysis	H_2SO_4 and heat	Carboxylic acid
Amide	Elimination	P_2O_5, distil	Nitrile
Carboxylic acid	Reduction	$LiAlh_4$ in dry ether	Alcohol
Carboxylic acid	Substitution	$SOCl_2$, PCl_3 or PCl_5, reflux	Acyl chloride
Carboxylic acid	Elimination	P_2O_5, distil	Acid anhydride
Carboxylic acid	Esterification	ROH, conc. H_2SO_4 cat.	Ester
Ester	Hydrolysis	Reflux, H^+ or OH^+	Carboxylic acid
Haloalkane	Elimination	Hot, conc. KOH, alcoholic solution	Alkene
Haloalkane	Substitution	KCN, ethanolic solution, reflux	Nitrile
Haloalkane	Substitution	Conc. NH_3, heat in sealed tube	Amine
Haloalkane	Substitution	$NaOH(aq)$, reflux	Alcohol

Ketone	Reduction	$NaBH_4$, alcoholic or alkaline aq. solution, heat; or $LiAlh_4$ in dry ether	Alcohol
Nitrile	Reduction	$LiAlh_4$ (ether)	Amine
Nitrile	Hydrolysis	H^+ (aq), H_2O, reflux	Carboxylic acid

Read more about "Organic Chemistry Reaction Map [New tab] (https://www.compoundchem.com/2014/02/17/organic-chemistry-reaction-map/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

19.6b A Short Guide to Arrows in Chemistry

Infographic on a short guide to arrows in chemistry.

Chemical reaction arrows:

- **Reaction arrow**: These arrows point from the reactants to the products of a chemical reaction. Reaction conditions, reagents or catalysts may be written above or below the reaction arrow.
- **Multiple arrow**: Chemists use stacked multiple arrows to indicate that there are several reaction steps between the reagents and the products shown on either side of the arrows.
- **Broken arrow** (an arrow with an 'x' through it or an arrow with slanting parallel lines): Chemists use these arrows to indicate chemical reactions that do not take place. The reactants shown cannot be transformed into the products shown.
- **Reversible reaction arrow** (two arrows running parallel pointing opposite directions): Chemists use these arrows to indicate that a reaction is reversible – the reactants react to produce the products, but the products can also react to make the reactants.
- **Equilibrium arrow** (two parallel half-headed arrows pointing opposite directs): These arrows show that a reversible reaction is at equilibrium: the forward and reverse reactions occur at the same rate. The length of the arrows can be varied to show if reactants or products are favoured.
- **Retrosynthesis arrow** (two parallel lines with an arrow head pointing in one direction): Organic chemists us these arrows to show that the molecule on the left can be made from the stating material on the right, often through several reaction steps.

Electron movement arrows:

- **Resonance arrow** (one double headed arrow pointing opposite directions): Chemists use these arrows to show different resonance forms of the same molecule. The forms differ in electron arrangements; the true structure of the molecule is an average.

- **Curly arrow** (an arched arrow or half headed arched arrow): Curly arrows show electron movement in reaction mechanisms in organic chemistry. A double headed arrow shows the movement of an electron pair, while a single headed arrow shows the movement of a single electron.

Read more about "A short guide to different arrows in chemistry [New tab] (https://www.compoundchem.com/2022/12/12/arrows/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

19.7a The Twelve Principles of Green Chemistry: What it is, & Why it Matters

Green chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and the environment. While no reaction can be perfectly "green", the overall negative impact of chemistry research and the chemical industry can be reduced by implementing the 12 Principles of Green Chemistry whenever possible.

1. Waste prevention: Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.
2. Atom economy: Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.
3. Less hazardous chemical synthesis: Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.
4. Designing safer chemicals: Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.
5. Safer solvents and auxiliaries: Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.
6. Design for energy efficiency: Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature and pressure are optimal).
7. Use of renewable feedstocks: Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.
8. Reduce derivatives: Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.
9. Catalysis: Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.
10. Design for degradation: Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. Real-time pollution prevention: Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. Safer chemistry for accident prevention: Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

Read more about The Twelve Principles of Green Chemistry: What it is, & Why it Matters [New tab] (https://www.compoundchem.com/2015/09/24/green-chemistry/) by Andy Brunning on Compound Interest, CC BY-NC-ND 4.0.

19.7b Dandelion chemistry: Diuretics and the tyres of the future

Dandelions' Medicinal Uses

The Frech name for dandelion is pissenlit ('wet the bed') from their supposed ability to act as a diuretic, increasing the production of urine. Research attributes this to several diuretic compounds, but evidence for the effect is mixed. Dandelions' high potassium content helps replace potassium lost through urine.

Potassium content of dandelion leaves versus bananas: Dandelion leaves 397 mg per 100 g. Bananas 358 mg per 100 g. (Source: US Department of Agriculture – FoodData Central)

Studies show dandelion extracts or compounds have anti-inflammatory, anti-carcinogenic and anti-oxidative actions. These effects are mostly due to polyphenols and sesquiterpenese, also responsible for the bitter flavour of the leaves.

Taraxinic acid β-D-glucopyranoside – A sesquiterpene lactone in dandelion, also thought to be a contact allergen.

Rubber from Dandelions

The sticky white liquid that seeps out from dandelion stems when they're picked contains a natural latex, which can be turned into rubber. The roots of Russian dandelions (*Taraxacum koksaghzy*) contain a particularly high percentage of latex, making them ideal for rubber production.

Percentage of the USSR's rubber provided by the Russian dandelion during rubber shortages in World War II. 1941: 30%

Main constituent of rubber: cis-1,4-polyisoprene

In the past decade, tyre manufacturers have been developing dandelion rubber tyres. Currently bike tyres made from dandelion rubber are commercially available and tyres for cars and trucks will be available within ten years.

Read more about Dandelion chemistry: Diuretics and the tyres of the future [New tab] (https://www.compoundchem.com/2022/05/26/dandelion/) by Andy Brunning on Compound Interest, CC BY-NC-ND 4.0.

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