TECHNIQUE 1

SAFETY IN THE LABORATORY

As you begin your study of experimental organic chemistry, you need a basic understanding of safety principles for handling chemicals and equipment in the laboratory. Consider this chapter to be required reading before you perform any experiments.

The organic chemistry laboratory is a place where accidents can and do occur and where safety is everyone's business. While working in the laboratory, you are protected by the instructions in an experiment and by the laboratory itself, which is designed to safeguard you from most routine hazards. However, neither the experimental directions nor the laboratory facilities can protect you from the worst hazard—your own or your neighbors' carelessness.

In addition to knowledge of basic laboratory safety, you need to learn how to work safely with organic chemicals. Many organic compounds are flammable or toxic. Some can be absorbed through the skin; others are volatile and vaporize easily into the air in the laboratory. Despite the hazards, organic compounds can be handled with a minimum of risk if you are adequately informed about the hazards and necessary safe handling procedures and if you use common sense while you are in the laboratory.

At the first meeting of your lab class, local safety issues will be discussed—the chemistry department's policies on safety goggles and protective gloves, the location of safety showers and eye wash stations, and the procedures to be followed in emergency situations. The information in this chapter is intended to complement your instructor's safety rules and instructions.

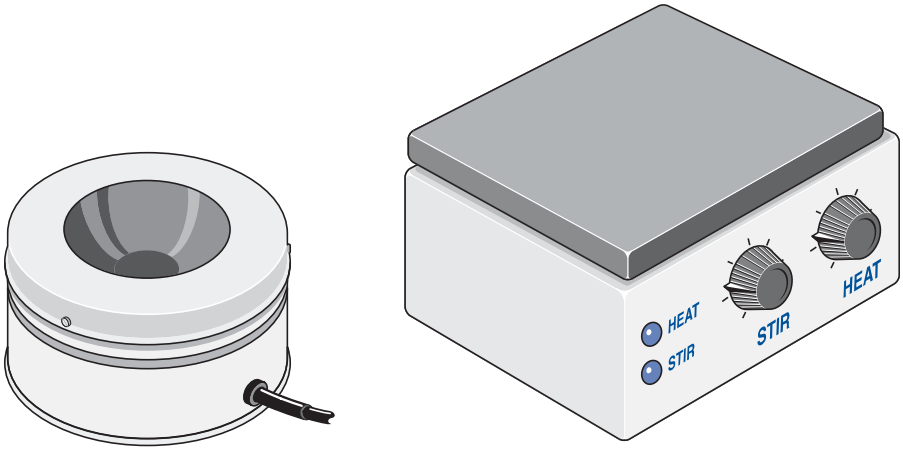
1.1 Causes of Laboratory Accidents

Laboratory accidents are of three general types: accidents involving fires and explosions, accidents producing cuts or burns, and accidents occurring from inhalation, absorption through the skin, or ingestion of toxic materials.

Fires and Explosions

Fire is the chemical union of a fuel with an oxidizing agent, usually molecular oxygen, and is accompanied by the evolution of heat and flame. Most fires involve ordinary combustible materials—hydrocarbons or their derivatives. Such fires are *extinguished* by removing oxygen or the combustible material or by decreasing the heat of the fire. Fires are *prevented* by keeping flammable materials away from a flame source or from oxygen (obviously, the former is easier).

Four sources of ignition are present in the organic laboratory: *open flames, hot surfaces* such as hot plates or heating mantles, *faulty electrical equipment*, and *chemicals.* The most obvious way to prevent a fire is to prevent ignition.



Ceramic heating mantle

Hot plate/stirrer

FIGURE 1.1
Heating devices.

Open flames. Open-flame ignition of organic vapors or liquids is easily prevented: **Never bring a lighted Bunsen burner or a match near a low-boiling-point flammable liquid.** Furthermore, because vapors from organic liquids can travel over long distances at bench or floor level (they are heavier than air), an open flame within 10 ft of diethyl ether, pentane, or other low-boiling organic solvents is an unsafe practice. In fact, the use of a Bunsen burner or any other flame in an organic laboratory should be a rare occurrence and done only with the permission of your instructor.

Hot surfaces. A hot surface, such as a hot plate or heating mantle, presents a trickier problem (Figure 1.1). An organic solvent spilled or heated recklessly on a hot plate surface may burst into flames. The thermostat on most hot plates is not sealed and can spark when it cycles on and off. The spark can ignite flammable vapors from an open container such as a beaker. Remove any hot heating mantle or hot plate from the vicinity before pouring a volatile organic liquid because the vapors from the solvent can be ignited by the hot surface of a hot plate or a heating mantle.

Faulty electrical equipment. Do not use appliances with frayed or damaged electrical cords as their use could lead to an electrical fire.

Chemical fires. Chemical reactions sometimes produce enough heat to cause a fire and explosion. For example, in the reaction of metallic sodium with water, the hydrogen gas that forms in the reaction can explode and ignite a volatile solvent that happens to be nearby.

Cuts and Injuries

Cuts and mechanical injuries are hazards anywhere, including the laboratory.

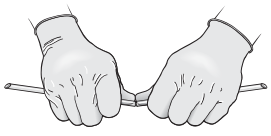


FIGURE 1.2
Breaking a glass rod properly.

Breaking glass rods or tubing. When you purposely break a glass rod or a glass tube, do it correctly. Score (scratch) a small line on one side of the tube with a file. Wet the scored line with a drop of water. Then, holding the tube on both sides with a paper towel and with the scored part away from you, quickly snap it by pulling the ends toward you (Figure 1.2).

Inserting glass into stoppers. Insert thermometers or glass tubes into corks, rubber stoppers, and thermometer adapters carefully and correctly. First, lubricate the end of the glass tube with a drop of water or glycerol. Then, while holding the tube with a towel **close** to the lubricated end, insert it slowly by firmly rotating it into the stopper. Never hold the thermometer by the end away from the stopper—it may break and the shattered end may be driven into your hand.

Chipped glassware. Check the rims of beakers, flasks, and other glassware for chips. Discard any piece of glassware that is chipped because you could be cut very easily by the sharp edge.

Inhalation, Ingestion, and Skin Absorption

Inhalation. The hoods in the laboratory protect you from inhalation of noxious fumes, toxic vapors, or dust from finely powdered materials. A hood is an enclosed space with a continuous flow of air that sweeps over the bench top, removing vapors or fumes from the area.

Because many compounds used in the organic laboratory are at least potentially dangerous, the best practice is to run every experiment in a hood, if possible. Your instructor will tell you when an experiment *must* be carried out in a hood. **Make sure that the hood is turned on before you use it.** Position the sash for the optimal airflow through the hood. If the optimum sash position is not indicated on the hoods in your laboratory, consult your instructor about how far to open the sash.

Ingestion. Ingestion of chemicals by mouth is easily prevented. **Never taste any substance or pipet any liquid by mouth.** Wash your hands with soap and water before you leave the laboratory. **No food or drink of any sort should be brought into a laboratory or eaten there.**

Absorption through the skin. Many organic compounds are absorbed through the skin. Wear the appropriate gloves while handling reagents and reaction mixtures. If you spill any substance on your skin, notify your instructor immediately, and wash the affected area thoroughly with water for 10–15 min.

1.2 Safety Features in the Laboratory

Organic laboratories contain many safety features for the protection and comfort of the people who work in them. It is unlikely that you will have to use the safety features in your lab, but in the event that you do, you must know what and where they are and how they operate.

Fire Extinguishers

Colleges and universities all have standard policies regarding the handling of fires. Your instructor will inform you whether evacuation of the lab or the use of a fire extinguisher takes priority at

your institution. **Learn where the exits from your laboratory are located.**

Fire extinguishers are strategically located in your laboratory. There may be several types, and your instructor may demonstrate their use. Your lab is probably equipped with either class BC or class ABC dry chemical fire extinguishers suitable for solvent or electrical fires.

Fire Blankets

Fire blankets are used for one thing and one thing only—to smother a fire involving a person's clothing. Fire blankets are available in most labs.

Safety Showers

Safety showers are for acid burns and other spills of corrosive, irritating, or toxic chemicals on the skin or clothing. If a safety shower is nearby, it can also be used when a person's clothing or hair is ablaze. The typical safety shower dumps a huge volume of water in a short period of time and thus is effective for both fire and acid spills, when speed is of the essence. **Do not use the safety shower routinely, but do not hesitate to use it in an emergency.**

Eye Wash Stations

You should always wear safety goggles while working in a laboratory, but if you accidentally splash something in your eyes, *immediately* use the eye wash station to rinse them with copious quantities of slightly warm water for 10–15 min. Learn the location of the eye wash stations in your laboratory and examine the instructions on them during the first (check-in) lab session.

First Aid Kits

Your laboratory or a nearby stockroom may contain a basic first aid kit consisting of such items as adhesive bandages, sterile pads, and adhesive tape for treating a small cut or burn. **All injuries, no matter how slight, should be reported to your instructor immediately.** Your instructor will indicate the location of the first aid station and instruct you in its use.

1.3 Preventing Accidents

Accidents can largely be prevented by common sense and knowledge of simple safety rules.

Personal Safety

1. Think about what you are doing while you are in the laboratory. Read the experiment before the laboratory session starts and perform laboratory operations with careful forethought.
2. It is a law in many states and common sense in the remainder to **wear safety glasses or goggles at all times in the laboratory.** Your institution may have a policy regarding wearing contact lenses in the laboratory; learn what it is and follow it. Wear clothing that covers and protects your body. **Shorts, tank tops, and sandals (or bare feet) are not suitable attire for the lab.** Avoid loose clothing and loose long hair, which are fire hazards or could become entangled in an apparatus. Laboratory aprons or lab coats may be required by your instructor. Always wash

your hands with soap and water at the end of the laboratory period.

3. **Never eat, chew gum, drink beverages, or apply cosmetics in the lab.**
4. Be aware of what your neighbors are doing. Many accidents and injuries in the laboratory are caused by other people. Often the person hurt worst in an accident is the one standing next to the place where the accident occurred. Make yourself aware of the procedures that should be followed in case of any accident. [See Technique 1.4].
5. **Never work alone in the laboratory.** Being alone in a situation in which you may be helpless can be life threatening.
6. Women who are pregnant or who become pregnant should discuss with the appropriate medical professionals the advisability of working in the organic chemistry laboratory.

Precautions When Handling Reagents

Never taste, ingest, or sniff directly any chemical. Always use the hood when working with volatile, toxic, or noxious materials. Handle all chemicals carefully, and remember that many chemicals can enter the body through the skin and eyes, as well as through the mouth and lungs.

Protective attire. Wear a lab coat or apron when working with hazardous chemicals. Cotton is the preferred fabric because synthetic fabrics could melt in a fire or undergo a reaction that causes the fabric to adhere to the skin and cause a severe burn.

Disposable gloves. Disposable gloves are available in all laboratories. **Wear gloves** to prevent chemicals from coming into contact with your skin unnecessarily. Table 1.1 lists a few common chemicals

TABLE 1.1 Chemical resistance of common types of gloves to various compounds

	GLOVE TYPE		
Compound	Neoprene	Nitrile	Latex
Acetone	good	fair	good
Chloroform	good	poor	poor
Dichloromethane	fair	poor	poor
Diethyl ether	very good	good	poor
Ethanol	very good	excellent	excellent
Ethyl acetate	good	poor	fair
Hexane	excellent	excellent	poor
Methanol	very good	fair	fair
Nitric acid (conc.)	good	poor	poor
Sodium hydroxide	very good	excellent	excellent
Sulfuric acid (conc.)	good	poor	poor
Toluene	fair	fair	poor

The information in this table was compiled from the Web site http://www.inform.umd.edu/CampusInfo/Departments/EnvirSafety/Is/gloves.html and from "Chemical Resistance and Barrier Guide for Nitrile and Natural Rubber Latex Gloves," Safeskin Corporation, San Diego, CA, 1996.

and the chemical resistance to each one provided by three common types of gloves. A more extensive chemical resistance table for types of gloves may be posted in your laboratory. Additional information on disposable gloves and tables listing glove types and their chemical resistance are also available from many Internet Web sites, for example:

http://www.microflex.com
http://www.ansellpro.com
http://www.des.umd.edu/ls/gloves
http://www.hazmat.msu.edu:591/glove_guide
http://www.admin.cam.ac.uk/offices/safety

Chemical hazards. Consult your instructor if you are in doubt about the safe handling procedures for any chemical. If you are handling a particularly hazardous compound, wear the appropriate type of gloves and know what the safe handling procedures for it are *before* you begin the experiment.

Flammable solvents. Flammable solvents with boiling points of less than 100°C, such as diethyl ether, methanol, pentane, hexane, and acetone, should be distilled, heated, or evaporated on a steam bath or heating mantle, **never on a hot plate or with a Bunsen burner**. Use an Erlenmeyer flask fitted with a cork—**never an open beaker**—for temporarily storing flammable solvents at your work area.

Order in the Laboratory

Keep your laboratory space clean and neat. In addition to your own bench area, the balance and chemical dispensing areas should be left clean and orderly. **If you spill anything while measuring out your chemicals, notify your instructor and clean it up immediately.** After weighing a chemical, replace the cap on the container and dispose of the weighing paper in the appropriate receptacle. Keep gas and water valves closed whenever they are not in use. Floors can become very slippery if water is spilled; wipe up any spill immediately.

Burns and Other Injuries

Remember that both glass and the tops of hot plates look the same when hot as when cold. When heating glass, do not touch the hot spot. Do not put hot glass on a bench where someone else might pick it up.

Steam and boiling water cause severe burns. Turn off the steam source before removing containers from the top of a steam bath or steam cone. The screw attached to the rounded handle that controls a steam line can become very hot; be careful not to touch it when you turn the steam on or off. Handle containers of boiling water very carefully.

Explosions

Never heat a closed system! Also, never completely close off an apparatus in which a gas is being evolved: always provide a vent in order to prevent an explosion.

1.4 What to Do if an Accident Occurs

If an accident occurs, act quickly, but think first. The first few seconds after an accident may be crucial. Acquaint yourself with the following instructions so that you can be of immediate assistance.

Fire

Your laboratory instructor will inform you on the first day of lab about the proper response to a fire. **It is important to know the policy of your institution concerning when to evacuate the building and when to use a fire extinguisher.**

In case of a fire in the lab, get out of danger and then immediately notify your instructor. If possible, remove any containers of flammable solvents from the fire area.

Know the location of the fire extinguishers and how they operate. A fire extinguisher will always be available. If you use one, aim low and direct its nozzle first toward the edge of the fire and then toward the middle. Tap water is not always useful for extinguishing chemical fires and can actually make some fires worse, so always use the fire extinguisher.

Be sure you know where the fire blanket and safety showers are located. If a person's clothing catches fire, **drop the person to the floor** and roll the person's body tightly in a fire blanket. If the blanket is wrapped around a person who is standing, it may direct the flames toward the person's face. If your clothing is on fire, do not run. Rapid movement fans flames.

General Policy Regarding Accidents

Always inform your instructor immediately of any accident that happens to you or your neighbors. **Let your instructor decide whether a physician's attention is needed.** If a physician's attention is necessary, an injured person should always be accompanied to the medical facility; the injury may be more serious than it initially appears.

Minor Cuts and Burns

Learn the location of the first aid kit and the materials it contains for the treatment of simple cuts and burns. **Notify your instructor immediately if you are cut or burned or if any chemical is spilled on your skin. Seek immediate medical attention** for anything except the most trivial cut or burn.

Cuts. Press on the cut to help slow the bleeding. Apply a bandage when the bleeding has ceased. If the cut is large or deep, seek immediate medical attention.

Heat burns. Apply cold water for 10–15 min to any heat burn. Seek immediate medical attention for any extensive burn.

Chemical burns. The first thing to do if any chemical is spilled on your skin, unless you have been specifically told otherwise, is to wash the area well with water for 10–15 min. This treatment will rinse away the excess chemical reagent. For acids, bases, and toxic chemicals, thorough washing with water will save pain later. Skin contact with a strong base usually does not produce immediate pain

or irritation, but serious tissue damage (especially to the eyes) can occur if the affected area is not immediately washed with copious amounts of water. Specific treatments for chemical burns are published in *The Merck Index*. Seek immediate medical treatment for any serious chemical burn.

Chemical splash in the eyes. If a chemical gets into your eyes, immediately go to the eye wash station and wash your eyes with a copious amount of slightly warm water. Position your head so that the stream of water from the eye wash fountain is directed at your eyes. **Hold your eyes open** to allow the water to flush the eyeballs for 10–15 minutes. Because this position is difficult, assistance may be required. Do not hesitate to call for help. Do not use very cold water because it can damage the eyeballs. Seek medical treatment immediately after using the eye wash for *any* chemical splash in the eyes.

If you are wearing contact lenses, they must be removed for the use of an eye wash station to be effective, an operation that is extremely difficult if a chemical is causing severe discomfort to your eyes. Therefore, **it is prudent not to wear contact lenses in the laboratory.**

1.5 Chemical Toxicology

Most substances are toxic at some level, but the level varies over a wide range. A major concern in chemical toxicology is quantity or dosage. It is important that you understand how toxic compounds can be handled safely in the organic laboratory.

The toxicity of a compound refers to its ability to produce injury once it reaches a susceptible site in the body. A compound's toxicity is related to its probability of causing injury and is a species-dependent term. What is toxic for people may not be toxic for other animals and vice versa. A substance is ***acutely toxic*** if it causes a toxic effect in a short time; it is ***chronically toxic*** if it causes toxic effects with repeated exposures over a long duration.

Fortunately, not all toxic substances that accidentally enter the body reach a site where they can be deleterious. Even though a toxic substance is absorbed, it is often excreted rapidly. Our body protects us with various devices: the nose, scavenger cells, metabolism, and rapid exchange of good air for bad. Many foreign substances are detoxified and discharged from the body very quickly.

Action of Toxic Substances on the Body

Although many substances are toxic to the entire system (arsenic, for example), many others are site specific. Carbon monoxide, for example, forms a complex with the hemoglobin in our blood, diminishing the blood's ability to absorb and release oxygen; it also poisons the action of mitochondrial aerobic metabolism.

In some cases, the metabolites of a compound are more toxic than the original compound. An example is methanol poisoning. The formic acid that is formed in the body's metabolism of methanol affects the optic nerve, causing blindness. The metabolism of some relatively harmless polycyclic aromatic hydrocarbons produces

potent carcinogenic compounds. As far as the body is concerned, it does not matter whether the toxicity is due to the original substance or to a metabolic product of it.

Toxicity Testing and Reporting

Consumers are protected by a series of laws that define toxicity, the legal limits and dosages of toxic materials, and the procedures for measuring toxicities.

Acute oral toxicity is measured in terms of LD_{50} (***LD*** stands for "lethal dose"). $\boldsymbol{LD_{50}}$ represents the dose, in milligrams per kilogram of body weight, that will be fatal to 50% of a certain population of animals. Other tests include dermal toxicity (skin sensitization) and irritation of the mucous membranes (eyes and nose). *The Merck Index* is a useful reference for the toxicity of organic compounds and lists the LD_{50} of many compounds.

The toxicity of virtually all chemical compounds that are commercially available has been reported, and every year the toxicities of many more compounds become known. Chemists and biologists have learned a great deal about toxicities in the past few decades. A wall chart of toxicities for many common organic compounds may be hanging in your laboratory or near your stockroom.

1.6 Where to Find Chemical Safety Information

Material Safety Data Sheets

All laboratories must make available a Material Safety Data Sheet (MSDS) for every chemical used in the laboratory. Every MSDS contains information on a list of topics required by law that describe the physical properties, hazards, safe handling and storage practices, and first aid information for the chemical. Manufacturers are required to prepare an MSDS for every chemical sold; the content is the same for a specific chemical, but the format in which the information is presented differs from one company to another. An MSDS from one company may be easy to read while that from another may be more difficult to understand.

MSDS information for thousands of compounds can be obtained easily on the Internet. The Web sites for chemical companies provide MSDSs for specific compounds as free, downloadable PDF files. Example companies are Sigma-Aldrich and Acros Organics:

http://www.sigmaaldrich.com

http://www.acros.com

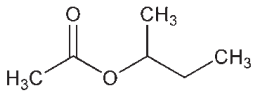
If your college or university subscribes to them, the following Web sites have downloadable PDF files of MSDSs:

http://www.MSDSonline.com

http://www.chemwatch.na.com

In addition to a complete MSDS, Chemwatch also provides mini MSDSs that briefly summarize the essential safety information for compounds in clear, concise language and pictograms.

1536. *sec*-Butyl Acetate. [105-46-4] Acetic acid 1-methylpropyl ester; acetic acid *sec*-butyl ester. $C_6H_{12}O_2$; mol wt 116.16. C 62.04%, H 10.41%, O 27.55%. Prepd from *sec*-butanol and acetic anhydride: R. Altschul, *J. Am. Chem. Soc.* **68**, 2605 (1946). Prepn of *d*- and *l*-form: J. Kenyon *et al.*, *J. Chem. Soc.* **1935**, 1072. Manuf: *Faith, Keyes & Clark's Industrial Chemicals*, F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 171-177.



***dl*-Form.** Liquid. d_{27} 0.865. bp_{761} 111-111.5°. n_D^{27} 1.3848. Flash pt, open cup: 88°F (31°C). Slightly sol in water; sol in alcohol, ether.

***d*-Form.** [66610-38-6] Acetic acid (1*S*)-1-methylpropyl ester. $[\alpha]_{546.1}^{18}$ +10.52° (neat).

***l*-Form.** [54657-08-8] Acetic acid (1*R*)-1-methylpropyl ester. Liquid, bp 116-117°. d_4^{19} 0.873. $[\alpha]_{546.1}^{19}$ −20.19° (neat). $[\alpha]_{546.1}^{19}$ −18.86° (c = 5.046 in ethanol). n_D^{18} 1.3899.

Caution: Potential symptoms of overexposure are irritation of eyes; headache; drowsiness; narcosis; dryness of upper respiratory system and skin. *See NIOSH Pocket Guide to Chemical Hazards* (DHHS/NIOSH 97-140, 1997) p 38.

FIGURE 1.3
Monograph 1536, for *sec*-Butyl acetate from page 256 of *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 14th ed. (Reproduced with permission from *The Merck Index*, Fourteenth edition. Copyright © 2006 by Merck & Co., Inc., Whitehouse Station, NJ, USA. All rights reserved.)

The Merck Index

A brief synopsis of safety information for common organic compounds can be found in *The Merck Index*. The entry for sec-butyl acetate lists the caution information at the end (Figure 1.3).

Hazardous Materials Identification Systems

The labels on chemical containers carry warnings about the hazards involved in handling and shipping the compounds. The four-diamond symbol and a globally harmonized system of pictograms are the most commonly used hazardous materials identification systems.

Four-diamond symbol. Chemical suppliers put a color-coded, four-diamond symbol—developed by the National Fire Protection Association—on the container label of all reagents they sell (Figure 1.4). The four diamonds provide information on the hazards associated with handling the compounds:

fire hazard (top, red diamond)
reactivity hazard (right, yellow diamond)
specific hazard (bottom, white diamond)
health hazard (left, blue diamond)

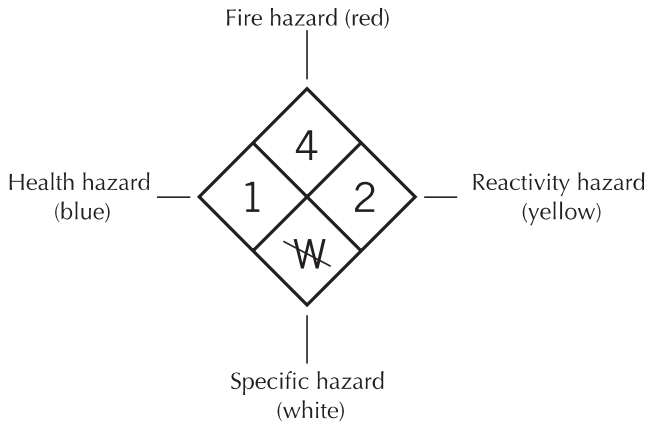


FIGURE 1.4
Four-diamond label for chemical containers indicating health, fire, reactivity, and special hazards. The symbol in the specific hazard diamond indicates that the compound is reactive with water and should not come into contact with it.

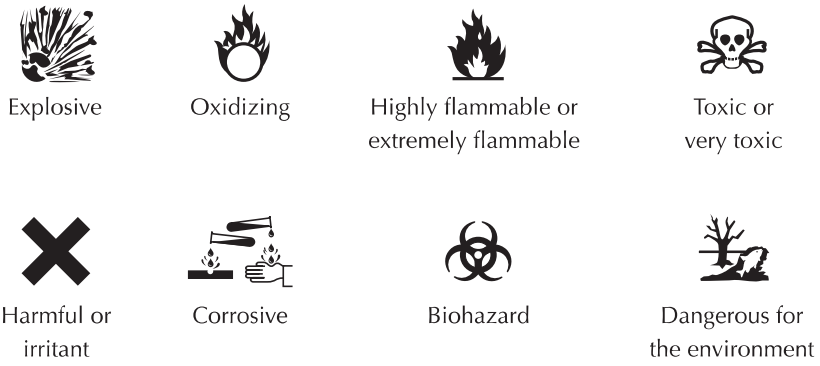


FIGURE 1.5 Globally Harmonized System (GHS) pictograms indicating chemical hazards.

The numerical values in the diamonds range from 0 to 4—0 indicates no chemical hazard and 4 indicates extreme chemical hazard.

Globally Harmonized System (GHS) of pictograms. Many chemical suppliers also indicate hazards by printing the universally understandable pictograms approved at the UN-sponsored Rio Earth Summit in 1992 on the labels of their reagents (Figure 1.5). Since then the pictograms have become a widely accepted standard on chemical labels around the world.

Other warnings found on chemical labels. Chemical labels may also include warnings such as "Irritant," "Lachrymator," "Cancer suspect agent," "Mutagen," or "Teratogen." Definitions of these terms follow:

Irritant: Substance causes irritation to skin, eyes, or mucous membranes.
Lachrymator: Substance causes irritation and watering of the eyes (tears).
Cancer suspect agent: Substance is carcinogenic in experimental animals at certain dose levels, by certain routes of administration, or by certain mechanisms considered relevant to human exposure. Available epidemiological data do not confirm an increased cancer risk in exposed humans.
Mutagen: Substance induces genetic changes.
Teratogen: Substance induces defects in a developing fetus.

Further Reading

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