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Safety in the chemical laboratory

The chemistry laboratory is a dangerous environment in which to work. The dangers are often unavoidable, since chemists regularly have to use hazardous materials. However, with sensible precautions, the laboratory is probably no more dangerous than your home, be it house or apartment, which, if you stop to think about it, also abounds with hazardous materials and equipment – household bleach, pharmaceutical products, herbicides and insecticides, natural or bottled gas, kitchen knives, diverse electrical equipment, the list goes on and on – all of which are taken for granted. In the same way that you learn to cope with the hazards of everyday life, so you learn good laboratory practice, which goes a long way to help minimize the dangers of organic chemistry.

The experiments in this book have been carefully chosen to exclude or restrict the use of exceptionally hazardous materials, while still highlighting and exemplifying the major reactions and transformations of organic chemistry. However, most chemicals are harmful in some respect, and the particular hazards associated with the materials **should not be ignored**. Unfortunately, it has not been possible to exclude totally the use of some chemicals, such as chloroform and dichloromethane, which are described as ‘cancer suspect agents’, but if handled correctly with proper regard for the potential hazard, there is no reason why such compounds cannot be used in the organic chemistry laboratory. Ultimately, laboratory safety lies with the individual; *you* are responsible for carrying out the experiment in a safe manner without endangering yourself or other people, and therefore it is *your* responsibility to learn and observe the essential safety rules of the chemical laboratory.

Prior to starting any experiment, a risk assessment should be prepared to identify the hazards, the likelihood of harm and any steps you can undertake to reduce the level of risk. The material safety data sheets (MSDSs) for any chemicals you are planning to use will provide valuable information. The risk assessment should also consider the end product and any intermediates that may be produced, as these may have hazardous properties.

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Companion website: www.wiley.com/go/cranwell/EOC

Legislation varies between the United Kingdom, Europe and the United States, therefore the references given in this section are generally for the UK only. Further information for a UK laboratory can be found at the following websites:

http://www.hse.gov.uk/coshh/basics/assessment.htm
http://www.hse.gov.uk/risk/controlling-risks.htm

1.1 Essential rules for laboratory safety

The essential rules for laboratory safety can be expressed under two simple headings: **ALWAYS** and **NEVER**.

Most of these rules are common sense and need no further explanation. Indeed, if asked to name the single most important factor that contributes towards safety in the laboratory, the answer is simple: common sense.

ALWAYS

- familiarize yourself with the laboratory safety procedures
- wear eye protection and a laboratory coat
- dress sensibly
- wash your hands before leaving the laboratory
- read the instructions carefully before starting any experiment
- check that the apparatus is assembled correctly
- handle all chemicals with great care
- keep your working area tidy
- attend to spills immediately
- ask your instructor if in doubt
- carry out a risk assessment

NEVER

- eat or drink in the laboratory
- smoke in the laboratory
- apply makeup in the laboratory
- inhale, taste or sniff chemicals
- fool around or distract your neighbours
- run in the laboratory
- work alone
- carry out unauthorized experiments

1.1.1 Laboratory safety procedures

Your laboratory will have certain safety procedures with which you must be familiar. Some of these procedures are legal requirements; others will have been laid down by the department. Make sure you know:

- where all the exits to the laboratory are, in the event of an evacuation because of fire or other incident;
- the precise location of fire extinguishers, fire blankets, sand buckets, safety showers and eye-wash stations;
- what type the fire extinguishers are and how to operate them, especially how to remove the safety pin.

If you are unsure of which type of extinguisher to use then do not attempt to fight the fire; the use of an incorrect type can, and probably will, make things worse.

1.1.2 Eye protection

You must wear eye protection at all times in the laboratory. Even if you are just writing in your notebook, your neighbour may be handling hazardous materials. The use of corrosive chemicals is not the only hazard for eyes, as many solvents are just as painful and irritating. Eyes are particularly vulnerable to damage from sharp objects such as broken glass and from chemicals, and therefore must always be protected to prevent permanent damage. Protection should be in the form of approved safety goggles or safety glasses (http://www.hse.gov.uk/foi/internalops/oms/2009/03/om200903app3.pdf). Ordinary prescription glasses do not provide adequate protection, since they do not have side shields and may not have shatter-proof lenses. If you are going to do a lot of laboratory work, it is probably worth obtaining a pair of safety glasses fitted with prescription lenses. Alternatively, wear goggles over your normal glasses for full protection. Contact lenses are often forbidden in chemical laboratories, because in the event of an accident, chemicals can get under the lens and damage the eye before the lens can be removed. Even if contact lenses are permitted, then you must wear well-fitting goggles for protection. Inform your instructor, the laboratory staff and your neighbours that you are wearing contact lenses so that they know what to do in case of accident. Although no experiments in this book require them, full face shields should be worn for particularly hazardous operations. If a chemical does get into the eye, you must take swift action. The appropriate action is discussed in Section 1.4.5.

Contact lenses

1.1.3 Dress

Dress sensibly in the laboratory. The laboratory is no place to wear your best clothes, since however careful you are, small splashes of chemicals or acids are inevitable. For this reason, shorts or short skirts are unsuitable for laboratory work and are forbidden in many institutions. A laboratory coat should always be worn, and loose-fitting sleeves that might catch on flasks and other equipment should be rolled back. Long hair is an additional hazard, and should always be tied back. Proper shoes should be worn; there may be pieces of broken glass on the laboratory floor, and sandals do not provide adequate protection from glass or from chemical spills.

1.1.4 Equipment and apparatus

Never attempt to use any equipment or apparatus unless you fully understand its function. This is particularly true of items such as vacuum pumps, rotary evaporators and cylinders of compressed gas, where misuse can lead to the damage of expensive equipment, your experiment being ruined or, most serious of all, an accident. Remember the golden rule:

If in doubt, ask.

Before assembling the apparatus for your experiment, check that the glassware is clean and free from cracks or imperfections. Always check that the apparatus is properly clamped, supported and correctly assembled *before* adding any chemicals. Again, if in any doubt as to how to assemble the apparatus, ask.

1.1.5 Handling chemicals

Chemicals are hazardous because of their toxic, corrosive, flammable or explosive properties. Examples of the various categories of hazardous chemicals are given in the next section, but all chemicals should always be handled with great care. The major hazard in the organic chemistry laboratory is fire. Most organic compounds will burn when exposed to an open flame and many, particularly solvents that are often present in large quantities in the laboratory, are highly flammable. A serious solvent fire can raise the temperature of the laboratory to well over 100 °C within minutes of it starting. Good laboratory practice demands that there should be no open flames in the organic chemistry laboratory. Steam baths, heating mantles and hotplates should be used wherever possible to heat reaction mixtures and solvents. **Never** transfer a flammable liquid without checking that there are no open flames in the vicinity. Remember that solvent vapour is heavier than air and will therefore travel along bench tops and down into sinks and drains; never pour flammable solvents down the sink.

Always check for flammable solvents before lighting a burner

Never pour flammable solvents down the sink

Avoid inhaling the vapours from organic compounds at all times, and whenever possible use a reliable fume hood. The use of a good fume hood is essential for operations involving particularly toxic materials and for reactions that evolve irritating or toxic vapours.

Wear gloves when handling corrosive chemicals

Avoid skin contact with chemicals at all times. This is particularly important when handling corrosive acids and chemicals that are easily absorbed through the skin. It is best to wear disposable gloves that offer appropriate protection to the chemicals being handled (see MSDS for information); this minimizes the risk of chemicals coming into contact with the skin, but you must always be alert to the risk of seepage under the glove that will exacerbate the dangers due to the material being held in close contact with the skin. The risk is also reduced by good housekeeping, ensuring that your bench and areas around the balance are kept clean and tidy. When highly corrosive or toxic chemicals are being handled, thin disposable gloves are inadequate and thick protective gloves must be worn. However, remember to remove gloves before leaving the laboratory; **do not contaminate door handles and other surfaces with soiled gloves.**

The gloves you use need to be appropriate for the task being undertaken. There are breakthrough times and chemical compatibility tests that will determine what to wear.

For the legislation surrounding chemical/microorganism gloves within Europe, see EN 374 (http://www.hse.gov.uk/foi/internalops/oms/2009/03/om200903app5.pdf).

1.1.6 Spills

All chemical spills should be cleared up immediately. Always wear gloves when dealing with a spill. Solids can be swept up and put in an appropriate waste container. Liquids are more difficult to deal with. Spilled acids must be neutralized with solid sodium hydrogen carbonate or sodium carbonate, and alkalis must be neutralized with sodium bisulfate. Neutral liquids can be absorbed with sand or paper towels, although the use of sand is strongly advised, since paper towels are not appropriate for certain spills. **Generation of gases as a result of using water or a damp paper towel could occur.**

If the spilled liquid is very volatile, it is often best to clear the area and let the liquid evaporate. When highly toxic chemicals are spilt, alert your neighbours, inform your instructor and ventilate and clear the area immediately.

If you are unsure of how to proceed then seek advice, as you could make things worse.

1.2 Hazardous chemicals

One of the fundamental rules of laboratory safety requires you to read the instructions before starting any experiment. In Europe, hazard symbols must conform to the Globally Harmonized System for labelling and packing (http://www.unece.org/trans/danger/publi/ghs/pictograms.html). Some examples of the commonly used symbols are shown in Fig. 1.1, and examples of each type of hazardous chemical are given in the following sections.

1.2.1 Flammable reagents

Always follow the general guidelines (Section 1.1.5) when handling flammable reagents.

Solvents constitute the major flammable material in the organic chemistry laboratory. The following organic solvents are all commonly used and are highly flammable: hydrocarbons such as *hexane*, *light petroleum* (*petroleum*

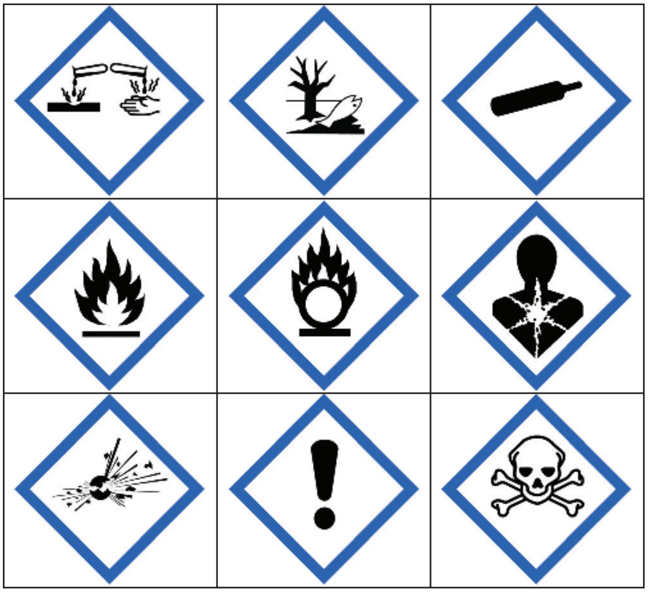

Fig. 1.1 Common hazard warning signs. Source: Reproduced from www.unece.org/trans/danger/publi/ghs/pictograms.html.

ether), *benzene* and *toluene*; alcohols such as *ethanol* and *methanol*; esters such as *ethyl acetate*; ketones such as *acetone*.

Ethers require a special mention because of their tendency to form explosive peroxides on exposure to air and light. *Diethyl ether* and *tetrahydrofuran* are particularly prone to this and should be handled with great care. In addition, diethyl ether has a very low flash point and has a considerable narcotic effect.

Carbon disulfide is so flammable that even the heat from a steam bath can ignite it. The use of this solvent should be avoided at all times.

Additionally, some gases, notably *hydrogen*, are highly flammable, as are some solids, particularly finely divided metals such as *magnesium* and *transition metal catalysts*. Some solids such as *sodium* and *lithium aluminium hydride* are described as flammable because they liberate hydrogen on reaction with water.

1.2.2 Explosive reagents

Some chemicals constitute explosion hazards because they undergo explosive reactions with water or other common substances. The alkali metals are common examples: *sodium metal* reacts violently with water; *potassium metal* reacts explosively with water.

Other compounds contain the seeds of their own destruction. This usually means that the molecule contains a lot of oxygen and/or nitrogen atoms, and can therefore undergo internal redox reactions, or eliminate a stable molecule such as N_2. Such compounds are often highly shock sensitive and constitute a considerable explosion hazard, particularly when dry. Examples include *polynitro compounds*, *picric acid*, *metal acetylides*, *azides*, *diazo compounds*, *peroxides* and *perchlorate salts*. These are avoided in procedures described in this book.

If you have to use potentially explosive reagents, wear a face mask and work on the smallest scale possible and behind a shatter-proof screen. Never do so without consulting an instructor and alert others before commencing the procedure.

1.2.3 Oxidizers

Oxidizers are an additional hazard in the chemical laboratory, since they can cause fires simply by coming into contact with combustible material such as paper.

Nitric and *sulfuric acids*, in addition to being highly corrosive, are both powerful oxidizers.

Reagents such as *bleach*, *ozone*, *hydrogen peroxide*, *peracids*, *chromium(VI) oxide* and *potassium permanganate* are all powerful oxidizers.

1.2.4 Corrosive reagents

Always wear appropriate protective gloves when handling corrosive reagents. Spills on the skin should be washed off immediately with copious amounts of water.

The following acids are particularly corrosive: *sulfuric, hydrochloric*, *hydrofluoric*, *hydrobromic*, *phosphoric* and *nitric acid*, as are organic acids such as *carboxylic acids* and *sulfonic acids*. *Hydrofluoric acid* is particularly corrosive and should be treated with the greatest care because of its tendency to cause extreme burns and nerve damage if spilled.

Phenol is a particularly hazardous chemical and causes severe burns, in addition to being extremely toxic and rapidly absorbed through the skin.

Alkalis such as *sodium hydroxide*, *potassium hydroxide* and, to a lesser extent, *sodium carbonate* are also extremely corrosive, as are *ammonia*, *ammonium hydroxide* and organic bases such as *triethylamine* and *pyrrolidine*.

Bromine is an extremely unpleasant chemical. It causes severe burns to the skin and eyes and must be handled in a fume hood. In addition, its high density and volatility make it almost impossible to transfer without spills when using a pipette.

Thionyl chloride, *oxalyl chloride*, *aluminium chloride* and other reagents that can generate HCl by reaction with water are also corrosive and cause severe irritation to the respiratory system.

1.2.5 Harmful and toxic reagents

The distinction between *harmful* and *toxic* is one of degree; most organic compounds can be loosely described as harmful, but many are much worse than that, and are therefore classified as toxic. Commonly encountered compounds that are particularly toxic and therefore must always be

Always handle toxic chemicals in a fume hood

handled in a fume hood include: *aniline*, *benzene*, *bromine*, *dimethyl sulfate*, *chloroform*, *hexane*, *hydrogen sulfide*, *iodomethane*, *mercury salts*, *methanol*, *nitrobenzene*, *phenol*, *phenylhydrazine*, *osmium tetraoxide*, *potassium cyanide* and *sodium cyanide*. You must always be aware of the difference between *acute* and *chronic* toxicity. The effects of acute toxicity are usually recognizable more or less immediately (for example, inhalation of ammonia) and appropriate remedial action can be taken promptly. Chronic effects are much more pernicious, exerting their influence during long periods of exposure and generally manifesting their effects only when irrecoverable long-term damage has been caused. Many compounds are classed as *cancer suspect agents*, for instance. This need not negate their use in the laboratory, but does require particularly stringent precautions to avoid exposure and these compounds must always be handled in an efficient fume hood.

When using the fume hood, make sure that the glass front (sash) is pulled well down. This ensures sufficient air flow to prevent the escape of toxic fumes. As a general rule, never start any experiment involving a highly toxic chemical until you have read and understood the instructions and safety information, fully appreciate the nature of the hazard, and know what to do in the event of an accident.

1.2.6 Suspected carcinogens

The exposure of healthy cells to certain chemicals (carcinogens) is known to result in tumour formation. The period between the exposure and the appearance of tumours in people can be several years, or even decades, and therefore the dangers are not immediately apparent. The utmost care is required when handling such chemicals. This means that the chemical is either known to cause tumours in people or in animals, or is strongly suspected of doing so.

The following compounds or compound types should be treated as suspected carcinogens: biological alkylating agents such as *iodomethane*, *epoxides* and *dimethyl sulfate*; *formaldehyde*; *hexane*; *benzene*; aromatic amines such as *2-naphthylamine* and *benzidine*; polynuclear aromatic hydrocarbons (PAHs) such as *benzpyrene*; *hydrazines* in general, *hydrazine* itself and *phenylhydrazine*; *nitrosamines*; *azo compounds*; *chromium(VI) compounds*; chlorinated hydrocarbons such as *carbon tetrachloride*; *chloroform* and *vinyl chloride*; *thiourea* and *semicarbazide hydrochloride*.

1.2.7 Irritants and lachrymators

Many organic compounds are extremely irritating to the eyes, skin and respiratory system. To minimize the chance of exposure to the reagent or its vapours, the following chemicals should always be handled in a fume hood: *benzylic* and *allylic halides*, α-halocarbonyl compounds such as *ethyl bromoacetate*, *isocyanates*, *thionyl chloride* and *acid chlorides*.

Some organic compounds, in addition to being irritants, also have a particularly penetrating or unpleasant odour. These are usually indicated by the word **stench**, and examples include *pyridine*, *phenylacetic acid*, *dimethyl sulfide* and many other sulfur-containing compounds, *butanoic acid*, *skatole* and *indole*. Again, these chemicals should be confined to a well-ventilated fume hood.

1.3 Disposal of hazardous waste

Waste disposal is one of the major environmental problems of modern society and the safe disposal of potentially hazardous chemical waste places a great burden of responsibility and expense on those in charge of laboratories. It is important that everyone who works in the organic chemistry laboratory appreciates the problems and exercises their individual responsibility to their fellow citizens and to the environment by not disposing of chemical waste in a thoughtless manner. In addition to statutory legal requirements, each laboratory will have its own rules and procedures for the disposal of chemical waste; we can only offer general advice and suggest some guidelines. More information about disposal methods can be found in the texts listed the end of this Chapter.

Think before disposing of any chemical waste

1.3.1 Solid waste

Solid waste from a typical organic chemistry laboratory comprises such things as spent drying agents and chromatographic supports, used filter papers, discarded capillaries from melting-point apparatus and broken glass. Common sense is the guiding principle in deciding how to dispose of such waste. Unless the solid is toxic or finely divided (e.g. chromatographic silica; see Section 3.3.6, subsection ‘Disposal of the adsorbent’), it can be placed in an appropriate container for non-hazardous waste. Filter papers can be disposed of in this way unless, of course, they are contaminated with toxic chemicals. Toxic waste should be placed in special appropriately labelled containers. It is the responsibility of your laboratory staff and your instructor to provide these containers and see that they are clearly labelled; it is *your* responsibility to use them. Some toxic chemicals need special treatment to render them less toxic before disposal. This often involves oxidation, but your instructor will advise you when this is necessary.

Broken glass, discarded capillaries and other ‘sharp’ items should be kept separate from general waste and should be placed in an appropriately labelled glass or sharps bin. Chromatography silica should be transferred to polythene bags in a fume hood after removal of excess solvent, moistened with water and the bags sealed for later disposal.

1.3.2 Water-soluble waste

It is very tempting to pour water-soluble laboratory waste down the sink and into the public sewer system. It then becomes a problem for someone else, namely the water authority. This is bad practice. It is best not to dispose of anything down the sink and to place any waste in an appropriate container. If in doubt, consult local health and safety rules.

Never pour solvents down the sink

1.3.3 Organic solvents

Never mix chlorinated and non-chlorinated solvents

Organic solvents are the major disposal problem in the organic chemistry laboratory. They are usually immiscible in water and highly flammable, and often accumulate very quickly in a busy laboratory. Waste solvent should be poured into appropriately labelled containers, never down the sink. The containers are then removed from the laboratory for subsequent disposal by an authorized waste contractor in accordance with local legislation. There should be two waste solvent containers – one for hydrocarbons and other non-chlorinated solvents, and one for chlorinated solvents. Chlorinated solvents have to be handled differently during the combustion process since they generate hydrogen chloride. It is therefore very important that you do not mix the two types of waste solvent. If the waste container is full, ask the laboratory staff or your instructor for an empty one; do not be tempted to use the sink as an easily available receptacle. **Burning of solvents is very tightly controlled by the Environment Agency (EA) in the United Kingdom and the Environmental Protection Agency (EPA) in the United States, so the use of licensed waste routes is preferable.**

1.4 Accident procedures

In the event of a laboratory accident, it is important that you know what to do. Prompt action is always necessary, whatever the incident. **Tell your instructor immediately** or, if you are incapacitated or otherwise occupied in dealing with the incident, ensure that someone else informs the instructor. It is the instructor's responsibility to organize and coordinate any action required.

1.4.1 Fire

For anything but the smallest fire, the laboratory should be cleared. Do not panic, but shout loudly to your colleagues to leave the laboratory. If you hear the order from someone else, do not become inquisitive: **get out**.

1.4.2 Burning chemicals

The most likely contenders for chemical fires are organic solvents. If the fire is confined to a small vessel such as a beaker, it can usually be contained by simply placing a bigger beaker over the vessel. Sand is also very useful for extinguishing small fires, and laboratories are often equipped with sand buckets for this purpose. Remove all other flammable chemicals from the vicinity, and extinguish any burners. Since most flammable solvents are less dense than water, **water must never be used in an attempt to extinguish a solvent fire**; it will have the effect of spreading the fire rather than putting it out. For larger fires, a fire extinguisher is needed; a carbon dioxide or dry chemical type should be used. However, the use of fire extinguishers is best left to your instructor or other experienced persons; incorrect use can cause the fire to spread. If the fire cannot be quickly brought under control using extinguishers, a general fire alarm should be sounded, the fire services summoned and the building evacuated.

1.4.3 Burning clothing

If your clothes are on fire, shout for help. Lie down on the floor and roll over to attempt to extinguish the flames. Do not attempt to get to the safety shower unless it is very near.

If a colleague's clothes catch fire, your prompt action may save his or her life. Prevent the person from running towards the shower; running increases the air supply to the fire and fans the flames. Wrap the person in a fire blanket or make them roll on the floor. Knock them over if necessary; a few bruises are better than burns. If a fire blanket is not immediately to hand, use towels or wet paper towels, or douse the victim with water. **Never use a fire extinguisher on a person**. If the safety shower is nearby then use it. Once you are sure the fire is out, make the person lie still, keep them warm and **send for qualified medical assistance**. Do not attempt to remove clothing from anyone who has suffered burns unless it is obstructing airways.

1.4.4 Burns

Minor heat burns from hot flasks, steam baths and the like are fairly common events in the organic chemistry laboratory. Usually the only treatment that such minor burns require is to be held under cold running water for 10–15 minutes. Persons with more extensive heat burns need immediate medical attention.

Any chemical that is spilled on the skin should be washed off immediately with copious amounts of running water; the affected area should be flushed for at least 15 minutes. If chemicals are spilled over a large area of the body, use the safety shower. It is important to get to the shower quickly and wash yourself or the affected person with large volumes of water. Any contaminated clothing should be removed, so that the skin can be thoroughly washed. **Obtain immediate medical attention**.

1.4.5 Chemicals in the eye

If chemicals get into the eye, time is of the essence, since the sooner the chemical is washed out, the less the damage. The eye must be flushed with copious amounts of water for at least 15 minutes using an eye-wash fountain or eye-wash bottle, or by holding the injured person on the floor and pouring water into the eye. You will have to hold the eye open with your fingers to wash behind the lids. **Always obtain prompt medical attention, no matter how slight the injury might seem**.

1.4.6 Cuts

Minor cuts from broken glass are a constant potential hazard when working in the chemistry laboratory. The cut should be flushed thoroughly with running water for at least 10 minutes to ensure that any chemicals or tiny pieces of glass are removed. Minor cuts should stop bleeding very quickly and can be covered with an appropriate bandage or sticking plaster. If the bleeding does not stop, obtain medical attention.

Major cuts, that is, when blood is actually spurting from the wound, are much more serious. The injured person must be kept quiet and made to lie down with the wounded area raised slightly. A pad should be placed directly over the wound and firm pressure should be applied. **Do not apply a tourniquet**. The person should be kept warm. **Prompt medical assistance is essential**; an ambulance and doctor should be summoned immediately.

1.4.7 Poisoning

No simple general advice can be offered. **Obtain medical attention immediately**.

Further reading

There are a number of texts that deal with laboratory safety practices in general and with the specific properties of, and disposal of, hazardous chemicals. These texts are written by safety experts and give far more detail than is possible in this book. If in doubt, consult the experts.

L. Bretherick, *Bretherick's Handbook of Reactive Chemical Hazards*, 7th edn, Academic Press, Oxford, 2008.
R.J. Lewis, *Hazardous Chemicals Desk Reference*, 6th edn, John Wiley & Sons, Hoboken, NJ, 2008.
G. Lunn and E.B. Sansone, *Destruction of Hazardous Chemicals in the Laboratory*, 3rd edn, John Wiley & Sons, Hoboken, NJ, 2012.

Recommended URLs:
http://www.hse.gov.uk/coshh/basics/assessment.htm
http://www.hse.gov.uk/risk/controlling-risks.htm
http://www.unece.org/trans/danger/publi/ghs/pictograms.html