EXPERIMENT 3 – PREPARATION OF DIPHENYLACETYLENE

PRELIMINARY QUESTIONS

THE MATERIAL SAFETY DATA SHEETS (ON THE CD-ROM) OF ALL THE CHEMICALS HANDLED IN THIS PRACTICAL MUST BE CONSULTED BEFORE ATTEMPTING THESE QUESTIONS AND THE PRACTICAL

1. (i) To which Dangerous Goods Class does bromine belong?

(ii) Bromine has a subsidiary risk class, i.e., it has a secondary classification other than the Dangerous Goods classification. What is this subsidiary risk class?

2. Indicate whether the following hazardous health effects are true or false with respect to bromine:

- on inhalation, severely irritates the mucous membranes
- can cause blindness if gets into one's eyes
- if inhaled, can cause difficulty in breathing
- causes nausea on inhalation
- burns the skin on contact
- overexposure can give rise to a blue colouration of the blood (cyanosis)
- on inhalation, causes damage to genetic material
- can cause an allergic reaction on repeated contact
- causes cancer on inhalation
- has a low exposure standard (TWA - time weighted average)
- has a low STEL (short term exposure limit)
- on inhalation, can give rise to birth defects
- on inhalation, can cause oedemas

INTRODUCTION

In this experiment you will prepare diphenylacetylene using an addition/elimination sequence of reactions.

Learning objectives:

Besides the general laboratory techniques you will use, this experiment will illustrate both addition and elimination reactions, both of which are covered in your lecture notes and textbook. Electrophilic addition to alkenes and elimination to form alkenes are two sides of the same coin and are often used to manipulate functionality in a molecule, as demonstrated in this experiment.

On completing this experiment, you will have carried out both an addition and an elimination reaction and will be familiar with the mechanisms for both.

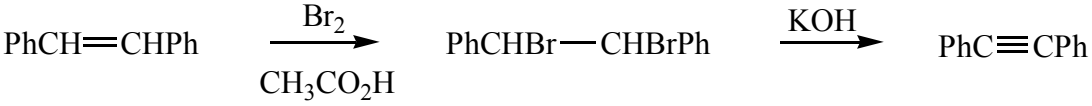
Assessment criteria:

(i) *It is important that it is clear to the assessor that you understood the experiment and the basic theory behind the reactions you carried out. This can be shown adequately by discussing the significance of your results (including analysis of spectra), writing mechanisms for the reactions involved and addressing the questions asked in the manual.*

(ii) *Accuracy of results as shown by visual inspection of your products as well as yield, melting points and IR spectra generally reflect a degree of competency in mastering laboratory techniques and will therefore contribute to the assessment of this practical.*

(iii) *Clarity and layout of your report will also contribute to your assessment. If you are unsure of how to construct a reasonable report, it is recommended that you follow the semester 1 weekly report layout guide and the "What to include in weekly reports" page (both on the CD-ROM) as well as using the sample report (CD-ROM) as a guide.*

This experiment demonstrates the utility of an addition/elimination sequence of reactions in preparing diphenylacetylene. Bromination (see McMurry, 5th ed. p 234-236) of *trans*-stilbene leads to the formation of 1,2-dibromo-1,2-diphenylethane which is then converted into diphenylacetylene.



The second reaction in this sequence is actually a two-step process involving the loss of two molecules of hydrogen bromide. The dehydrobromination (McMurry, 5th ed. p 233) is carried out at high temperature with potassium hydroxide in the high-boiling solvent triethylene glycol (b.p. 290°C) in order to obtain a reasonably short reaction time.

PROCEDURE ***CAUTION:*** *Exercise the greatest care in handling the solution of bromine in acetic acid and wear nitrile gloves while doing so. The bromination must be carried out in the fumehood. Check your calculations with a demonstrator before proceeding.*

1,2-dibromo-1,2-diphenylethane

In a 100 ml conical flask dissolve *trans*-stilbene (2 g) in acetic acid (40 ml) by heating with swirling on a steam bath until dissolution occurs. Allow the solution to cool to approximately 40-45°C (*not* lower), then add a small portion (about 1 ml) of 2M bromine in acetic acid. Swirl the solution until the bromine colour disappears. The dibromide may start to separate out. Continue adding portions of the bromine solution (**how much will you need?**) until its colour just persists, then cool the mixture to room temperature. Collect the precipitated product by vacuum filtration (in the fumehood) and wash it with cold methanol (3 x 20 ml). Suck air through the product on the Buchner funnel for 15 minutes to dry it. The melting point of this product is too high to be measured conveniently (m.p. 241°C

dec.); **you should, however, record an IR spectrum, yield and % yield.** The crude product may be used directly in the next step.

Diphenylacetylene

Place 1,2-dibromo-1,2-diphenylethane (1 g), triethylene glycol (3 ml) and six pellets of potassium hydroxide (approx. 0.5 g) in a large test tube. Heat the mixture in an oil bath to 160-170°C with frequent (careful!) stirring using a glass rod. Keep the mixture at this temperature for 5 min, cool and add water (15 ml). Collect the product diphenylacetylene by vacuum filtration, wash with a small portion (approx. 10 ml) of cold water and suck dry on the funnel for 10 min. Recrystallise the crude product from ethanol, using charcoal for decolourisation if necessary (*very* little ethanol is required, so be careful!). If the recrystallisation is allowed to proceed undisturbed, very large spars of colourless crystals are formed. If desired (or if the yield is low!), concentration of the mother liquor (using a steam bath) affords a second crop of pure product. **Record the yield, % yield, m.p. and IR spectrum of your product.**

QUESTIONS

1. Would the 1,2-dibromo-1,2-diphenylethane obtained in part 1 be optically active? Explain.

2. Draw a reaction energy profile for the formation of both products in this sequence.

3. In a chemical laboratory such as the Teaching Laboratory where there is such a wide range of chemicals, one must always be aware of the dangerous properties of the chemicals. This is especially important when one is handling, storing and transporting bulk chemicals. An accident involving bulk chemicals can present a health risk to the local population and also an environmental risk.

   In the United Kingdom, the emergency services have established a system whereby all Dangerous Goods have associated with them a code, the Hazchem Emergency Action Code (Hazchem code). This code has been adopted in Australia. The code is a summary of the immediate action that should be taken by the emergency services when attending an accident involving bulk Dangerous Goods. The code indicates what fire-fighting medium should be used, what clothing and equipment would be appropriate for fighting the fire, whether there is a risk of violent reaction or explosion, what action to take if there is a spill, and whether evacuation ought to be considered.

   The code together with the UN number (see Experiment 9) and Dangerous Goods symbol of the chemical is included as part of the Emergency Information Panel that is found on all transport vehicles carrying bulk Dangerous Goods.

   The Hazchem code is made up of a number followed by a maximum of two letters.

   - The Number

The number refers to what type of extinguisher should be used to fight a fire involving the chemical in question or how to disperse a spill:

1 Water jets

2 Spray or water fog

3 Foam

4 Dry powder

A lower numbered type of extinguisher can be replaced with a higher numbered one but never one lower.

- The Letters

The first letter indicates whether or not there is risk of explosion or violent reaction, whether full protective clothing and breathing apparatus are needed and whether the substance should be diluted or contained in the case of a spill. There are thirteen letters in all. The letters can be written either normally (black letter, e.g., S) or in "reversed" print (white letter in a black square, e.g., S or black letter in square brackets, e.g., [S]). The letter in "reversed" print has the same meaning as the normal letter except when it is a fire situation. A list of the letters used and their meanings is given in Table 1.

Table 1 – Letters used in the Hazchem code and their meanings.

Letter	Danger of reaction or explosion	Protective gear	Spillage Action
P	YES	full protective clothing[1]	dilute[4]
R	NO	full protective clothing	dilute
S	YES	breathing apparatus[2]	dilute
[S] or S	YES	breathing apparatus (for fire only)[3]	dilute
T	NO	breathing apparatus	dilute[5]
[T] or T	NO	breathing apparatus (for fire only)	dilute
W	YES	full protective clothing	contain
X	NO	full protective clothing	contain
Y	YES	breathing apparatus	contain
[Y] or Y	YES	breathing apparatus (for fire only)	contain
Z	NO	breathing apparatus	contain
[Z] or Z	NO	breathing apparatus (for fire only)	contain
E			consider evacuation

[1]Full protective clothing **includes breathing apparatus.**

[2]Breathing apparatus **means breathing apparatus and protective gloves.**

[3]Breathing apparatus (for fire only) **means breathing apparatus for fire situations only.**

[4]Dilute **means that the chemical can be safely diluted with water and washed into drains.**

[5]Contain **means that the chemical should be prevented from entering drains or waterways as it is toxic or immiscible with water.**

Using the information given above and the material safety data sheets for acetic acid, bromine, potassium hydroxide and ethanol, complete the following table.

UN Number	Structure	Shipping Name	Hazchem code	Appropriate Actions
		Acetic acid		
		Bromine		
		Potassium hydroxide		
		Ethanol		

4. You have used a lot of different chemicals in the practicals during this semester. The usage of these chemicals, however, is not restricted to controlled laboratory situations. Many of these chemicals are also commonly used outside the laboratory. In order to make people aware of the properties of these chemicals, the labelling, storage and sale of a lot of common chemicals are controlled under the state poisons acts under the guidance of a national standard, the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP). The drugs and poisons are categorised into 8 schedules.

   (i) Look at the material safety data sheet for bromine. What schedule does it come under?

   (ii) Look in the resource folder at the extract from the SUSDP and determine what types of poisons are covered by this schedule.

   (iii) Have a look around your home for scheduled poisons (try the medicine cabinet). Find one example, list the poison, its schedule number and what type of chemical that schedule covers.

   (iv) Methanol was used in this practical in part 1. It also has many uses outside the laboratory. For example, it can be used as an antifreeze in car radiators, as fuel for picnic stoves and used to denature alcohol, etc. Being a common chemical does not mean that it is harmless; ingestion of only 30 ml of methanol can be fatal. When labelling scheduled poisons for sale to the general public, under the state poisons act, the label must contain a statement as to which poison schedule the drug comes under, key warning statements (e.g., keep out of reach

of children), the concentration of the substance, safety directions and first aid instructions.

In the servery is a 500 ml bottle of methanol. Find and list the obligatory labelling components mentioned above that appear on the container. The label is missing one of the obligatory labelling components. Which is it and how should it appear on the label?