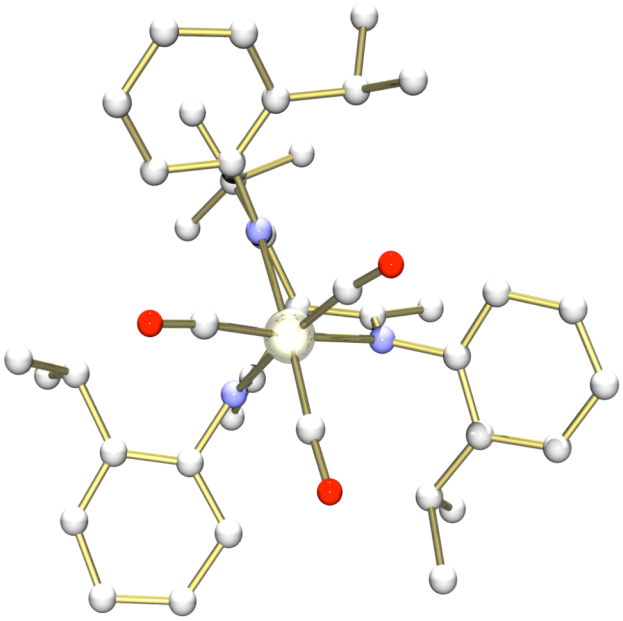
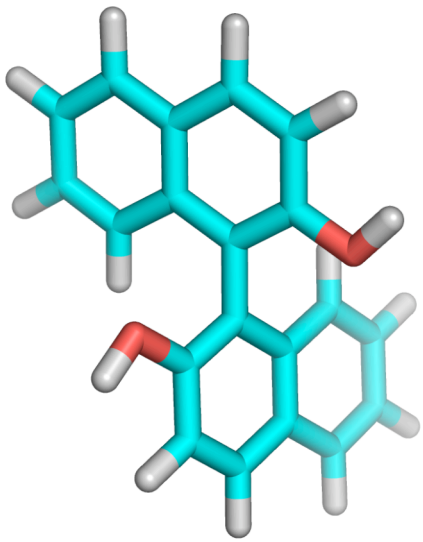
MANCHESTER 1824

The University of Manchester

SCHOOL OF CHEMISTRY

YEAR 3 SYNTHESIS LAB 2006-7





Notes and Instructions for Students

Weeks 7-12

SCHOOL OF CHEMISTRY

Year 3 Synthesis Lab 2006-7

Table of Contents.

Introduction: Aim of the course

Welcome to the third-year Synthesis Teaching Laboratories which is your last experience of set experiments before commencing on your own research projects next semester. The overall aims of these sessions are to (i) refresh and further your knowledge of aspects of organic and inorganic synthetic chemistry, (ii) to refresh and further develop practical synthetic chemical skills, and (iii) develop your ability to acquire, sensibly interpret, draw valid conclusions based upon, and present reasonable hypotheses to explain, experimental data. This prepares you for research. Some of the experiments and write-ups may therefore be more involved and extended than those of other set practicals you have previously encountered.

Course Structure, Location and Duration.

The Synthesis course will take place in the Synthesis Labs on the **second floor** of the new Undergraduate Teaching Labs. The laboratory will be open for you to carry out experiments on Thursdays from 10am – 4 pm, and on Fridays from 10am-1pm.

A lab layout map is attached at the end of this lab manual.

Lockers and Apparatus in the Synthesis Labs

You will be allocated a locker with an individual kit set. In addition, some specific (generally larger equipment/glassware) will be located in a set of shared drawers in the centre of each bay. You are expected to show good laboratory practice in maintenance and care of your equipment and we expect you to replace any items which may become broken with a replacement item from stores. ***You will not be signed out as having completed the lab if your lab kit is not left complete and so we will not return a lab mark. It is thus vital that you do ensue your kit is complete at the end of the lab sessions.***

Items in the lab and personal lockers

You will have access to lockers only for the duration of each lab session/day and you will need to bring a padlock and remove this at the end of each day. You must NOT bring items such as food and drink into the lab and can leave these in an external locker. You are also strongly advised to leave personal valuables, bags, coats and so on in the lockers. This will need to include items such as iPods which you will not be allowed to use during lab work.

Lab Entry and Conditions

You MUST put safety glasses on as you enter the lab and keep them on throughout your time in the lab. They are not to be worn on top of your head as a hair decoration and are not an optional extra! ***If you are seen not wearing safety glasses you will be warned once. Subsequent non-compliance will result in your expulsion from the lab session; a mark of zero will be recorded for that experiment.***

You will not be allowed to do any experimental work without a completed COSHH risk assessment.

You are required to have your laboratory notebook **in the laboratory** at all times. ***If you do not have your laboratory notebook with you, you will not be allowed to carry out any laboratory work as all notes must be written into the notebook directly, NOT on scraps of paper.***

Overall structure

The first two weeks in your 3-week block in the Synthesis lab are devoted to principally organic experiments, and the final week to principally inorganic experiments, though you will come to appreciate much commonality in methods between the two.

The laboratory staff will be made up of members of academic staff (1-2 each session), laboratory technicians, and postgraduate student demonstrators. All staff are present to help you learn as much as possible from the course and help you where you are having difficulties. ***Please ask***; assistance should be freely given!

Demonstrator groups:

You will be divided into SIX groups of 10 or 11 students based on your lab locker location. Each group will be colour coded and will be labelled as Groups A-F for purposes only of the Synthesis lab. Your demonstrator should be readily identifiable (and be wearing a blue lab coat) and we have arranged the lab locations so any two facing/adjacent bays only are covered by the same demonstrator.

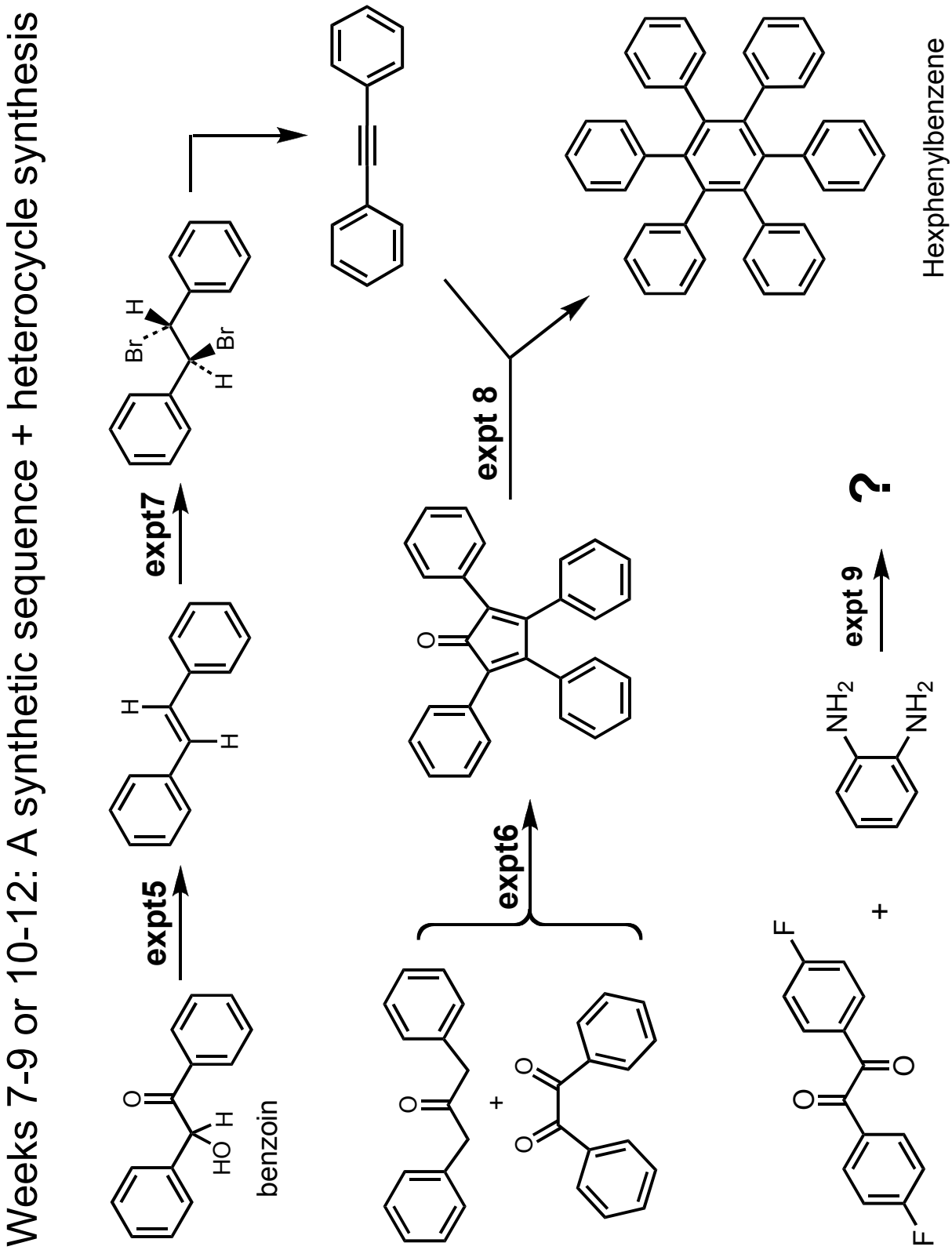
Course content summary

For the weeks 7-12, the whole of Year 3 will be split into Groups A' and B', and will alternately spend three weeks in the Synthesis lab and 3-weeks in the Measurements lab. You will thus either spend 3 weeks in the Synthesis lab during weeks 7-9, or you will be in the Synthesis lab during weeks 10-12, with your other 3-week block being spent in the Measurements lab. If your name is not on the lists provided to you at the start of *this* class then you are probably in the wrong place!

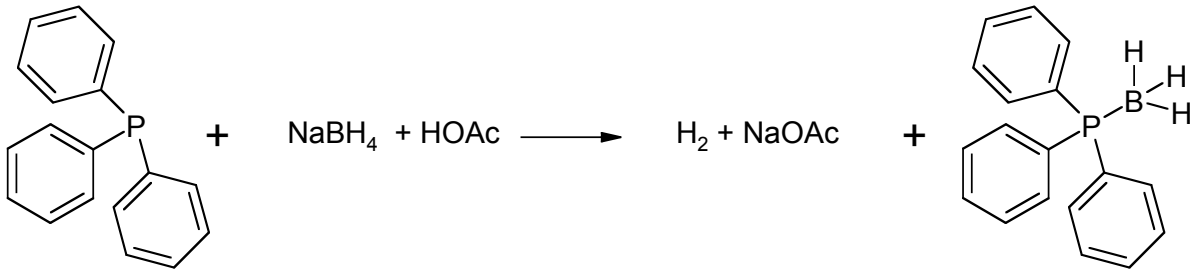
The organic experiments in this S-lab work are centred on a convergent synthetic sequence which aims to provide hexaphenylbenzene. The overall schematic is given overleaf also for information. There is also an additional stand-alone experiment involving the synthesis of a fluorinated heterocyclic compound.

The timetabling assumes you will have completed expts 5-7 by 1pm on the Thursday afternoon of your second week. IF YOU ARE NOT at this stage then even if you are timetabled to do expt 9 on that Thursday afternoon, you should in fact proceed with the synthetic sequence to ensure that you complete the synthesis of the hexaphenylbenzene, even if this means you are unable to complete expt 9 on the Friday of your second organic week.

The organic synthetic work will be carried out over the first 2 of your 3 weeks in the second synthesis lab section. In the third week of this block you will carry out an inorganic reaction sequence shown also below, which covers work across all three lab sessions that week.


Weeks 7-9 or 10-12: A synthetic sequence + heterocycle synthesis
benzoin
expt5
expt7
expt6
expt 8
expt 9
?
Hexphenylbenzene

Week 9 or 12: Inorganic sequence



$$2CuCl_2(aq) + Na_2SO_3 + H_2O \longrightarrow 2CuCl + 2NaCl + H_2SO_4$$

$$CuCl + Ph_3P + NaBH_4 \longrightarrow ? \longrightarrow ??$$

Work and Attendance:

You are expected to attend **ALL** sessions and are required to sign in and out of the laboratory. A list of attendance is required for safety reasons. Any absence will be notified to the School centrally on a weekly basis.

You MUST arrive for the lab no later than 15 minutes into the day/session period. Those arriving later into sessions compromise both their own chances of completing on time and thereby create problems at the end of the lab sessions for others, including technical staff.

Students arriving after this time on more than one occasion may be penalized.

Attendance at laboratory classes is a requirement for Chemistry degree programmes. Details of the School Policy are provided in the Programme Handbook.

To ensure students are treated fairly, it is vital that attendance registers are accurate. If you attend a laboratory class, make sure you have been marked as present.

However, students should be aware that attending for a short period, signing the attendance register and then leaving **will be noticed** as we have several secondary checking systems in place; such behaviour will be considered as unsatisfactory attendance and will both be recorded as absence and reported separately to the School administration for further action.

Copying and Plagiarism:

The School does not accept **any** form of copying/plagiarism in any work. Any lab report which involves submitted copied work, whether from another student or from the internet, will receive a zero mark. In addition, *ALL* work by this student over the course – past or future - will then be individually scrutinized for any evidence of further plagiarism. A student found to have been the source of material for other students to copy will also be severely penalized.

In this lab, such copying will be deemed to include also the submission of copies of other students' spectra (unless the work is part of a joint experiment where common data submission is agreed), submission of yields, mpt data etc. which is fabricated.

Safety: READ ME BEFORE YOU START WORK!

ALL substances should be treated as toxic. Absorption through the skin may be dangerous as well as ingestion through the mouth, nose, ears, eyes, etc. Some materials appear to have little immediate effect, but may cause problems in the long term. ***If at any time you are unsure of what you are doing ask for help. That is what the staff and demonstrators are present for.***

YOU MUST:

- Wear safety spectacles at all times in the laboratory AND BEFORE ENTERING.
- Note the location of the emergency exits and the first aid boxes.
- Note the location of the CO_2 fire extinguishers and fire blankets and familiarise yourself with their mode of operation
- Use pipette fillers at all times when pipetting chemicals.
- Wear protective gloves when using acids and bases or other harmful substances.
- Concentrated acids must only be dispensed in the fume cupboard.
- Label all samples with your name, date and what the substance is and mass.
- Dispose of waste acetone and other organic solvents in the specially marked bottles provided.
- Dispose of broken glass in glass bins. A pan and brush are available in stores.
- Clear up any chemical spillage immediately.
- Return chemicals to shelves or hoods.
- Leave shared apparatus in clean working condition. (eg balance room!)
- Keep all areas, especially, the balance areas clean.
- You must not eat, drink, or run in the laboratory.
- Be aware of the danger of fires. Many solvents are both volatile and flammable and may ignite if the liquid or the vapour comes in contact with flames or hot surfaces. Do not use a Bunsen burner until you are absolutely sure that no one is using a flammable solvent nearby, and always turn it off immediately after use.
- Be aware of the danger of cuts. Together with fires, cuts are the most common accidents we encounter. Check your glassware for breakages or sharp edges, and check carefully for cracks or 'star-cracks' in glassware which is to be used under suction (*e.g.* filtration flasks), or under pressure (*e.g.* chromatography columns). Keep ground glass joints clean so that they do not stick. Handle sample vials carefully – they can easily break when the caps are being fitted.

COSHH forms: *Availabale from Front Desk or Demonstrator*

These **must** show that you are aware of the hazards associated with the chemicals used in a particular experiment, and know how to minimise the risks.

You should prepare CoSHH (**C**ontrol **O**f **S**ubstances **H**azardous to **H**ealth) forms ***before*** the lab session so that you arrive with a completed form. CoSHH forms are then to be countersigned and dated by your group demonstrator *before* experimental work begins.

You will ONLY be allowed to start any new experiment once a completed COSHH form is provided, checked and signed by demonstrating personnel.

If you wait till you arrive this will significantly delay the start of your practical work and will compromise your chances of completing in the time available.

- You will need to enter the chemicals to be used, with a **short** assessment of their hazards. Details of actual lethal doses are not required, but your assessment should include any particularly hazardous routes of ingestion, code letters, such as, M for Mouth, S for Skin, L for Lungs, F for Flammable could be used as a coded indicator.
- Methods of decontamination must also be included.
- Some information can be found on bottle labels, in catalogues and some may have to be looked up in the special texts, which are held in the library. A list of useful references is given at the end of this note.

Examples:

- **Acetone:** Not highly toxic. F, S, L. Can be decontaminated with water.
- **Dilute hydrochloric acid:** Not highly toxic. M. Decontaminate with water, sodium bicarbonate.

Data to include in your CoSHH forms can be obtained in several ways. Some is provided in this manual, some can be obtained from a chemical catalogue (eg Aldrich), or via the internet. Some books are also sources of information:

The BDH Safety Data Book
The Sigma Aldrich Catalogue of Safety Data
Hazards in the Chemical Laboratory, 2nd edition, by E.D. Muir
Hazards in the Chemical Laboratory, 4th edition, by L. Bretherick.

ACCIDENTS

It is imperative that accidents are dealt with **immediately**.

IT IS IMPORTANT THAT IF AN ACCIDENT OCCURS A MEMBER OF STAFF IS INFORMED IMMEDIATELY

Splashes to the skin and eyes should be washed immediately with copious amounts of water, removal of reagents insoluble in water will be facilitated by cleaning the contaminated area with soap; dry burns should be treated by covering the afflicted area with a dry sterile dressing contained in the first aid box. If you inhale gas or dust particles and feel faint immediately leave the area and inform a demonstrator or a member of staff. If, in the unlikely event that you do ingest a chemical, immediately wash your mouth out with copious amounts of water and inform a demonstrator or member of staff immediately. You should then seek medical advice.

All lab technical staff are trained in first aid.

GOOD LAB PRACTICE

In this lab we want you to employ good practice throughout, based on your training in Year 1 and 2. Primary amongst this are safety and cleanliness. In addition to considering safe practice at all times, you must show good habits in use of shared equipment use of balances, spectrometers and rotary evaporators.

BALANCES: ONLY transfer compounds into vessels OUTSIDE the balance. NEVER EVER spatula or tip material into or onto vessels on the balance pan!!! IF you do inadvertently spill any material around the balance YOU must clean this up IMMEDIATELY. To not do so is not only very poor lab practice but is both highly incosdierate and potentially dangerous to your fellow students who then need to work around the unknown chemical waste you leave behind.

EVAPORATORS: Leave these CLEAN. If your sample solvent bumps then wash it out! Dispose of solvents collected in the solvent waste containers.

IR SPECTROMETERS: CLEAN plates after use and retrun them to jars or containers to preserve from moisture. Do NOT LEAVE items and samples scattered about and leave equipment as you found it.

Laboratory Notebook.

The reasons for keeping a laboratory notebook are several in number and include: to record what you have done and your raw data, so as to enable you to repeat the experiment at a later date; to enable you to write a report; to enable someone else to repeat the work that you have done; and to avoid the possibility of losing scraps of paper that have important information written on them. Most importantly, your lab notebook is the primary documentary record of what you did, when you did it. Laboratory Notebooks can be used as legal documents in court cases, for example in disputed cases of intellectual property rights (IPR). It must be hard-backed and properly bound, not spiral-bound; it should not be possible to add or remove pages.

Your notebook will be inspected and commented on by staff and demonstrators during the course to make sure it is being kept to a satisfactory standard.

You Must:

- Put your name on the cover or inside cover;
- have an index and numbered pages;
- put the date on the tops of the pages;
- put the title of the experiment;
- put the equations or structural formula diagrams for the experiment, so you know what you're doing and can work out which is the limiting reagent;
- have a list of reagents, how much you used in g and moles and the number of equivalents;
- include your hazard assessment;
- include a calculation of the theoretical yield based on the limiting reagent;
- comment on how you did the experiment: short statements are okay and a full discussion isn't necessary, but should be detailed enough to enable you to repeat the experiment and should be written as you carry out the work; observations and problems encountered and how they were overcome.

On the next page is an example of a couple of pages from a working notebook. Notice it is not pristine in appearance.

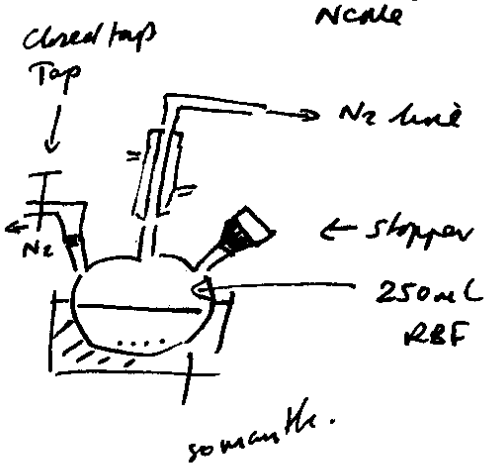
Sample pages from a notebook.

(53)

27 May 2003.

Preparation of $[W(CO)_3(NCMe)_3]$.

$$[W(CO)_6] \xrightarrow[NCMe]{\text{Reflux}} [W(CO)_3(NCMe)_3] + 3\ CO\uparrow$$



Weight bottle + $W(CO)_6$ = 5.33 g
Weight bottle = 1.30 g
Weight $W(CO)_6$ 4.03 g

moles $[W(CO)_6] = \frac{4.03}{351.91} = 0.0115$

Volume of NCMe = 100 mL

The glassware was assembled under nitrogen atmosphere $[W(CO)_6]$ added to deoxygenated NCMe.
Mixture heated to reflux for 3 days under a nitrogen atmosphere affording yellow solution

30 May 2003

Solution cooled and about volume reduced by half under reduced pressure

Flask placed in fridge and left overnight for crystals to form.

(54)

31 May 2003

Yellow crystals collected by filtration and dried under vacuum

Weight bottle + prod 5.41 g
Weight bottle = 1.47 g
1.94 g

Yield 3.94 g

Theoretical yield FW $[W(CO)_3(NCMe)_3]$ 4n

W 183.85
CO 28.01 x 3
NCMe 41.05 3
399.04

Max no moles product 0.0115

expected 0.0115 x 391.04 = 4.50 g

% $\frac{3.94}{4.50} \times 100$ 88%

(based upon $[W(CO)_6]$ limiting reag)

Mpt decomposes 143 (turns black)

Synthesis Laboratory Assessment.

You will be assessed on three criteria:

1. The quality and quantity of your prepared samples: *Purity, yield, dryness.*

2. The quality of your laboratory note-taking: *Laboratory notebook assessed before sign-out.*

3. The quality of your formally written experiment report, including spectral interpretation and answers to questions.

You must hand in a **separate report** for each experiment. Details for each experiment are given in the script, but in general, write-ups should include:

> a **brief** statement of aims

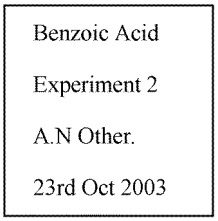
> an experimental section written in past tense, passive voice, in Chemical Society style, as found in journals such as 'Dalton Transactions' or Organic & Biological Chemistry',

> annotated copies of spectra (either those you record or those provided to you)

> answers to questions.

Method for Handing In.

- You must write your name, experiment number and date clearly on your write up and hand it in at the Student Reception Area G20.
- There will be a record of receipt of this. Only reports received in this way will be marked. **THERE WILL BE NO EXCEPTIONS.**
- Do not hand in any work to staff via their pigeon holes: it will be returned to you unmarked via your pigeon hole. **THERE WILL BE NO EXCEPTIONS.**
- Samples must also be handed-in in a glass vial which has been properly labelled, using a sticky label. See diagram below. Your demonstrator will record you have handed your sample(s) in.



Specimen Sample Label

also state *mass* of submitted sample.

YEAR 3 SYNTHESIS LAB 2006-7

INDEX OF EXPERIMENTS

WEEKS 7-9 (Group B') and 10-12 (Group A')

To facilitate better use of your time we have grouped the class into two subsections for some of the second week of experiments, indicated as below with reference to demonstrator groups A-C and D-F. You may thus not all be doing the same experiments at the same time. This may help with access to general equipment (eg evaporators and spectroscopic equipment). It is important that you plan your time well and arrive at the sessions on time, which will ensure you complete all experimental work.

Week 7/10	
Thursday	Preparation of stilbene from benzoin
Friday	Conversion of Stilbene to Diphenylacetylene

Week 8/11	Group A	Group B	Group C	Group D	Group E	Group F
Thursday **am**	Synthesis of Tetraphenylcyclopentadienone					
Thursday **pm**	hexaphenyl-benzene	hexaphenyl-benzene	hexaphenyl-benzene	fluorinated heterocycle	fluorinated heterocycle	fluorinated heterocycle
Friday	fluorinated heterocycle	fluorinated heterocycle	fluorinated heterocycle	hexaphenyl-benzene	hexaphenyl-benzene	hexaphenyl-benzene

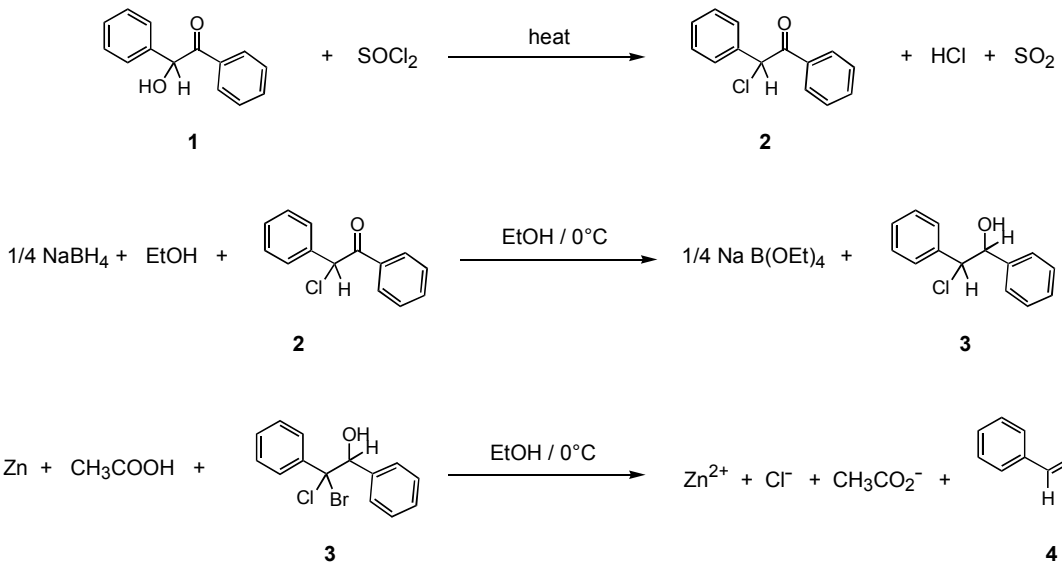
Week 9/12	Group A	Group B	Group C	Group D	Group E	Group F
Thursday **am**	**4 tasks: synthesis of CuCl, Phosphinecopper borohydride, and Ph_3BH_3, and analysis**					
Thursday **pm**	Consult your demonstrator on when you will do Ph_3PBH_3 operation under Nitrogen; work other tasks around this.					
Friday						

HAND-IN DEADLINES: ***NO*** *reports will be accepted after these deadlines.*

	GROUP A	**GROUP B**
Experiments 5 and 7	2pm, Monday week 9	2pm, Monday week 12
Experiments 6, 8 and 9	2pm, Monday week 10	2pm, Monday week 12
Experiment 10	2pm, Monday week 11	2pm, Monday week 1, Semester 2

5 Preparation of Stilbene from Benzoin:

Abstract: Benzoin, **1**, is converted in three steps to stilbene without isolation of intermediates. Reaction of deoxybenzoin with thionyl chloride first yields desyl chloride, **2**. Reduction with borohydride then yields the chlorohydrin, **3**, and reductive elimination with zinc yields *E*-stilbene, **4**.



Properties of Reactants and Products

Benzoin, **1**: $C_{14}H_{12}O_2$; FW = 212	Solid, mp 340°	Unknown toxicology; avoid contact or ingestion.
Thionyl chloride	Liquid, bp 76 ºC; d 1.64	Toxic and corrosive; **lachrymator and skin irritant; avoid skin and eye contact, inhalation.**
Desyl Chloride **2**, $C_{14}H_{11}OCl$; FW = 230.5	Waxy solid, mp 37°	Toxic and corrosive; **powerful lachrymator and skin irritant; avoid skin and eye contact.**
1,2-diphenylepichlorohydrin, **3**, $C_{14}H_{13}OCl$; FW = 232.5	Oil	Unknown toxicology; **assume corrosive and lachrymatory;**
E-stilbene, 4, $C_{14}H_{12}$ FW 180	Solid, mp l24-l25°	Mildly toxic by ingestion; Orl LD 50 920mg/kg (mus)
Sodium Borohydride, $NaBH_4$ FW 38	Solid; Mp 497° (decomp)	Toxic and corrosive; avoid contact and ingestion; reacts vigorously with acid to release hydrogen gas
Zinc dust: Zn FW 65.4	Solid: mp 419°	May react vigorously with acids or oxidisers; irritant and toxic.
Ethanol: C_2H_5OH FW = 46	Liquid bp 78°; d 0.785	Flammable; may react vigorously with oxidisers; irritant and intoxicant; LD50 3530mg.kg

Acetic Acid (glacial) $C_2H_4O_2$ FW 60.1	Liquid bp 116 ºC d 1.049	Flammable; Strong irritant and vesicant; skin burns; LD50 3530 mg/kg(OR)
40-60 Petrol: C_5H_{10} mainly	Liquid	Highly flammable; may form explosive mixtures with air; harmful by ingestion, inhalation and irritant.

Techniques

Recrystallization; drying and filtration, UV.

Procedure

Some general comments: - This is a three-stage procedure. Although the intermediates (**2** and **3**) are not isolated, it is good experimental practice to check as you go along that things are working to plan. IR spectroscopy provides a simple and effective check on the functional group change conversion of the hydroxyl group to a chloride in the first step. In the second step, UV spectroscopy permits simple observation of loss of the conjugated aromatic ketone in **2** ($\lambda_{max} \approx 250$nm) as the reduction proceeds.

The reactions: -

Stage 1: CAUTION Thionyl chloride is toxic and corrosive, and the reaction releases HCl and SO_2, toxic, corrosive and irritant gasses. Operations should be carried out as far as possible in a fume hood. **Note also that desyl chloride, 2, the product of the reaction of benzoin and thionyl chloride, is a powerful lachrymator and skin irritant. Avoid skin contact, and keep your hands away from your eyes during the procedure. In the event of contact irrigate with plenty of water and dilute baking soda solution.**

It is important that a mixture of benzoin and thionyl chloride is not allowed stand at room temperature for any length of time, so before starting, place a stirrer hotplate and sand bath in a fume hood and preheat the sand bath to about 90°C.

Place finely powdered benzoin (2.0g.) in a 100 ml RB flask with an anti-bumping granule. Add thionyl chloride (2 mL), and warm in the sand bath, swirling gently until all the benzoin dissolves. Then place the flask in the sand bath and heat for 5 minutes. Cool, and add ether (30 mL) to the flask and swirl to dissolve.. Pour the ether solution over ice (30g) in a beaker. Rinse the flask with a little more ether (*ca* 20ml) and add these to the beaker. Stir the contents of the beaker vigorously until all the ice has melted then transfer to a separating funnel and separate the layers. Extract the aqueous layer with a more ether and then dry the combined ether extracts over calcium chloride pellets. Decant or filter through a fluted filter paper into a weighed 100 ml RB flask and remove the ether on a rotary evaporator to leave the desyl chloride as a viscous oil which may crystallize on cooling. Run an IR spectrum (film on NaCl plates) and compare with that of benzoin, available in the database, to confirm the conversion of the replacement of the hydroxyl group by chloride.

Stage 2: Add 95% ethanol (30 mL) and a magnetic flea to the crude desyl chloride in its RB flask. Clamp in an ice-water bath on a magnetic stirrer, and fit with a thermometer. Stir to dissolve. Add one

small drop of the mixture to 3 mL of 95% ethanol in a UV cell and run the UV spectrum (200 to 300nm).

Weigh out sodium borohydride (0.18 g) on to a small watch glass and quickly break up any lumps with a dry spatula. Add the borohydride in a single portion to the cooled stirred desyl chloride solution and stir until the reduction is complete (about 10 minutes) as shown by loss of the 250 nm band in the UV spectrum of a sample taken as described above.

Stage 3: Add glacial acetic acid (2.0 mL) to the reaction flask. Note any evolution of hydrogen from reaction of excess borohydride and acetic acid. Add zinc dust (1.0g), and fit the flask with a reflux condenser. Stir under reflux for 1 hour.

Product isolation: - Cool the reaction mixture. Stilbene may precipitate at this stage. Decant the solution, *including* any white crystals, into a separating funnel, leaving any unreacted zinc in the flask. Rinse the zinc with a portion *t*-butyl methyl ether (25 mL) and add this to the separating funnel. Dissolve any zinc salts by addition of water (50 mL of water containing 1 ml of conc. hydrochloric acid) to the separating funnel. Shake vigorously, and separate the layers, retaining the organic layer. Extract the aqueous layer with a fresh portion of *t*-butyl methyl ether (25 mL). Dry the combined organic extracts over anhydrous calcium chloride (3.0 g). Decant or filter through a fluted filter paper into a weighed RB flask, and evaporate the solvent to leave a crystalline solid. Weigh the flask to obtain the crude yield.

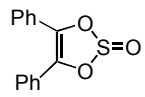
Purify the product by dissolving in the minimum amount of hot 95% ethanol (about 10 ml). Cool to obtain shiny white plates of *E*-stilbene, and isolate by suction filtration on a weighed Buchner or Hirsch funnel and suck dry. Yield is usually about 1.0 g. Determine its melting point and run a UV spectrum to determine λ_{max} and ε_{max}.

The write-up: - Reminder: Do NOT hand in your lab book or complete your write up in a lab notebook. Submit reports separately please.

This should be the usual description of what you saw and did, written in Chemical Society experimental section style. Submit your product in a labeled dated vial.

In addition, you should deal with the following points: -

1) If benzoin and thionyl chloride are allowed to stand without heating, a slow reaction occurs yielding the cyclic sulphite shown opposite. Write a mechanism for this conversion. Why does this reaction not take place if benzoin is heated with thionyl chloride?

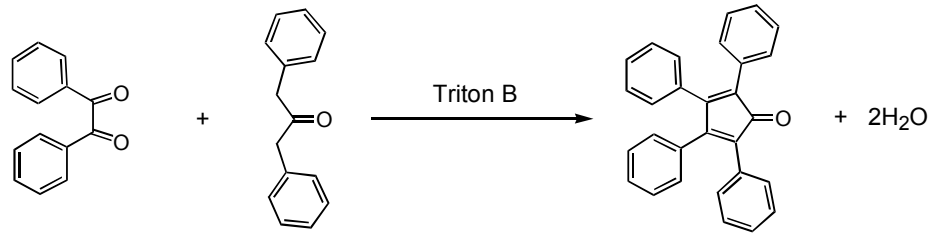


2) Make models of both *E*- and *Z*-stilbene and include sketches of the features of these structures. Comment on the differences between them and effects this may have on spectroscopic data. Which would you expect to be more stable and why? You may find the models available on the Year 3 Labs web info helpful.

3) How many stereoisomers of **3** are there? Sketch and label the diastereoisomers and show which are enantiomeric pairs.

6. Synthesis of tetraphenylcyclopentadienone:

Abstract: Base catalysed condensation of 1,3-diphenylacetone, **1**, with benzil, **2**, yields tetraphenyl-cyclopentadienone, **3**.



1 **2** **3**

Properties of Reactants and Products

Benzil, **1**. $C_{14}H_{10}O_2$ FW = 212	Yellow solid, mp 96°;	Low toxicity by ingestion; orl LD50 3g/kg (mus)
1,3-Diphenylacetone, **2** $C_{15}H_{14}O$ FW = 210	Solid mp 35°;	Unknown toxicity; avoid contact or ingestion.
Benzyltrimethylammonium hydroxide $PhCH_2N^+Me_3$ OH	Supplied as 40% solution in methanol	Flammable, toxic and corrosive. Avoid contact and ingestion.
Tetraphenylcyclopentadienone $C_{29}H_{20}O$ MW 384	Purple solid mp 219°	Unknown toxicity; avoid ingestion or contact.
Triethylene glycol, $C_6H_{14}O_4$ FW 150.7	Deliquescent liquid: bp 290° d 1.125	Flammable liquid. Low toxicity.
Methanol: CH_3OH FW = 32	Liquid bp 78°; d 0.785	Flammable; more here

Techniques

Filtration, crystallization, IR and UV analysis.

Procedure

The reaction: - Preheat a sand bath on a hot plate to 120°C. Place benzil, **1**, (1.0g) and 1,3-diphenylacetone, **2**, (1.0g.) and triethylene glycol (5 mL) in a 25 x 150mm test tube. Heat on the sand bath until the benzil is dissolved then remove from the heating. Add 0.5 ml. of commercially available 40% benzyltrimethylammonium hydroxide in methanol (sold as Triton B) using the autopipette supplied. Return to the sand bath and stir with a thermometer until the temperature just rises above 100^0C. The mixture turns very dark, and crystallization of the deep purple product may be observed. *Product isolation and characterization:* - Remove the test tube from the sand bath and allow to cool

slowly until the temperature is about 70°C, then cool to room temperature in a cold water bath. Add methanol (5 mL) to complete precipitation of the product. After 5 minutes, collect the product on a **weighed** Hirsch funnel. Use a little cold methanol to aid transfer and rinsing of the product on the funnel. Suck dry and weigh to obtain the crude yield (usually about 1.5g.) of deep purple crystals.

The material may be purified by suspending 1g of crude material in fresh triethylene glycol (5 mL) and heating to 220 ºC to dissolve. Slow cooling yields well-formed crystals, mp 219 °C, which can be isolated by filtration. Wash with a little methanol and suck dry.

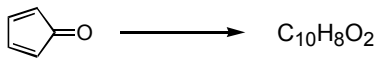
Record an IR spectrum (as KBr disc or powder) and a UV spectrum (dichloromethane solution scanning 200 to 500nm).

The write-up: -

This should be the usual description of what you saw and did, written in Chemical Society experimental section style. Show your product in a labeled dated vial to your demonstrator and it will then be filed in the Year 3 cabinet.

In addition, you should deal with the following points: -

1) Cyclopentadienone itself is extremely reactive. All attempts to isolate it yield a dimer. Suggest a structure for this dimer. How might contributing resonance forms of cyclopentadienone explain its high reactivity compared to tetraphenyl-cyclopentadienone (which is stable in monomeric form)?



cyclopentadienone

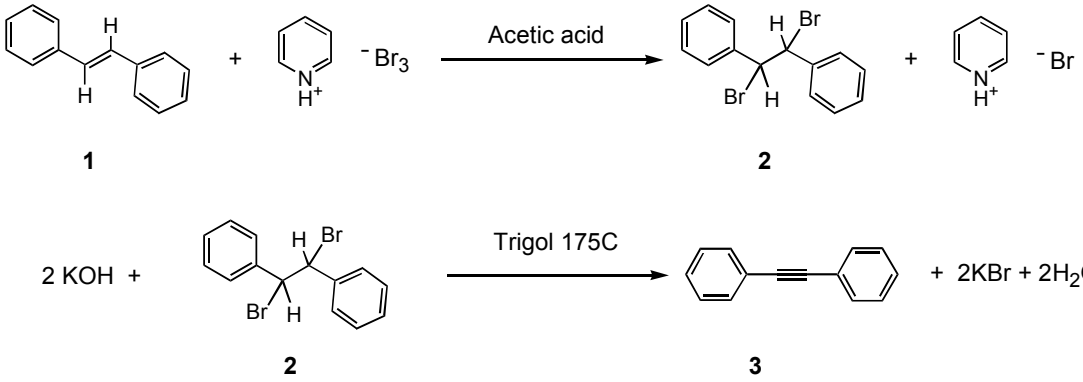
2) Why is tetraphenylcyclopentadienone so strongly colored? Look carefully at its UV spectrum before answering this.

3) The which important general class to reactions does this preparation of tetraphenyl-cyclopentadienone belong? Devise a restrosynthetic analysis of **3** and write a mechanism for the conversion of **1** and **2** into **3**.

4) Diphenylacetone is made from ethyl phenylacetate ($PhCH_2COOEt$). Provide a retrosynthetic analysis of **2** which could use this as the starting material.

7 Conversion of Stilbene to Diphenylacetylene

Abstract: Stilbene is converted to 1,2-diphenylacetylene in a two-stage procedure. Addition of bromine to *E*-stilbene yields *meso*-1,2-dibromostilbene, **2**. Reaction of **2** with potassium hydroxide in a high boiling solvent yields diphenylacetylene, **3**.



Properties of Reactants and Products

Pyridinium perbromide, C_5H_6N Br_3; FW = 340	Solid, bp 238°; ρ = 0.79	Toxic and corrosive; avoid inhalation, ingestion or contact;
E-stilbene, 4, $C_{14}H_{12}$ FW 180	Solid, mp l24-l25°	Mildly toxic by ingestion; Orl LD 50 920mg/kg (mus)
1,2-Dibromostilbene, $C_{14}H_{12}Br_2$ FW 340	Solid mp 236-7°	No toxicity data; treat with caution. avoid ingestion or contact
Diphenylacetylene, $C_{14}H_{10}$ FW 178	Solid mp 61°	Unknown toxicological properties. Avoid contact, inhalation or ingestion.
Triethylene glycol, $C_6H_{14}O_4$ FW 150.7	Deliquescent liquid: bp 290° d 1.125	Flammable liquid. Low toxicity.
Potassium Hydroxide KOH FW 56	deliquescent solid	Corrosive and toxic; dissolves exothermically in water; avoid **all** skin or eye contact.

Techniques

Drying and filtration; UV-vis spectroscopy; filtration; recrystallisation.

Procedure

Stilbene Dibromide:- CAUTION pyridinium perbromide is a convenient crystalline source of bromine. However, it should does release molecular bromine in solution, and its hazards on contact are the same as those of bromine liquid. Dissolve stilbene, **1**, (1.0g) in glacial acetic acid (20 mL) in a 100 mL conical flask, by warming gently on a steam bath in a fume food. Add pyridinium perbromide (2.0g) and continue warming for about five minutes. Reaction takes place almost immediately and cooling the flask induces crystallization of the product. Allow the flask to stand at room temperature for five minutes to complete crystallization. Do not chill in ice; glacial acetic acid freezes at 10 ºC. Isolate your product by suction filtration on a weighed Buchner or Hirsch funnel. Use a little ice-cold methanol to rinse the flask and wash the product on the filter. Suck dry and weigh to obtain the yield. The material is usually suitable for the next stage. Check its melting point before proceeding, and retain a small quantity (0.05g) for submission with your report. Use the rest in the second stage.

Diphenylacetylene: - Preheat a sand bath on a hot plate to about 180 ^{0}C. Place stilbene dibromide (1.0 g), triethylene glycol (4.0 ml) and potassium hydroxide pellets (0.5 g., *ca* six pellets) in a 20 x 150 mm test tube. Insert a thermometer in a small test tube containing just enough triethylene glycol to cover the bulb and slide this into the larger test tube, so that you can measure the temperature in the reaction without the thermometer coming into with the corrosive solution of KOH in hot triethylene glycol. Clamp the tubes and thermometer in the hot sand bath and heat to 160 ^{0}C then keep the internal temperature at between 160 and 170 °C for five more minutes. Potassium bromide may precipitate from the triethylene glycol.

Product Isolation and characterization: - Remove the thermometer and small tube, before cooling to room temperature. Add cold water (10 mL) to precipitate the diphenylacetylene, and allow to stand for a few minutes to ensure complete precipitation, before collecting the crystals by suction filtration on a weighed Hirsch funnel. Suck as dry as possible then record the crude yield. Purify by recrystallisation from 95% ethanol. Slow cooling yields beautiful colorless spars (usually about 0.5g).

The write-up: -

This should be the usual description of what you saw and did, written in Chemical Society experimental section style. Show your product in a labeled dated vial to your demonstrator and it will then be filed in the Year 3 cabinet.

In addition, you should deal with the following points: -

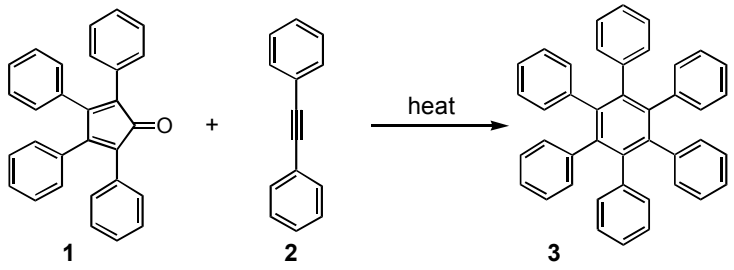
1) How many stereoisomers are there of 1,2-dibromostilbene? Sketch all of them in their minimum energy conformations, and indicate which of them are enantiomeric pairs.

1) The dibromostilbene formed in this reaction is the *meso* isomer? Is this the result of the expected stereochemistry for addition of bromine to alkenes? Sketch the structure(s), which might result starting from *Z*-stilbene.

2) The formation of diphenylacetylene from dibromostilbene can reasonably be viewed as two sequential 1,2-eliminations of HBr. Write mechanisms and show clearly the expected stereochemistry of the eliminations.

8 Synthesis of Hexaphenylbenzene

Abstract: On heating, tetraphenylcyclopentadienone **1** reacts with diphenylacetylene, **2** to yield hexaphenylbenzene, **3**.



Properties of Reactants and Products

Diphenyl ether FW 170.2	$C_{12}H_{10}O$	Liquid bp 258 ºC; d 1.071	High boiling flammable liquid; Irritant. Avoid inhalation, ingestion or contact
Tetraphenylcyclopentadienone $C_{29}H_{20}O$ MW 384		Purple solid mp 219°	Unknown toxicity; avoid ingestion or contact.
Diphenylacetylene, FW 178	$C_{14}H_{10}$	Solid mp 61º	Unknown toxicological properties. Avoid contact, inhalation or ingestion.
Hexaphenylbenzene $C_{42}H_{30}$ FW 534.7		Solid: mp 465 º	Unknown toxicological properties. Avoid contact, inhalation or ingestion.

Techniques

High temperature cycloaddition and crystallization.

Procedure

General comments: - The reaction involves a Diels-Alder cycloaddition with tetraphenyl-cyclopentadienone supplying the diene component and the triple bond of diphenylacetylene supplying the dienophile. Diphenylacetylene is not a very reactive dienophile and high temperature is necessary to force the reaction. Excess diphenylacetylene, bp *ca* 300 °C, is therefore used as the solvent. This has the added advantage that all the highly colored tetraphenylcyclopentadienone should be consumed in the reaction. Both diphenylacetylene and the product hexaphenylbenzene are colorless, so the reaction may be monitored by color change in the reaction mixture. Heating is by microburner or heatgun – seek demonstrator advise. If your materials are pure, and you avoid localized heating, the color change is easy to see.

The reaction: - Place tetraphenylcyclopentadienone (0.5g.) and diphenylacetylene (0.5g.) in a 25 x 150 mm test tube held in a clamp. Heat the mixture to >300 °C – this can be done using a microburner or a heatgun and *do not insert a thermometer into the test tube*; the temperature will be too high! The reactants melt, and bubbling may be seen (why?). Soon white crystals of the high-melting product begin to form. Continue heating, letting the diphenylacetylene reflux in the test tube until the mixture is colorless or light brown rather than deep purple.

Product isolation: - Remove excess diphenylacetylene by filling a smaller test tube with ice-water and lowering it into the heated reaction test tube so that the vapor of the refluxing diphenylacetylene condenses on it. Periodically, lift out the cold tube and clean off the recovered diphenylacetylene. Repeat this process until no more diphenylacetylene condenses on the cold tube. The residue in the reaction test tube should be almost pure hexaphenylbenzene, which may solidify, even at these high temperatures. Allow to cool a little,

Isolation and characterization: - Add diphenyl ether (10mL), to the semi-crystalline mass and heat to dissolve the crude hexaphenylbenzene in the high temperature sand bath. Remove from the sand bath. If there is no suspended insoluble material, allow to cool, and the product crystallizes as white plates. If there is some dark undissolved material, use a Pasteur pipette to transfer the hot solution (care) to a clean test tube, leaving behind the insoluble material, before cooling and precipitation.

Dilute the solvent with toluene (10mL) and collect the product by filtration on a **weighed** Hirsch funnel. Wash with a little toluene. The yield of colorless plates is usually 0.6 to 0.7 g. Run an IR spectrum. *Do not attempt to determine a melting point;* the recorded melting point is 465^0C, which is higher than of lead and not accessible with our mp kits!

The write-up: -

This should be the usual description of what you saw and did, written in Chemical Society experimental section style. Show your product in a labeled dated vial to your demonstrator and it will then be filed in the Year 3 cabinet.

In addition, you should deal with the following points: -

1) Write a mechanism for the reaction of tetraphenylcyclopentadienone with diphenylacetylene. Clearly identify the intermediate. What is the gas which is evolved from this reaction?

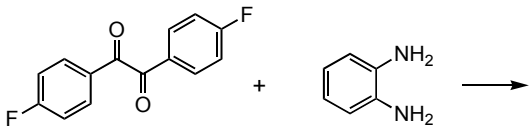
2) Make a model, or an accurate sketch of hexaphenylbenzene. Can this be a planar structure? If not, show clearly how the six peripheral phenyl groups might be arranged around the central one.

3) Why is the IR spectrum of this large molecule so simple?

4) On heating, tetraphenylcyclopentadienone reacts smoothly with dimethyl acetylenedicarboxylate, with evolution of a gas, at 120 °C, yielding a new compound, $C_{34}H_{26}O_4$. Suggest a structure for this compound and explain why the reaction does not require the same high temperature as that with diphenylacetylene.

9 Preparation of a fluorinated heterocycle

Abstract: A fluorinated aromatic (4,4-difluorbenzil) is reacted with 1,2-phenylenediamine to produce a heterocyclic F-containing product.



Properties of Reactants and Products

4,4-difluorobenzil $C_{14}H_8FO_2$ FW = 227		Treat as toxic.
1,2-phenylenediamine $C_6H_8N_2$ FW = 108		Toxic: CAUTION – can cause dermatitis and cause serious eye damage. Wear gloves.
Ethanol: C_2H_5OH FW = 46	Liquid bp 78°; d 0.785	Flammable; may react vigorously with oxidisers; irritant and intoxicant; LD_{50} 3530mg/kg

Techniques

Recrystallization, analysis of ^{19}F NMR.

Procedure

In this experiment you make a fluorine-containing heterocyclic compound through the condensation of amines and carbonyl derivatives. The experiment also demonstrates one of the consequences of introducing fluorine into a molecule.

In one small test tube dissolve 4,4-difluorobenzil (0.22 g, 1 mmol) in ethanol (4 mL) and in second test tube dissolve 1,2-phenylenediamine (0.11g, 1 mmol) in ethanol (2mL). This may require some warming for up to 30 mins. Once the reagents have dissolved add to the 4,4-difluorobenzil solution (make sure all the solution is transferred - wash with a little ethanol if necessary) to the 1,2-phenylenediamine solution. Heat the mixture in a water bath at 50 ºC for 30 min. Add just enough water dropwise to the warm solution until a slight cloudiness persists. Let the mixture cool and then place in an ice/water bath to complete the crystallization. Recover the product by vacuum filtration. Recrystallize the crude product from ethanol and water in a similar manner. Record the melting point and the infrared spectrum of this crystalline sample. Assess the purity of the sample by tlc.

The write-up:-

This should be the usual description of what you saw and did, written in Chemical Society experimental section style. Show your product in a labeled dated vial to your demonstrator and it will then be filed in the Year 3 cabinet. Once you have a sample, your demonstrator will ensure you receive copies of NMR spectra for your write-up.

In addition, you should deal with the following points: -

1) You need to identify the structure of the product.

2) You should draw a mechanism for the reaction.

3) Interpret the ^{1}H, ^{19}F and ^{13}C spectra of the product.

4) Draw the structure of a fluorinated drug in clinical use.

10 Inorganic Reactions of Sodium Borohydride

Aims

to perform syntheses under anaerobic and anhydrous conditions

to investigate complexes and reactions using spectroscopies and chromatography

Objectives

to carry out a risk assessment from hazard data sheets

to prepare triphenylphosphineborane, [Ph_3PBH_3], **A**

to prepare a transition metal borohydride complex, [$(Ph_3P)_2CuBH_4$], **B**

to interpret multinuclear NMR spectra

to interpret mass spectra

to use infra-red spectroscopy in characterisation

to use melting points to establish purity

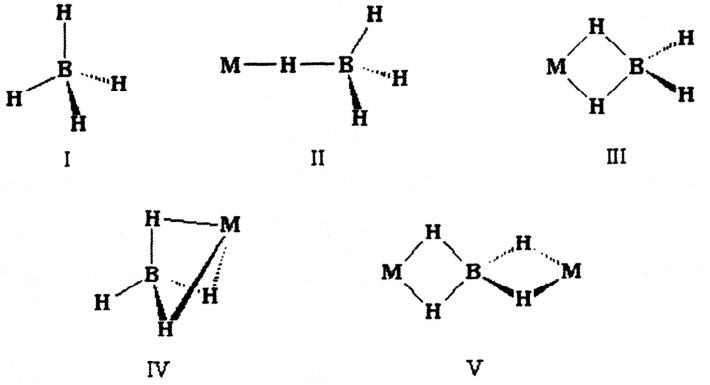
to perform Thin Layer Chromatography to establish purity

Introduction

The borohydride (or tetrahydroborate) anion, BH_4^-, is widely used in organic chemistry as a reducing agent. However, it also has many uses in inorganic chemistry, of which two will be explored in this experiment.

Controlled oxidation of the borohydride anion results in the formation of borane (BH_3). Since borane has an empty p-orbital on the boron atom it normally exists as a dimer (B_2H_6) which has bridging hydride ligands involved in electron deficient three centre, two electron bonds. However, when BH_3 is generated in the presence of electron pair donors, L, it can form adducts, $L \rightarrow BH_3$. Adducts with thf, SMe_2, pyridine and Me_3N are widely used as mild organic reducing agents, while BH_3 is used as a protecting group for phosphines.

The borohydride anion can also form complexes with transition metals, which may adopt a variety of structural types. It may act as an isolated anion (I), or bond covalently to a metal through monodentate (II), bidentate (III), or tridentate (IV) hydride bridges. Furthermore, it can potentially act as a bridging ligand between two metals (V). These structures may be distinguished by the characteristic vibrations in their infra-red and Raman spectra.



SAFETY WARNING – during these preparations gaseous boron hydrides, once considered as rocket fuel, may be produced if glassware or solvents are wet with water and/or the reaction solutions are allowed to come into contact with moist air. These are toxic and spontaneously explosive on contact with most air. Therefore, the reaction solutions used to prepare A and B must be kept under a dinitrogen atmosphere and all glassware must be thoroughly dried prior to use. The resultant solids are air stable.

Experimental

a) Preparation of triphenylphosphine borane, Ph_3PBH_3 (A)

- Using the hazard data sheets provided (obtain from a demonstrator) prepare a risk assessment for the experiment. This should be checked and signed by a demonstrator before you begin experimental work.

Equipment

Nitrogen Line or Nitrogen/vacuum double manifold	Buchner flask
dropping funnel	Buchner funnel and suitable filter paper
Condenser	Refrigerator (or ice)
250 mL 3-necked round bottomed flask	Vacuum grease
Stopper for one neck (for solids addition).	Fittings to attach B19 cones to tubing(2)
ice bowl	Suba seal
Stirrer bar	Heater/stirrer
Silica tlc plates.	

Procedure

WORK IN PAIRS for this part only.

METHOD

Collect glassware and place in a drying oven. Grind your solid reagents (separately) in a dry mortar and pestle.

Fit a three-necked 250 mL round-bottomed flask with a condenser and a dropping funnel. Attach the condenser and dropping funnel to a nitrogen line while still hot from the oven; seal the third neck with a Suba Seal. Insert a small needle into the suba seal. Flush with a strong flow of nitrogen. Check that you can feel the flow emanating from the needle. Leave like this for *at least* 10 minutes [Alternatively you can use a nitrogen/vacuum double manifold. Consult a demonstrator]. Once purged with nitrogen, quickly replace the suba seal with a B19 glass stopper. Leave the nitrogen switched on to ensure a slow but steady stream of bubbles through the oil bubbler. Remove the stopper from the third neck

and add 18 mL of dry THF solvent and a stirrer bar. To this, with stirring, add 4.75 g (18 mmol) of triphenylphosphine powder. Now add 1.03 g (27 mmol) sodium borohydride and seal the vessel again. Place the magnetically stirred solution in an ice bath. Into the dropping funnel add 1.8 mL of acetic acid in 7.2 mL dry THF, and re-seal the system. Add the THF/acetic acid mixture *dropwise* (CARE!) over a 30-minute period. An appreciable amount of frothing will occur as hydrogen gas is evolved, but this is readily controllable with the use of a magnetic stirrer. As soon as all the acid has been added, remove the ice bath, and continue to stir at room temperature for 1 hour. After 1 hour, switch off the nitrogen and open apparatus to air. Carefully add 20 mL water to the reaction mixture, and then add 2 mL acetic acid in 25 mL water. Product crystallisation should occur spontaneously, or by brief storage in a refrigerator or in ice. When complete crystallisation has occurred, filter the product via suction and wash with cold water, then with cold methanol, then with diethylether, and air dry.

- Record the Yield (g, %)

- Record the melting point. If unsatisfactory (consult a demonstrator) re-crystallise by dissolving in chloroform and precipitating by addition of diethyl ether.

- Show your sample to a demonstrator who will examine it, and if satisfactory, give you typical NMR, Mass, and IR spectra for interpretation.

(perform all subsequent steps as individuals)

b) Preparation of Copper(I) chloride

Copper(I) chloride is prepared by reducing copper(II) ions with sulfur dioxide or sulfite ions in the presence of chloride ions. The copper(I) ions once formed react with chloride ions to form the insoluble copper(I) chloride.

Prepare three solutions:

(a) dissolve sodium sulfite (2.5 g) in 12 cm^3 of water,

(b) dissolve copper(II) chloride (3.25 g) in 6 cm^3 of water,

(c) prepare a sulfurous acid solution by dissolving sodium sulfite (0.25 g) in 250 cm^3 of water and add 4 cm^3 of 2M hydrochloric acid.

- Add slowly, with constant stirring, the sodium sulfite solution to the copper(II) chloride solution.

- Dilute the suspension of copper(I) chloride so formed with about half the sulfurous acid solution, allow the precipitate to settle, and decant most of the supernatant solution.

- Filter the solid by suction on a sintered glass disc, wash the precipitate on to the sinter with the remaining sulfurous acid solution. Take care that the copper(I) chloride, CuCl, is always covered by a layer of solution.

- Finally wash the product with portions of glacial acetic acid, abs. EtOH, and Et_2O. Dry the product in a warm oven. Copper(I) chloride is slowly oxidized by moist air to give the basic copper(II) chloride, $CuCl_2.3Cu(OH)_2$, so it must be stored in stoppered containers or used immediately. Commercial "CuCl" is often coloured pale green for this reason.

c) Preparation of bis(triphenylphosphine)tetrahydroborato copper(I), (B)

- Prepare a solution of triphenylphosphine (2.16g) in chloroform (25 cm^3).

- Add finely powdered anhydrous copper (I) chloride (0.4g) with stirring over about five minutes (if all the copper chloride has not dissolved within this time, the reaction mixture should be filtered).

- To this solution a suspension of powdered sodium borohydride (0.15 g) in ethanol (1 to 2 cm^3) is added over ten minutes.

- After the addition is complete, the reaction mixture is stirred for fifteen minutes.

- Pour the reaction mixture into water (5 cm^3): a small amount of decomposition may occur, with some gas evolution and a small amount of elemental copper being formed.

- Separate the organic phase (chloroform solution) from the aqueous phase in a separating funnel and wash with water (2 x 2.5 cm^3).

- After separation, dry the chloroform layer (over anhydrous sodium sulphate).

- Filter off the drying agent.

- Add diethyl ether (20 cm^3) to the resulting solution to obtain colourless crystals of your product, bis(triphenylphosphine) copper tetrahydroborate.

- Filter off the product, wash with diethyl ether and dry in air.

- Record the yield (g, %).

d) Further Investigation

- Record the melting point of both compounds **A** and **B**.

- Record the infra-red spectra of both compounds, and of Ph_3P and $NaBH_4$, as nujol mulls.

- Prepare a solution of a small quantity of $(Ph_3P)_2CuBH_4$ in toluene and warm to 60°C. Record your observations and retain a small sample of the solution obtained for TLC analysis.

e) Thin Layer Chromatography

- Ready prepared TLC plates are available from the demonstrator.

- Prepare a mixture of 20 cm^3 of diethyl ether and 10 cm^3 of 40-60°C petroleum ether and place in the bottom of a large beaker.

- Line the beaker with filter paper to aid solvent saturation of the atmosphere and cover with a watch glass.

- Prepare solutions of 5-10 mg of $(Ph_3P)_2CuBH_4$, Ph_3PBH_3 and Ph_3P in 1-2 cm^3 of CH_2Cl_2.

- Using fine capillaries, apply spots comprising two different concentrations of each sample in a line about 1 cm from the base of the plate.

Note: this is most easily achieved by applying a capillary dipped in the appropriate solution, about 5 successive times and 10 successive times respectively, for each sample, allowing the CH_2Cl_2 to evaporate between each application.

- On a second plate apply samples of $(Ph_3P)_2CuBH_4$, Ph_3PBH_3, Ph_3P and the toluene solution saved from the decomposition reaction above.

- Place the plates into the beaker (one at a time if necessary) and replace the cover.

- Allow the chromatograms to run until the solvent front is *near* (not at) the top of the silica plate.

- Remove the plate from the tank and mark the solvent front before it evaporates.

- Allow the plate to dry thoroughly in air.

- Develop in a tank containing a few crystals of iodine, or view using UV.

- Keep your TLC plate, mark around the spots in pencil and submit with your write up.

Questions

1. Write a balanced equation for the formation of triphenylphosphineborane, $[Ph_3PBH_3]$, **A**.
2. Identify the bands in the infra-red spectrum of $[Ph_3PBH_3]$, **A**, arising from BH_3 and PPh_3.
3. Interpret the NMR spectra of $[Ph_3PBH_3]$, **A**, as fully as possible (see Table 2).
4. Interpret the mass spectrum of $[Ph_3PBH_3]$, **A**, as fully as possible. *Note:* These are positive ion mode electrospray mass spectra recorded from methanol solution. Sometimes sodium cations are picked up from the glass to give positive ions.
5. Identify the bands in the infra-red spectrum of $[Cu(PPh_3)_2BH_4$, **B**, arising from BH_4 and PPh_3.
6. Interpret the mass spectrum of $[Cu(PPh_3)_2BH_4]$, **B**, as fully as possible. See note at 4, above. Propose a reasonable structure for the gas-phase ion observed. (ignore the fragment at 293 and other minor peaks).
7. From the infra-red spectrum of $[Cu(PPh_3)_2BH_4]$, **B**, (using Table I) deduce the bonding mode of the $[BH_4]^-$ ion.
8. Describe the reaction sequence that leads to the preparation of $[(Ph_3P)_2CuBH_4]$, **B**, and draw a diagram of its likely structure.
9. Interpret the NMR spectra of **B**. Explain the differing conclusion drawn from IR and NMR analysis.
10. Calculate the R_f values of PPh_3, $[Ph_3PBH_3]$ (**A**) and $[Cu(PPh_3)_2BH_4]$ (**B**) and comment on the purity of the compounds that you prepared.
11. Describe the decomposition of $[Cu(PPh_3)_2BH_4]$, **B**, and using your observations and any information obtained from the TLC of the toluene solution write an equation for the decomposition reaction.

12. Find a recent literature reference to the use of either phosphine boranes or copper borohydride complexes in organic or inorganic synthesis, (note: different examples for each member of a pairing) and summarise the results in one or two sentences, with a chemical diagram, and a citation to the source.

Table 1: Infrared-Active Vibrations in various MBH_4 Configurations

Structure	**Frequency Range, cm^{-1}**	**Type of Internal Coordinate Change**	**Comments**
I **(ionic)**	2200-2300	B-H_t stretching	**Strong, Broad**
	1050-1150	BH_2 deformation	**Strong, Broad**
II **(monodentate)**	2300-2450	B-H_t stretching	**Strong,probably a doublet**
	2000	B-H_b stretching	**Strong**
	2000-1700	M-H_b stretching	**May be very broad**
	1000-1150	BH_3 deformation	**Strong band, possibly with weaker one at slightly higher frequency**
III **(bidentate)**	2400-2600	B-H_t stretching	**Strong doublet, 50-80 cm^{-1} splitting**
	1650-2150	B-H_b stretching	**Strong band, possible shoulder**
	1300-1500	Bridge stretching	**Strong, broad**
	1100-1200	BH_2 deformation	**Strong**
IV **(tridentate)**	2450-2600	B-H_t stretching	**Strong singlet**
	2100-2200	B-H_b stretching	**Doublet, 50-80 cm^{-1} splitting**
	1150-1250	**Bridge deformation**	**Strong**

Continued over/

Table 2. Isotope data for selected nuclei

Isotope	Abundance (%)	Nuclear spin, *I*	Isotope	Abundance (%)	Nuclear spin, *I*
^{1}H	99.985	½	^{31}P	100	½
^{10}B	19.8	3	^{63}Cu	69.2	$^{3}/_{2}$
^{11}B	80.2	$^{3}/_{2}$	^{65}Cu	30.8	$^{3}/_{2}$

Notres: Nuclei with I > ½ are quadrupolar. Some nuclei are more quadrupolar than others. Multiplicity is given by (2nI + 1). Consult Akitt & Mann, 'NMR and Chemistry' or Ebsworth, Cradock and Rankin, 'Structural methods in Inorganic Chemistry', for guidance. In short, quadrupolar nuclei speed up relaxation, resulting in broad lines and distorted relative intensities and coupling constants in multiplets.

Write up and assessment

Your write-up of this experiment must comprise:

1) A brief introduction stating aims, followed by a record (in past tense, passive voice) of what you did, i.e. an experimental section, consult Dalton Transactions for guidance on style. For each of parts (a) to (e) record your observations and the yield (g, %), appearance and melting point of products as required (out of *25 marks*).

2) Present the annotated spectra (IR, NMR, mass) and TLCs (with R_f values) in your report.

3) Answer questions 1 to 12 (out of *55 marks*).

The other marks (to a total of 100) are for provision of good quality samples of your products, and for accurate recording of your experimental work, quantities (g and moles), yields, and other observations in your laboratory notebook on the day.

Floor Plan Synthesis Labs