Guide for contributors to the Australian Journal of Education in Chemistry

Introduction

The Australian Journal of Education in Chemistry publishes refereed articles contributing to education in Chemistry. Suitable topics for publication in the Journal will include aspects of chemistry content, technology in teaching chemistry, innovations in teaching and learning chemistry, research in chemistry education, laboratory experiments, chemistry in everyday life, news and other relevant submissions.

Manuscripts are peer reviewed anonymously by at least two reviewers in addition to the Editors. These notes are a brief guide to contributors. Contributors should also refer to recent issues of the Journal and follow the presentation therein.

Articles

Articles should not exceed six pages in the printed form including tables illustrations and references - ca. 5000 words for a text only document. Short, concisely written articles are very welcome. Please use headings and subheadings to give your article structure.

1. We prefer to handle all submissions electronically. Our preference is for Microsoft Word files in Mac format. However, you can send files from any common Windows, DOS or Macintosh word processor.
2. On another separate page provide an abstract of 50 to 100 words;
3. All photographs should be scanned and saved in JPEG format.
4. All chemistry structures, and schemes should follow the guidelines set for ACS publications. It is preferred that Schemes, Tables etc be arranged to fit in a column 7 cm wide, although full page width will be accepted.

Reference Styles

AusJEC reference styles are based on the most recent edition of the Publication Manual of the American Psychological Association OR the Journal of Chemical Education.

Copyright

Your manuscript should not have been published already nor should it have been submitted for publication elsewhere. If AusJEC publishes your manuscript then it will become the copyright of the Royal Australian Chemical Institute. The RACI will, however, allow you to use the contents of your paper for most reasonable non-commercial purposes.

The AusJEC Team

Editors

Robert Bucat,
School of Chemistry and Biochemistry,
The University of Western Australia,
35 Stirling Highway,
Crawley WA 6009, Australia.
Bucat@chem.uwa.edu.au
Phone: (+61)(8) 9380 3158
Fax: (+61)(8) 9380 3432

Mauro Mocerino
Department of Chemistry,
Curtin University,
GPO Box U1987,
Perth WA 6845, Australia.
M.Mocerino@curtin.edu.au
Phone (+61)(8) 9266 3125
Fax (+61)(8) 9266 2300

Leslie Glasser
Department of Chemistry,
Curtin University,
GPO Box U1987,
Perth WA 6845, Australia.
L.Glasser@curtin.edu.au
Phone (+61)(8) 9266 3126
Fax (+61)(8) 9266 2300

David Treagust
Science and Mathematics Education Centre,
Curtin University,
GPO Box U1987,
Perth WA 6845, Australia.
D.F.Treagust@curtin.edu.au
Phone: (+61)(8) 9266 7924
Fax: (+61)(8) 9266 2503

All manuscripts should be sent to Mauro Mocerino

AusJEC Reviewing Panel

A.L. Chandrasegaran, Singapore
Vicky Barnett, Australia
Glen Chittleborough, Australia
Deborah Corrigan, Australia
Geoffrey T. Crisp, Australia
Bette Davidowitz, South Africa
Onno de Jong, The Netherlands
Kitty Drok, Australia
Loretta L. Jones, USA
Scott Kable, Australia
Bob Morton, Australia
Mark Ogden, Australia
W (Bill). P. Palmer, Australia
Marissa Rollnick, South Africa
Kim Chwee Daniel Tan, Singapore
Roy Tasker, Australia
Tony Wright, Australia
Brian Yates, Australia
Contents

* A Multi-Step Synthesis Involving a Protecting Group: An Advanced and Open-Ended Version of a Familiar Organic Chemistry Laboratory Exercise
  Jasmine R. Jensen, Hannah M. Wilson and Dennis P. Arnold

* Elementary Kinetics of a Dye–Bleach reaction: A low-mathematics kinetics experiment
  Anna Choy, Daniel Goldstein and Ronald Haines

* Chemometric study on the periodic properties of the representative elements
  João E. V. Ferreira, Antonio F. Figueiredo, Jardel P. Barbosa and José C. Pinheiro

* Green Chemistry and Guided-Inquiry Approaches to the Organic Chemistry Laboratory
  Elisabeth Rukmini

* Insights Gained from an Initial Trial of a Student-Centred Approach in an Introductory Chemistry Unit
  Allan R. Knight and Catherine C. Rowen

* A Tactile Limiting Reagent Exercise: Toys in the Classroom
  Tenaya Newkirk

* Determination of lifetime of α-chlorobenzyl cation in water by “Chloride Clock”: A competition kinetic experiment
  R. Sanjeev, V. Jagannadham and R. Veda Vrath

Supplementary Information

A Multi-Step Synthesis Involving a Protecting Group: ......
J. R. Jensen, H. M. Wilson and D. P. Arnold

* refereed papers

Secondary Division (Years 7-10) winner – Macinley Butson, Year 8, The Illawarra Grammar School NSW
Primary Division (Years K-6) winner – Hunter Murrin, Year 6, Wollondilly Anglican School, NSW
In this issue.....

**Jensen, Wilson** and **Arnold** describe a multi-step organic synthesis laboratory exercise that is an upgrade of a previously well known exercise. The basic process is a four-step synthesis from ethyl acetoacetate to a conjugated enone 4,4-diphenyl-but-3-en-2-one. Synthesis of some of the desired intermediates is relatively straightforward, although achievement of a high yield is challenging. Conducted over six four-hour sessions for upper-level undergraduates, it provides a combination of learning opportunities with respect to laboratory techniques (reduced-pressure distillation, low-temperature crystallisation, classical recrystallisation, trituration of a gum, and column chromatography), synthetic principles including protection and selectivity, and advanced interpretive spectroscopy (IR, $^1$H NMR and $^{13}$C NMR) to characterise five products - each with instructional features. Detailed student instructions and supplementary information on spectroscopic analysis are published in this issue.

A low-mathematics version of a kinetic study of a dye-bleach reaction has been developed and reported by **Choy, Goldstein** and **Haines**. The primary aim is to appreciate that the rate of a reaction depends on the concentrations of the reactant species. The exercise does involve drawing a graph and introduces the concept of reaction rate and its dependence on reactant concentration. To simplify the mathematics, the hypochlorite concentration during a reaction was expressed as the fraction of that in the most concentrated reaction mixture. Concentrations are determined using spectrophotometry. As an addition to the ACELL database, a full educational analysis is presented.

Chemometrics is the art of extracting chemically relevant information from data produced in chemical experiments. **Ferreira** et al. describe how statistical analysis can be used to draw some conclusions about the behaviour of the representative (main block) elements from their periodic properties of atomic radius, first ionisation energy, electron affinity, and electronegativity. The broad objective was to classify these elements as either metals or non-metals, using principle component analysis (PCA) and hierarchical cluster analysis (HCA). Elements are shown to have more metallic character if they have greater atomic radius, but lower first ionisation energy, electron affinity and electronegativity. There is some discussion of the ambiguity of allocation to metals or non-metals, and the variability of ways of classifying elements as metalloids, especially in the case of hydrogen.

**Rukmini** reports the introduction of a green chemistry laboratory experiment, based on guided-inquiry principles, into the sophomore organic chemistry course. Prior to the lab activity, students were provided with an introduction to the notion of green chemistry and the commonly acknowledge twelve principles of green chemistry. With this context, students were required to read a published paper on the acetylation of some amines using a green catalyst. The experimental procedure was not provided by the instructor, but was derivable from the article. In responding to guiding questions about the paper, it was intended that students would learn the reasons for performing the reaction, the decision to use PMA as a catalyst, combinatorial chemistry, and the relative cost efficiencies of processes. Findings from an evaluation of the exercise are included.

In the light of reduced attendance at lectures and tutorials with the introduction of online learning opportunities, a trial was conducted to deliver a bridging chemistry unit using the principles of Process-Oriented Guided-Inquiry Learning (POGIL) to assess the effect on attendance, engagement and achievement. Outcomes were compared with a group of students presented with traditional didactic lectures. **Knight and Rowen** report evidence of a positive experience for those engaged in the POGIL stream, with limitations. No significant differences in levels of achievement or in engagement were observed between the two groups.

**Newkirk** submits a description of a physical limiting reagent exercise using toys. Students are given that the design of Mr. Potato Head follows an “equation” comprising 1 body, 1 pair of eyes, 2 ears, 2 arms, 1 pair of feet, 1 mouth and 3 accessories. Kits with different numbers of components are distributed to the students to find (a) the “limiting reagent” in each case, (b) the “theoretical yield”, and (c) the amount of “excess reagents”. Guidance is provided by questions on a worksheet.

**Sanjeev** et al. describe an experiment in UV spectroscopy as part of a “discovery chemistry” curriculum. The reaction used as a vehicle for learning is the decomposition of benzyl-gem-dichloride. Students record the time-dependent UV spectrum and apply the steady state principle to find the lifetime of the intermediate α-chlorobenzyl carbocation. Conditioning questions are asked before the students conduct the experiment. Pertinent questions following the experiment are designed to enhance conceptualisation of thermodynamic and kinetic reactivity of intermediate carbocations, and their relative stabilities, as well as some insights into application of the Hammett relation.
A Multi-Step Synthesis Involving a Protecting Group: An Advanced and Open-Ended Version of a Familiar Organic Chemistry Laboratory Exercise

Jasmine R. Jensen, Hannah M. Wilson, and Dennis P. Arnold*

School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, G.P.O. Box 2434, Brisbane, Australia 4001; Email: d.arnold@qut.edu.au

Abstract
A comprehensive exercise in organic synthesis and interpretive spectroscopy for upper-level undergraduates is described. Protection of ethyl acetoacetate to yield ethyl 3-oxobutanoate ethylene ketal (product [A]), is followed by double addition of phenylmagnesium bromide with isolation of the protected keto-alcohol 2-(2-methyl-1,3-dioxolan-2-yl)-1,1-diphenylmethanol [B], selective hydrolysis of the ketal to 4-hydroxy-4,4-diphenylbutan-2-one [C], then reduction of [C] to 1,1-diphenylbutan-1,3-diol [D] and dehydration of [C] to conjugated enone 4,4-diphenyl-but-3-en-2-one [E]. Purification techniques include reduced-pressure distillation, low-temperature crystallisation, classical recrystallisation, titration of a gum, and column chromatography. Products are characterised by IR, ¹H NMR, and for [C] and [E], ¹³C NMR spectroscopy.

Introduction
In 1973, Paulson et al. published an undergraduate experiment entitled “The Ethylene Ketal Protecting Group in Organic Synthesis”.¹ Other groups have made modifications and improvements to it. We adopted this experiment in our fifth semester organic synthesis class in the early 1990s, and have run it successfully ever since. We have made several changes to both the original steps and those added by Rivett² and Baar et al.³ Our current version offers several significant and instructive features, that make this experiment an outstanding one for an advanced synthesis class. This classic experiment is now a thoroughly engaging exercise with a unique combination of laboratory techniques, synthetic principles of protection and selectivity, allied closely with advanced interpretive spectroscopy.

We use the sequence ethyl acetoacetate to products [A]—[E], shown in Figure 1. It includes selectively deprotecting the ketal-alcohol [B] to keto-alcohol [C] without dehydration to enone [E].² More vigorous conditions produce the enone in nearly quantitative yield. We added the reduction step [C] to diol [D], an excellent candidate for NMR analysis, as it has an asymmetric carbon. Previous publications have not reported detailed NMR results, but we have found many instructive aspects to the spectra of these compounds.

With 300 or 400 MHz NMR instruments increasingly available to undergraduates, it is opportune to share our enthusiasm for this experiment with other teachers.

Hazards
Hazards are minimal. The hazards of compounds are standard for an advanced undergraduate exercise. The students are provided with relevant information in their handout. Precautions are explained when using bromobenzene, iodine, diethyl ether, toluene, sodium hydroxide, methanol, solid carbon dioxide, and alkane-based solvents, when using heat sources so as to avoid heat and electrical injury, and with apparatus under reduced pressure. Students must wear safety glasses, laboratory coats and closed shoes.

Results and Discussion
The distinguishing features of our procedure and their educational benefits are described below.

(a) Organic chemistry laboratory techniques. Ethyl acetoacetate to [A]: azeotropic distillation to remove water in the ketal formation; distillation under reduced pressure (residual pressures of 20 – 50 torr). [A] to [B]: Grignard reagent formation and addition to an ester to form a tertiary alcohol, with protecting group intact; crystallisation at low temperature. [B] to [C]: selective hydrolysis; classical recrystallisation. [C] to [D]: small-scale reduction; crystallisation by titration. [C] to [E]:

Figure 1. The reaction sequence [A] to [E].
acid-catalyzed dehydration; column chromatography to isolate a coloured product. “Good” yields of purified products are [A] 60%; [B] 30–50%; [C] 70%; [D] 70%; [E] 80%. The total yield of [B] depends on how keen the students are in trying to get second and third crops in the low-temperature crystallisation.

(b) Knowledge and understanding of organic reactions. All the steps are instructive, especially in the context of reaction mechanisms. Cyclic ketal formation under water removal conditions affords an opportunity to discuss the mechanism of hemi-ketal and ketal formation and also aspects of thermodynamics and chemical equilibrium. Alert students will question why transesterification of ethyl acetoacetate with ethane-1,2-diol does not occur. In 2011, Alber et al. reported their variation on this experiment,\(^1\) in which they used the five-carbon homologues. They found transesterified ketal in 9.4% yield. We have never identified specific contaminants in the distilled [A], although very minor peaks are sometimes visible in NMR spectra.

Use of a Grignard reagent leads to discussion of organometallic reagents in general, as well as nucleophilic acyl substitution of an ester carbonyl group followed by addition to form the symmetrical tertiary nucleophilic acyl substitution of an ester carbonyl group organometallic reagents in general, as well as.

Peaks are sometimes visible in NMR spectra. 1,2 In reference 3, product [B] was not isolated, so these workers did not notice the failure of the IR and NMR spectra for all five products are provided in the Supplementary Information. Previously reported versions of this exercise omitted detailed analysis of the spectra, which is understandable when only 60 MHz spectra were available.\(^1,2\) In reference 3, product [B] was not isolated, so these workers did not notice the radical difference between the spectra of [A] and [B], which are revealed at 300 or 400 MHz. Most students easily predict the \(^1\)H spectrum of [A], as their concepts of organic structures in three dimensions up to this point are often naïve and confined to an “answer-the-exam-question” view of tetrahedral carbon atoms. The faces of the ketal ring in [A] are intrinsically non-equivalent, but even at 400 MHz a sharp singlet is observed for the 4Hs of the ring. However, the rug is pulled when the spectrum of [B] is recorded. Figure 2 shows a comparison of the upfield regions of the spectra of [A] and [B]. In Figure 3, an expansion of the ketal region of [B] is displayed; a clear AA′BB′ system is observed. The large difference in chemical shifts between the two faces of the ketal ring is presumably due to the proximity of the phenyl groups and/or the OH group. Moreover, the phenyl proton signals are separated well enough at 400 MHz to appear as a recognizable AA′BB′C system.

The deprotection to keto-alcohol [C] illustrates the reverse of step 1 and the effects of excess water on the ketone/ketal equilibrium. We use the conditions reported by Rivett, namely 0.17 M HCl + acetone 1:10.\(^2\) Dehydration to enone [E] is avoided by heating for only 15 minutes.

Formation of [E] requires more vigorous conditions, namely 10 M HCl + acetone 1:6 and 30 minutes boiling. Students should discuss in their reports why [C] is dehydrated so easily (tertiary doubly benzylic, conjugated product) and why it is coloured (conjugation again). [E] is interesting, as some samples become very dark on standing. We think this is due to residual acid in the product, and thorough washing with bicarbonate is important. It’s an interesting problem to offer the students: “samples of [E] containing traces of acid often discolor on standing – write a mechanism to explain what might be occurring”.

(c) Instructive spectroscopic characteristics. The IR and NMR spectra of [A] (above) and [B] (below), recorded in CDCl\(_3\) solution.

In view of this remarkable difference between the spectra of [A] and [B], we grew single crystals of [B] and determined its crystal structure (Figure 4).\(^5\) This revealed an intramolecular hydrogen bond between one ketal oxygen and the alcohol O–H. In the crystal this results in a chiral structure, which is not maintained in solution due to thermal motion.

Product [C] has a simple NMR spectrum, but its solid-state IR spectrum (neat, ATR) differs from sample to sample, with some spectra exhibiting two sharp OH stretches, and others only one, at about 3475 cm\(^{-1}\). This is probably due to variable proportions of the two
crystal modifications found for [C]. Most samples crystallise as long, fibrous needles, while some (including those used for the X-ray crystal structure determination) comprise cubic blocks. Both intramolecular and intermolecular H-bonds were present in its X-ray crystal structure.\(^6\)

Figure 4. The structure of [B] in the solid state, as revealed by X-ray crystallography (adapted from the published data\(^5\)).

The \(^1\)H NMR spectrum of racemic 1,3-diol [D] provides a superb illustration of the effects of a stereogenic centre on the neighbouring CH\(_2\) protons. The aliphatic region of the spectrum shows at first sight a very complex appearance, as the methine proton is coupled to the methyl group, then with very different vicinal coupling constants to the methylene protons, and also usually to the attached OH proton, leading to a broad, unresolved but symmetrical multiplet. The diastereotopic protons appear as a pair of double doublets, somewhat distorted by "leaning", and the expected large geminal coupling constant of 14.4 Hz. The \(^1\)H spectra for the students’ samples of [D] recorded in CDCl\(_3\) show interesting inter-sample differences in the appearances of the OH proton signals. The downfield signal representing the diphenylcarbinol OH generally appears as a fairly sharp singlet. The secondary OH occasionally appears as a sharp doublet (due to coupling to the methine H), but in some samples, the proton exchange is much faster, and a single, very broad hump is observed for the two OH protons. The students supply the same mass of sample to the technician who records the spectra, so these variations must be due to small amounts of unidentified acidic/basic impurities, or incomplete drying of the sample. The students are provided with notes to assist them in interpreting the spectrum of [D] (see Appendix). If the complications involving the OH protons are eliminated by exchanging them with D\(_2\)O, the first-order pattern of the methine H is revealed, showing a quartet of doublets of doublets, with 14 lines visible of the 16 total, and nearly exact first-order intensity ratios (i.e. the 1:3:3:1 splitting due to the coupling with the methyl protons). High-resolution expansions that are provided to the students are shown in Figure 5. The \(J\) values are displayed on the Newman projection of one enantiomer in Figure 6; the dihedral angles and the vicinal coupling constants fit the expected Karplus pattern. In a report of the 60 MHz spectrum, fine structure was not recorded.\(^7\)

In the solid-state IR spectrum of [D], the OH stretch appears as a broad band at 3250 cm\(^{-1}\), showing the effects of H-bonding that is confirmed by the X-ray crystal structure.\(^8\) The H-bond links the 3-hydroxy H with the 5-hydroxy O, in a six-membered ring. When we published this work in 1996, it was the first example of an intramolecularly H-bonded 1,3-diol. In the crystal studied, there is no intermolecular H-bonding.

Lastly, the enone [E] is another case where observant students will notice subtle features. The \(^1\)H NMR signals for the phenyl groups are different in appearance from those of [B] and [C] (which can be visualised as AA’BB’C, although [C] is more tightly coupled), and of [D], which has a complex aromatic region spanning a narrow range. With careful integration, the phenyl region divides into complex multiplets representing 3H, 5H, 2H from low to high field, clearly not the 4H, 4H, 2H sequence of [B] and [C]. The CH\(_3\)CO– singlet appears at the unusual chemical shift of 1.86 ppm, instead of ca. 2.2 ppm in a “normal” methyl ketone, whereas the alkene CH appears exactly as expected at 6.6 ppm. More was revealed by the \(^13\)C spectrum, which is provided in the Supplemental Material, and includes four quaternary signals at 200.20, 153.95, 140.74 and 138.93, approximately as expected, but in the aryl/vinyl region near 130 ppm, at least six CH carbon signals appear, with overlap in the 128.4 region.

\(^6\) Figure 5. \(^1\)H NMR spectrum of [D] in CDCl\(_3\): expansions of (top) the signals for the diastereotopic methylene protons and (bottom) the methine proton; the OH signals and the coupling between the OH proton and the methine proton have been eliminated by exchange with D\(_2\)O; the FT size was increased to 512k.

\(^7\) Figure 6. Newman projections of one of the enantiomers of the predicted major conformer of [D],\(^8\) showing the observed coupling constants.
We have tried to analyze the spectra using COSY, NOESY, HMBC and HSQC spectra, but a complete assignment is elusive at 400 MHz. The =CH carbon was unambiguously assigned by HSQC to a signal at 127.67. The structure of this compound demands that the phenyl groups are non-equivalent, but many students do not initially realise this, and are surprised at how much the phenyl region of the spectrum of [E] differs from those of [C] and [D]. Furthermore, the chemical shift of the methyl group suggests that this group is located most of the time in the shielding zone of the adjacent phenyl ring. We minimised the structure using Spartan™, and found the most favoured conformation has CH₃ anti to =CH (as drawn in Figure 1), with minor out-of-plane rotations to accommodate the steric demands of the ortho Hs of the “lower” phenyl group (see Supplementary Material). However, the “upper” phenyl ring is rotated well out of co-planarity with the rest of the conjugated system, resulting in the unusual upfield resonance for the methyl group.

**Conclusions**

This exercise (conducted over six four-hour sessions) is received well by students; feedback is almost invariably positive. It meshes very well with our learning outcomes, and prepares advanced students for graduate research in related fields. The actual procedures are virtually “student-proof”, in that reactions fail only if instructions are ignored, yet it is challenging for inexperienced students to get high yields, they are carrying out purification procedures that are new to them, and the characterisation of the five products is spiced with interesting features. It was not until 2011 that one of the students drew attention to the significance of the unusual chemical shift of the methyl group of [E], a fact that had eluded us.

**Supplementary Material**

Hints and extra information for instructors, IR and NMR spectra of [A] to [E], and the calculated optimised geometry of [E]. At QUT, we use a Criterion-Based Assessment for the exercise, and instructors can obtain the matrices from the corresponding author on request.

**Acknowledgments**

DPA thanks the students who have performed the experiment and provided valuable feedback; academic colleagues and ex-colleagues, especially Dr Keith Douglas who discovered it, Drs John Bartley and Chris Carvalho who made invaluable suggestions; crystallographers Dr John McMurtrie and Dr Graham Smith; and the technical staff who provisioned and supported the classes and recorded countless NMR spectra.

**References**

Appendix 1: Student Instructions for the exercise as conducted at QUT
(footnotes relate to possible changes other instructors may like to consider).

A MULTISTEP SYNTHESIS INVOLVING A PROTECTING GROUP

BACKGROUND
It often happens in the design of a synthesis that one wishes to carry out a transformation on one functional group using a reagent that would also react with another functional group present in the same molecule. This may be done by temporarily protecting one of the groups by changing it into another that is unreactive to the reagent in question.

This exercise involves a multi-step synthesis starting with the versatile compound ethyl acetoacetate (ethyl 3-oxobutanoate). As a β-keto ester, this compound has four reactive sites – the ester, the ketone, and the two positions α to the carbonyl groups. You will be carrying out reactions at the first two of these sites. The structures of the intermediate and final products are not given in this handout; you are meant to deduce them, if not from the chemistry, certainly from the spectra of your products. A flow chart of the reaction scheme is shown below.

Two reports are required: an Interim Report after steps 1 and 2, and a Final Report covering the whole exercise. The instructions for the two reports are given in the Appendix.

HEALTH and SAFETY NOTES and CAUTIONS
Risk Assessments of all Hazardous Substances used in the exercise have been carried out, and they are deemed to be safe when used according to the instructions. Particular care should be taken when using bromobenzene, iodine, diethyl ether, toluene, sodium hydroxide, methanol, solid carbon dioxide, and alkane-based solvents. Heating mantles and water baths should be used carefully so as to avoid heat or electrical injury. A distillation under reduced pressure is used to purify product [A]; all glassware should be inspected carefully for cracks and scratches, and all work under reduced pressure should be performed slowly and carefully to avoid the possibility of glass breakages. Personal Protective Equipment must be used according to the rules of the University.

PROCEDURE
Step 1 (ethyl acetoacetate to [A])
To a 250 mL round-bottomed flask equipped with a reflux condenser and a Dean-Stark water separator, add ethyl acetoacetate (20 mL), ethane-1,2-diol (11 mL), p-toluenesulfonic acid (0.25 g) and dry toluene (60 mL). Boil the resulting solution until water collection ceases (usually about one-and-a-half hours). Cool the reaction mixture to room temperature, pour into a 250 mL separating funnel and wash with 10% sodium hydroxide (20 mL) followed by water (2 x 20 mL) and dry over anhydrous sodium sulfate. After filtration, remove the toluene by rotary evaporation.

Small-scale distillation kits with three-position collection adapter (“pig”) are supplied for the distillation, with plastic clips to hold the joints when they are not under vacuum. Transfer the residue to the 50 mL pear-shaped flask and distill at reduced pressure, using a water aspirator or laboratory vacuum to reduce the pressure, a micromantle to supply the heat, and a manometer to measure the residual pressure. Pre-weigh the empty collection flasks before distilling. Use a thin but continuous film of silicone vacuum grease on all ground glass joints, and check that all seals are in good condition – you must have a gas-tight seal in all parts of the system. Check that the vertical position of the thermometer bulb is correct. Insulate the still-head with a loose cover of aluminium foil. Place a boiling stick loosely in the liquid in the flask. Insert the manometer into the vacuum line by means of a T-piece. Check that all joints are sealed and that they rotate easily when turned (note that they will tighten under vacuum). The Instructor should check your assembled apparatus before you apply the vacuum.

If you are using a water aspirator as vacuum source, and the distillation has to be interrupted, the system must be vented to the atmosphere before turning off the water to the aspirator. Consult an Instructor if this is required.

Your aim is to separate any remaining toluene from the bulk of your product. This is done by slowly increasing the applied heat under full vacuum, while observing the collected distillate and the pressure and still-head temperature. You should collect at least a few drops of initial distillate in the first flask, but this depends on how much toluene is actually in your sample. The bulk of the sample should be collected in the largest flask, after the condensing vapour temperature rises significantly, probably to >100°. Record the boiling point and pressure when the major fraction is

1 The use of a “boiling stick” (actually a bamboo meat skewer broken in half) obviates the need for magnetic stirring or a glass capillary bleed; although boiling stones are not useful under vacuum, these sticks work very well under the conditions used.
collected. When the liquid in the distillation flask begins to darken, the heat should be removed. Do not distill to dryness. The Instructor will assist in releasing the vacuum.

Record the yield and the IR and $^1$H NMR spectra of product [A], and submit a representative sample for inspection.

**Step 2 ([A] to [B])**

The reaction and its work-up must be completed in the same session, otherwise the product may degrade. The ether solution of product [B] may be stored once the work-up is completed.

The apparatus consists of a 500 mL round-bottomed flask and a 3-necked adaptor. The latter holds a reflux condenser, addition funnel and a stopper. Two drying tubes are required, one on the condenser, the other on the addition funnel. You also need a dry 50 mL measuring cylinder. All glass parts of the apparatus must be dried in an oven at 100 °C for ten minutes. The plastic parts of the apparatus can be dried with a hair-drier. Assemble the apparatus rapidly, as soon as you remove the glassware from the oven, as glass rapidly re-absorbs water from the atmosphere. You can protect the inside surfaces by capping the open joints with drying tubes or stoppers if you cannot assemble the whole thing at once.

**Preparation of the Grignard Reagent.** Add magnesium turnings (2.0 g), then anhydrous ether (30 mL) and a crystal of iodine (about 2 x 2 x 2 mm) to the flask. Place anhydrous ether (20 mL) and bromobenzene (14 g) in the addition funnel. Ensure the liquids are thoroughly mixed. Then add about a quarter of this solution to the flask. Stir the suspension slowly. Do not add more bromobenzene solution until obvious signs of Grignard reagent formation have appeared — e.g., the iodine colour fading, cloudiness, bubbles. Consult an Instructor if the reaction does not start within ten minutes. Once the reaction starts, the boiling of the ether should increase then begin to subside. When this occurs, add the rest of the bromobenzene solution at a rate such that a steady reflux of the ether is maintained. After the addition is complete, heat the mixture under reflux by placing a bath of warm water (no more than 50 °C) around the flask for 15 minutes.

**Reaction of the Grignard Reagent with Product [A].** Dilute the solution of phenylmagnesium bromide by adding anhydrous ether (30 mL) and cool the flask in an ice bath. Place product [A] from step 1 (7 g) and anhydrous ether (50 mL) in the addition funnel. Mix the liquids thoroughly by swirling. Add this solution steadily to the well-stirred Grignard reagent. Keep the flask in the ice bath during the addition. The reaction is exothermic — your aim is to keep the reaction under control by balancing the rate of addition, and hence heat evolution, with the cooling provided by the ice bath. After the addition is complete, place a bath of warm water (no more than 50 °C) around the flask for 15 minutes. A solid will form, and stirring may become impossible — if so, don’t be concerned.

**Work-up procedure.** Cool the mixture in ice and carefully add a few mL of half-saturated ammonium chloride solution, with swirling and shaking. There may be an initial vigorous reaction if any unreacted Grignard reagent is present. After the initial reaction subsides, the condenser etc. may be removed from the flask for easier addition and agitation, and the solution may be added in larger portions. Take the flask to the fume cupboard for this operation. When the sticky grey solid has all been dispersed, two nearly clear layers should be present. After the initial reaction subsides, the condenser etc. may be removed from the flask for easier addition and agitation. The solution may be added in larger portions. Take the flask to the fume cupboard for this operation. When the sticky grey solid has all been dispersed, two nearly clear layers should be present (this may require up to 150 mL of ammonium chloride solution). You may have to dislodge the solid carefully with a spatula to disperse it. Transfer both layers to a 500 mL separating funnel, but if there is excess Mg metal present, avoid transferring it into the separating funnel. Separate the ether layer and store it in a covered Erlenmeyer flask.

Extract the aqueous layer twice with 20 mL portions of ether and combine all the ether solutions. Dry the ether solution over anhydrous sodium sulfate. Remove the drying agent by filtration, collecting the solution in a pre-weighed round-bottomed flask, and evaporate the ether on the rotary evaporator to leave the product as an oil. Record the crude yield.

Dissolve the residue in 25 mL of methanol, then cool slowly, first in an ice-salt bath, then further in a dry ice-ethanol bath. While the product is crystallizing, cool about 60 mL of methanol in a conical flask in the dry ice-ethanol bath. Collect the crystalline product as rapidly as possible, using vacuum filtration, and using the very cold methanol for transfer and washing of the product. You should turn off the vacuum briefly for the final wash with methanol, then apply full vacuum to dry the solid, and obtain an almost white product.

By collecting the mother liquor and washings, removing about two-thirds of the solvent on the rotary evaporator, and cooling again in ice/salt, then dry ice-ethanol, you may be able to recover another crop of crystals, which you should keep separate from the more pure first crop. Dry the crystals on the filter, then spread on a cover glass. Allow as much drying time as possible before preparing the NMR sample. Record yield, m.p., IR and $^1$H NMR spectra (using your best sample of crystals) and submit samples of all crops of crystals for inspection.

**You must submit an Interim Report of the first two steps (see Appendix), which includes your response to the following task.**

---

2 A brine wash could be used here, but we have not found it to be necessary.
Using flow diagrams, give reasons for each operation in the work-up procedures of steps 1 and 2, including equations for any reactions that occur, and indicating specifically the likely impurities that are carried through or removed at each stage.

**Step 3 ([B] to [C])**
Place product [B] (3 g) in a 250 mL round bottomed flask, add acetone (40 mL), and 1M HCl (6 mL). Boil under reflux on a water bath for 15 minutes. Add water (50 mL), with swirling, then extract with ether (2 x 30 mL). If the interface between the layers is difficult to see, try “salting-out” by adding some sodium bicarbonate solution to the separating funnel. Wash the combined ether layers with saturated sodium bicarbonate (15 mL), then saturated sodium chloride solution (15 mL), and dry over anhydrous sodium sulfate (because of the presence of acetone, it takes more time than usual to dry the solution).

Remove the drying agent, then evaporate the ether and recrystallise the product from “hexane fraction” or similar hydrocarbon solvent. Slow cooling should reward you with excellent crystals, and the actual crystallisation process is fascinating to watch and can be amazingly fast once it is initiated. You may wish to chase a second crop here also, but your primary goal should be the next two steps. Record the yield, m.p., IR and 1H and 13C NMR spectra of product [C]. Submit a representative sample of all crops you obtain for inspection.

**Step 4a ([C] to [D])**
Place product [C] (0.5 g) in a 100 mL round bottomed flask. Add a magnetic stirrer bar and ethanol (10 mL), and stir to dissolve most of the compound. Then add sodium borohydride (0.2 g) in small portions, with stirring, over 5 min. Stir for a further hour. During this time, carry out step 4b.

Evaporate most of the ethanol on the rotary evaporator – a white slurry should be obtained. To this add water (10 mL) with swirling (some effervescence may occur), then ether (10 mL), swirl to dissolve everything, and transfer both layers to a separating funnel. Separate the layers, then extract the aqueous layer with another 10 mL of ether. Combine the ether layers and wash with saturated sodium chloride (10 mL), dry over anhydrous sodium sulfate, filter, and evaporate the ether to yield crude product [D] as a colourless gum.

Crystallise the product by triturating with petroleum ether (b.p. 40-60 °C) (about 5 mL), with persistent scratching and cooling in an ice/salt bath. Alternatively, if it is convenient, good crystals are often obtained by covering the gum with about 5 mL of petroleum ether, and standing the stoppered flask for a week at room temperature. When the product is crystalline, collect it by vacuum filtration, and dry it. Record the yield, m.p., and IR and 1H NMR spectra. You will also be provided with a copy of an expanded 400 MHz NMR spectrum of authentic product [D], which has been recorded after deuteration of the OH groups. Your treatment of the NMR data for product [D] is one of the important elements in the assessment.

**Step 4b ([D] to [E]) (commence this section while stirring the [C] to [D] reaction)**
Place product [C] (0.5 g) in a 50 mL round bottomed flask, add acetone (15 mL), and concentrated HCl (2.5 mL). Boil under reflux on a water bath for 30 minutes. The solution should become pinkish-orange. Add water (30 mL), with swirling, then extract with ether (2 x 10 mL). Wash the combined ether layers with saturated sodium bicarbonate (3 x 10 mL), then water (2 x 10 mL).³ Dry the ether solution with anhydrous sodium sulfate, filter, and evaporate the ether to yield a yellow oil.

This crude product [E] may be purified by rapid column chromatography. Obtain a column with stopcock. If it does not have a sintered glass disc at the bottom, place a plug of cotton wool in the constriction. Clamp the column vertically, add 15 g of silica gel to the column, tap with rubber tubing to settle the packing, then place a 1 cm layer of sand on the top of the silica gel. Prepare 100 mL of 50/50 diethyl ether/petroleum ether (b.p. 40-60 °C). This mixture is referred to as “eluent” below. Keep the prepared mixture in a covered Erlenmeyer flask until needed.

The successive steps must follow each other quickly, so prepare everything in advance.

1. **Prewashing of column:** Add eluent to the column, without disturbing the top of the packing. Open the stopcock, adding more eluent until the packing is saturated and liquid drips from the bottom. Tapping the column with rubber tubing will displace large bubbles, but if you delay here, more bubbles will form, especially on a warm day. When the column is prepared, allow it to run until liquid is just above the sand, then close the tap. Proceed immediately to the next step.

2. **Application of the sample:** Dissolve your crude product [E] in about 1 mL of eluent, transfer this solution by Pasteur pipette to the top of the packing. Rinse the flask with a further 2 mL of eluent, and transfer the rinsings to the column. As with all types of chromatography, your aim is to apply the sample in a narrow, concentrated band.

3. **Elution of the product:** Open the stopcock to allow the sample to flow on to the packing. Add more eluent to avoid the column drying out. The product will travel rapidly as a yellow band. Collect this band in a clean, dry, pre-weighed 100 mL round bottomed flask. When the yellow band has eluted, allow the column to run dry. Dispose of the used silica gel as instructed.

³ A brine wash could be included, but we have not found it to be necessary.
Evaporate the solvent to leave the pure product [E] as a yellow oil. Leave the flask on the rotary evaporator in the hot water for several minutes after all solvent appears to have gone, to make sure the last traces of solvent are removed. Measure the yield, and record the IR and 1H and 13C NMR spectra. The product may discolor on standing, so show an Instructor the fresh material for checking.

**Appendix 2: Requirements for Reports**

(i) The **Interim Report** should include:

(a) **Experimental procedures** written in the style of a Chemistry research journal.

(b) **Results for products A and B**. Results and data should be collected here. Tabulate results such as physical constants, spectroscopic data and yields. The physical appearances of products should be described. Show your yield calculations as an Appendix – a tabular summary is easier to read.

(c) **Discussion of results**. This is the most important part of your report, since it gives an indication of your ability to interpret results and discuss them in a logical fashion. In this synthetic exercise, you should set out to prove that the required target molecules have indeed been made, and show that impurities, starting materials, solvents etc., are absent. The discussion should not be confined only to the spectra of your products, but must also include some chemistry (with brief mechanisms, but relate these to the particular compounds and reaction conditions) and purification methods. You should make appropriate reference to literature sources.

(d) **Bibliography**

(e) **Labelled samples of products A and B**.

(f) **The answer to the Question** given in the Procedure.

(ii) The **Final Report** should include:

(a) **Objectives**.

(b) **Abstract**. A summary of the results in a very succinct form – procedural details should not be included, but % yields should be. It should cover the whole exercise, i.e. products A – E.

(c) **Introduction**. General background material relevant to the exercise should be presented. This might include synthetic principles, protecting groups, important reagent types used (in a general sense), reaction mechanisms, techniques, etc. Some generic structures should be included. Material specifically related to the substances in the exercise should be treated under the heading Discussion.

(d) **Results for products C, D and E** (see (i)(b) above).

(e) **Discussion for products C, D and E** (see (i)(c) above). Some marks are allocated specifically for the detailed interpretation of the 1H NMR spectrum of D (see below).

(f) **Conclusion**. This should be related to the objectives and to what extent they were achieved. It is not the same as the Abstract. Please also express your opinions on the value of the exercise.

(g) **Bibliography**.

(h) **Samples of products C and D**.

**Appendix 3: Verbatim notes supplied to the students regarding the NMR spectrum of [D]**.

There is a very interesting variation between samples in the appearance of signals for the OH groups in this compound. Some of you will see two separate, fairly sharp signals, and even some coupling in one of the OH groups (it should be easy to see which one can do that). The other extreme shows one very broad (several ppm wide) resonance for both OH groups, while intermediate cases show two moderately broad signals. Some samples show the usual slightly broadened peak for water contaminant in the CDCl3, while in others, the water signal is smeared out almost into the baseline. This behaviour is due to the fact that weakly acidic OH groups are exchanging their protons (and those of water) at a rate such that the NMR technique cannot resolve their positions (this is an important tool in NMR for studying the rates of such processes).

This process of proton exchange (mediated by water in the solution) will occur at different rates in different samples, because it is catalysed by traces of acids and bases. So very pure solutes in very pure and dry solvent will probably show two sharp OH signals, even showing coupling between the OH and neighbourhood CH protons in some cases ("slow exchange limit"). However, in other samples, the two alcohol signals and the water signal are averaged, and in the "fast exchange limit", would appear as one sharp line at a mole fraction-weighted chemical shift. For intermediate rates of exchange, it could be anything in-between. Because the energies of the transitions in NMR are small, the NMR method is "slow" compared with other techniques such as UV/visible spectroscopy. It can be likened to a slow mechanical camera shutter, which shows a blurred image when the subjects are moving.

So, for the spectrum of your sample, just report the chemical shifts and appearances of your OH signals, with integrals. You do not have to go into details such as those above. For the aromatics, just describe them as 7.15-7.45 (complex multiplet), because even when this region is expanded, it cannot be analysed by first-order methods.

Assign the chemical shifts in the rest of the spectrum, discuss the presence/absence of impurities, and generally prove the structure and purity using this spectrum.

**Notes regarding the expanded and labelled spectrum provided:**

You are also given an expansion of the 1.0-4.0 ppm section of a 400 MHz spectrum. This sample has been treated (with D2O) so that the OH protons are unobservable and therefore there is no coupling from either OH proton to the
CH signals in the spectrum. You are required to analyse the coupling pattern of just the 1-4 ppm section using first-order theory, and explain how the appearance of the spectrum arises. You will have to think about the three-dimensional shape of the molecule, and the best way is to draw some Newman projections.

Coupling trees are the best approach to solving this problem. For best results, these should be plotted to scale (e.g. 1 Hz = 5 mm) on graph paper. The spectrum is first-order. The problem involves only the group of protons below, and the phenyl protons are not involved (to an observable extent) in any coupling to this group:
Elementary Kinetics of a Dye–Bleach reaction: A low-mathematics kinetics experiment

Anna Choy, Daniel Goldstein, and Ronald Haines

School of Chemistry, University of New South Wales, 2052, NSW, Australia, r.haines@unsw.edu.au

Abstract
There is increasing student demand for university-level elementary chemistry courses structured to suit the needs of students with little or no scientific background. Teaching chemical kinetics in such courses can be difficult because of the intrinsic mathematical nature of kinetics and the lack of mathematical background amongst the students. This paper presents a kinetics experiment which requires no mathematical background beyond the ability to draw a graph but which introduces the concept of reaction rate and its dependence on reactant concentration. The experiment uses household chemicals to illustrate the role of chemistry in everyday life. Concentrations are determined using spectrophotometry, which provides an easy introduction to scientific measurement since light absorption and its dependence on concentration is something students can see with their own eyes. This experiment was enhanced through the ACELL 2009 workshop.

Introduction
Kinetics is one of the foundation stones of Chemistry and arguably has a place in any first year chemistry course. However tertiary institutions who want to offer elementary Chemistry courses for students with no prior science background may find that a significant portion of their target audience also lacks the mathematics needed to describe the terms used in defining what chemical kinetics is about, and even the core quantities such as rate.

The experiment described here is based on an existing published experiment (1) which had been used in our first year laboratory for a number of years. The decolourisation of a food dye on reaction with hypochlorite is easy to monitor using a colorimeter or single beam spectrophotometer. The use of two domestic substances helps to establish a connection between the chemistry practised in the laboratory and the ubiquity of chemistry in the ‘real’ world.

The original experiment required the student to record the absorbance over a relatively long period, at least two half lives, to obtain data which could be graphed according to the integrated zero-th, first and second order rate equations to yield the order with respect to the dye concentration. Reactions were run with excess hypochlorite to obtain pseudo first order conditions. Data were usually of such good quality that the systematic deviation from a linear fit for the zero-th and second order graphs was immediately obvious on inspection. While this experiment worked well, the level of mathematical sophistication required for the data analysis was expected to exceed the mathematical skills of students entering a newly created Introductory Chemistry course designed for students with no high school chemistry background.

The experiment was redesigned into an initial rates experiment, using suitable bleach and dye concentrations and a much shorter observation period. The bleach concentration became an independent variable which the students control via a simple dilution regime while the rate can be seen from absorbance versus time graphs which are close to linear. By graphing absorbance versus time using the same scales for each of several bleach concentrations the effect of the bleach concentration on the rate becomes obvious without any mathematical analysis.

Some mathematical analysis of the results was asked of the students, however the procedure for this analysis was explicitly stated, so that it did not depend on prior mathematical training. Students were shown how to calculate the gradient of the absorbance versus time graphs and then plot the magnitude of the gradient against the concentration of hypochlorite, expressed as a fraction of the concentration in the most concentrated reaction mixture. This was a change as a result of a suggestion in the ACELL workshop: originally the experiment required students to calculate the concentrations of hypochlorite in the dye-bleach mixtures, starting from the concentration in the bleach provided. To simplify the mathematics the graph of rate versus concentration was changed to express the hypochlorite concentration as a simple fraction of that in the most concentrated reaction mixture.

Educational Template

Section 1 – Summary of the Experiment

1.1 Experiment Title
Elementary Kinetics of a Dye–Bleach reaction.

1.2 Description of the Experiment
The absorbance at 630 nm of a dilute solution of a blue food dye is measured over 4 minutes at 30 second intervals after adding sodium hypochlorite solution. The absorbance is plotted against time and the slope used as a measure of the reaction rate. This is repeated with the bleach diluted to 75%, 50%, and 25% of its original concentration to yield estimates of the rate at these concentrations. The rate is plotted against concentration to demonstrate the dependence of rate on concentration.

The primary aim is to demonstrate that the rate of a reaction depends on the concentrations of the reactants (note the target level of the students, see 1.3). Other aims include accustoming students to the definition of rate as variation of concentration with time, the use of
spectrophotometry in determining concentrations, practising data handling skills, and the chemical nature of some domestic substances.

1.3 Level of the Experiment
First year undergraduates with no previous chemistry background (i.e. effectively high school level) and very little mathematical background (nothing beyond plotting a graph and (optionally) estimating the slope).

1.4 Keyword Descriptions of the Experiment
Chemistry Domain: general chemistry
Specific Descriptors: kinetics, elementary, dye, bleach, oxidation

1.5 Course Context and Students' Required Knowledge and Skills
Students performing this experiment are enrolled in a course requiring no previous chemistry background (i.e. no high school chemistry is required). This course was run for the first time in 2009 and this experiment was devised to suit the needs of these students. The course has 2–3 lectures on kinetics towards the end of semester and this experiment is scheduled after these lectures and associated tutorials.

Skills required: handling pipettes and laboratory glassware, plotting data.

1.6 Time Required to Complete
Prior to Lab about 20 min (5 min to get safety data, 15 min to read experiment notes)
In Laboratory 2 hrs experiment and data analysis
After Laboratory N/A

1.8 Experiment History
A more comprehensive analysis of the kinetics of the dye–bleach reaction has been used for many years in a higher level first year course in the School of Chemistry at UNSW. That (3 hour) experiment involved measuring absorbance over an extended period and plotting three graphs according to various integrated rate equations to establish the order with respect to the dye concentration (using an in–house data plotting program). This was then repeated using a diluted bleach solution to establish the order with respect to the hypochlorite. The present (2 hour) experiment was devised by the author (RH) of this document to remove most of the mathematical analysis used in the existing experiment to suit the mathematical skills and chemistry background of the students in the new Introductory Chemistry course run for the first time in 2009. The resulting experiment therefore does not refer to concepts such as rate equations, order etc. but aims to demonstrate the simpler concept that rate does depend on concentration, with minimal mathematical analysis.

1.9 Any Other Comments
The changes from the earlier version of this experiment to the present one are aimed at reducing mathematical complexity (to the point of arriving at an almost semi–quantitative exercise) and reducing the time required for the experiment (required since all our lab classes are now of 2 hours duration, instead of 3 hours in previous years).

### Section 1 – Educational Analysis

<table>
<thead>
<tr>
<th>Learning Outcomes</th>
<th>Process</th>
<th>Indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>What will students learn?</td>
<td>I/D/P</td>
<td>How will students learn it?</td>
</tr>
<tr>
<td>Rate is the time variation of concentration.</td>
<td>I</td>
<td>Correct calculation of the slopes of absorbance versus time graphs.</td>
</tr>
<tr>
<td>Rate depends on concentration.</td>
<td>I</td>
<td>Response to questions in the report for the experiment.</td>
</tr>
<tr>
<td>Reaction is first order with respect to bleach concentration.</td>
<td>I</td>
<td>Response to questions in the report for the experiment.</td>
</tr>
</tbody>
</table>
2.2 Scientific and Practical Skills

<table>
<thead>
<tr>
<th>Activity</th>
<th>Grade</th>
<th>Description</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Using pipettes, diluting a solution.</td>
<td>P</td>
<td>Preparing the solutions used in the experiment.</td>
<td>Data falling within expected ranges, as checked by demonstrator in the lab</td>
</tr>
<tr>
<td>Using a spectrophotometer or colorimeter.</td>
<td>P</td>
<td>Filling, cleaning spectrophotometer cells, recording absorbances.</td>
<td>Successfully measuring absorbances.</td>
</tr>
<tr>
<td>Plotting data.</td>
<td>P</td>
<td>Plotting their data (choosing scales, labelling axes).</td>
<td>Acceptable graphs of their data, as assessed by demonstrator.</td>
</tr>
<tr>
<td>Drawing line of best fit.</td>
<td>P</td>
<td>Drawing the line of best fit on five graphs prepared in the course of the experiment.</td>
<td>Acceptable lines of best fit, as assessed by their demonstrator.</td>
</tr>
</tbody>
</table>

2.3 Thinking Skills

<table>
<thead>
<tr>
<th>Activity</th>
<th>Grade</th>
<th>Description</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculating concentrations after dilution.</td>
<td>D</td>
<td>Carrying out calculations of the concentration of the diluted bleach.</td>
<td>Correct calculations as checked by their demonstrator.</td>
</tr>
<tr>
<td>Interpretation of the graph of rate versus bleach concentration.</td>
<td>P</td>
<td>Answering questions in their report about the relationship of rate and concentration.</td>
<td>Correct response to questions as checked by their demonstrator.</td>
</tr>
<tr>
<td>Critical analysis of experimental procedure.</td>
<td>D</td>
<td>Executing the instructions to mix the bleach and dye solutions and transfer them quickly to the spectrophotometer or colorimeter.</td>
<td>Linearity of absorbance vs time graphs, consistent trend in gradient with variation in hypochlorite concentration.</td>
</tr>
</tbody>
</table>

2.4 Generic Skills

<table>
<thead>
<tr>
<th>Activity</th>
<th>Grade</th>
<th>Description</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Professional data recording skills.</td>
<td>D</td>
<td>Recording observations in pen, without whiteout. Recording numerical data with correct number of significant digits.</td>
<td>On the spot feedback from demonstrator.</td>
</tr>
<tr>
<td>Working in a group.</td>
<td>D</td>
<td>Communicating with lab partner to organise sharing lab tasks.</td>
<td>Successfully able to complete the experiment as a team.</td>
</tr>
</tbody>
</table>

Section 3 – Student learning experience

Explanatory notes

Two groups of students completed this laboratory exercise in 2010. One group of 45 students were in the introductory chemistry course for which the experiment was specifically designed. The second group of 47 students were in a chemistry course designed for a health-related study programme and had a wide range of chemistry backgrounds, with some having no recent secondary level chemistry and a weak mathematical background. In both cohorts the students worked in pairs for this exercise, in contrast to most of their other chemistry experiments which were performed individually.

The students’ response to the experiment was evaluated using the ACELL ‘Student Evaluation of an Experiment’ survey tool. This consists of 12 questions to assess the student reaction to the experiment, on a 5-point Likert scale, 2 questions regarding the time to complete the experiment and the overall learning experience, again each with a 5-point Likert scale, and 5 open response questions about how enjoyable the experiment was, what was learned from it, changes to the experiment and other comments. The Likert scale questions are phrased so that a response indicating agreement indicates a favourable perception of the experiment.

There is debate over the appropriate methods for analysing data from Likert scales (2) however to give some sense of the feedback from the students, eight questions (indicated with an asterisk in Table 1) achieved a numerical average (based on a -2 to +2 scale for ‘strongly disagree’ to ‘strongly agree’ ) greater than one standard deviation above ‘neutral’ and had modal scores of 1 or 2.

None of the questions received a numerical average or a modal score below a neutral response. The data in Table 1 is based on responses from the students in the introductory chemistry course. Responses from students in the health-related programme were not statistically different from those in the Introductory Chemistry course.
**Table 1:** Summary of student responses to the ACELL ‘Student Evaluation of an Experiment’ survey tool.

<table>
<thead>
<tr>
<th>Item</th>
<th>Mean†</th>
<th>Standard Deviation</th>
<th>% Agree or Strongly Agree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 This experiment helped me to develop my data interpretation skills. *</td>
<td>+0.84</td>
<td>0.69</td>
<td>67%</td>
</tr>
<tr>
<td>2 This experiment helped me to develop my laboratory skills. *</td>
<td>+1.21</td>
<td>0.64</td>
<td>88%</td>
</tr>
<tr>
<td>3 I found this to be an interesting experiment.</td>
<td>+0.63</td>
<td>0.87</td>
<td>51%</td>
</tr>
<tr>
<td>4 It was clear to me how this laboratory exercise would be assessed.</td>
<td>+0.53</td>
<td>0.96</td>
<td>53%</td>
</tr>
<tr>
<td>5 It was clear to me what I was expected to learn from completing this experiment.</td>
<td>+0.79</td>
<td>0.94</td>
<td>58%</td>
</tr>
<tr>
<td>6 Completing this experiment has increased my understanding of chemistry.</td>
<td>+0.49</td>
<td>0.98</td>
<td>49%</td>
</tr>
<tr>
<td>7 Sufficient background information, of an appropriate standard, is provided in the introduction. *</td>
<td>+1.33</td>
<td>0.68</td>
<td>88%</td>
</tr>
<tr>
<td>8 The demonstrators offered effective supervision and guidance. *</td>
<td>+1.56</td>
<td>0.91</td>
<td>88%</td>
</tr>
<tr>
<td>9 The experimental procedure was clearly explained in the lab manual or notes. *</td>
<td>+1.21</td>
<td>0.80</td>
<td>86%</td>
</tr>
<tr>
<td>10 I can see the relevance of this experiment to my chemistry studies. *</td>
<td>+1.07</td>
<td>0.77</td>
<td>74%</td>
</tr>
<tr>
<td>11 Working in a team to complete this experiment was beneficial. *</td>
<td>+1.70</td>
<td>0.51</td>
<td>98%</td>
</tr>
<tr>
<td>12 The experiment provided me with the opportunity to take responsibility for my own learning. *</td>
<td>+0.81</td>
<td>0.71</td>
<td>64%</td>
</tr>
<tr>
<td>13 I found that the time available to complete this experiment was ('nowhere near enough’, ‘not enough’, ‘about right’, ‘too much’, ‘way too much’)</td>
<td>+0.17</td>
<td>0.54</td>
<td>N/A</td>
</tr>
<tr>
<td>14 Overall, as a learning experience, I would rate this experiment as ('worthless’, ‘of little value’, ‘worthwhile’, ‘very valuable’, ‘outstanding’)</td>
<td>+0.34</td>
<td>0.48</td>
<td>N/A</td>
</tr>
</tbody>
</table>

† For items 1 to 12 a 5-point Likert scale mapped to numerical values from -2 (strongly disagree) to +2 (strongly agree) was used. A uniform neutral response would yield an average of 0, while a uniform 'strongly agree' response would yield an average of +2. For items 13 and 14 the five responses shown were mapped to numerical values from -2 to +2. N/A = not applicable.

* Indicates items with a positive mean larger than one standard deviation.

The open-ended questions received considerably more favourable responses than unfavourable responses. For example the question “Did you enjoy the experiment? Why or why not?” the favourable responses outweighed unfavourable responses by a 6:1 ratio. The open-ended questions and some typical responses are listed below.

**Q15. Did you enjoy doing the experiment? Why or why not?**
- "I found it more enjoyable than just learning the theory of it."
- "Yes, I was given a chance to use a new device."
- "Yes, as I have never done anything like this."
- "Somewhat, as it was tedious after a while."
- "Yes it was fun."
- "Yes, the results page was easy to fill out."

**Q16. What did you think the main lesson to be learnt from the experiment?**
- "How the rate of reaction changes with concentration."
- "How to complete/show your results in graphs."

**Q17. What aspects of the experiment did you find most enjoyable and interesting?**
- "I found using the spectrophotometer the most interesting because I haven't done it before."
- "Learning to use the equipment."
- "Teamwork."

**Q18. What aspects of the experiment need improvement and what changes would you suggest?**
- "More spectrophotometers."

Typical favourable responses included words such as 'simple', 'interesting', 'easy', 'team work.' Unfavourable responses often included 'boring', 'mechanical' and 'repetitive.' Few students offered suggestions for improvements to the experiment, but the majority of those who did requested more instruments, reflecting the ratio of about 20 student pairs to 12 spectrophotometers. Simpler colorimeters were
available, but most student pairs preferred to wait so that they could use the more sophisticated spectrophotometers.

A final open ended question asking for any additional comments on the experiment attracted few responses (12 out of 47) and those who responded mostly commented on the quality of the demonstrators.

Conclusion
The aim of developing this experiment was to remove much of the mathematical theory of reaction rates while retaining the observations essential to understanding the effect of concentration on rate. The responses to question 16 demonstrate the main lesson learned from the experiment was that the rate depended on the concentration of the reactants, which verifies that the aim of the experiment was achieved. Nowhere in the survey responses is there mention of difficulties with processing the data from the experiment, indicating that the simplification of the mathematics has also been successful. A fascination with new equipment also stands out in the survey results, as does a disinterest in experiments involving much repetition. The question with the largest score in Table 1 concerns the quality of supervision and guidance from demonstrators which reinforces the crucial importance of having good instructors in our laboratories. These outcomes, along with the very positive response to working in a group, should be noted when designing other undergraduate laboratory experiments.

References
Chemometric study on the periodic properties of the representative elements

João E. V. Ferreira¹, Antonio F. Figueiredo², Jardel P. Barbosa³ and José C. Pinheiro⁴

¹Instituto Federal de Educação, Ciência e Tecnologia do Pará. Campus Tucuruí. Rua Porto Colombo, 12. Vila Permanente. CEP 68455-695. Tucuruí, Pará, Amazônia, Brasil. joao.elias@yahoo.com.br
⁴Laboratório de Química Teórica e Computacional, Universidade Federal do Pará. Rua Augusto Correa, 1, Guamá, CEP 66075-110. Belém, Pará, Amazônia, Brasil.

Abstract
Advances in computation have given a great contribution to the chemical investigation, since they make possible to deal with many different types of information about atoms and molecules. In this work computer is used to study the periodic trends of the representative elements through Principal Component Analysis and Hierarchical Cluster Analysis. The pedagogical objective with this activity is to show how Chemometrics can be a useful tool to chemists.

Keywords: Representative elements, periodicity, principal component analysis, hierarchical cluster analysis

1. Introduction
Chemistry uses computers to simulate and calculate properties of simple and complex systems. Advances in computation brought software that made possible to deal with many different types of information about atoms and molecules. With access to spreadsheets, graphs and calculations have become much easier. Moreover it is possible to gather many data and construct a matrix that may give interesting contributions to the chemical investigation. However it seems that analyzing all data will require time. As a consequence most people only think of Statistics when faced with a lot of quantitative information to process. Then the salvation for chemists is Chemometrics, the art of extracting chemically relevant information from data produced in chemical experiments.

In this work Chemometrics is employed to classify the representative elements (also called main-group elements) into metals and non-metals based on their periodic properties. In the long-form periodic table they are found in groups numbered 1, 2 and 13 through 18 or, as an older classification, groups numbered 1 through 8 with each number followed by a letter A. Groups 1 and 2 are on the left side of the table and are called the s-block elements while groups 13 through 18 are on the right side and are called p-block elements. Every member of these groups has the same valence electron configuration and shows distinct and fairly regular variations in their properties with changes in atomic number.

The periodic table of the chemical elements is the principal organisational feature of Chemistry. So knowledge of periodicity helps understand chemical and physical properties of the elements and their compounds. The pedagogical objective with this activity is to show how Chemometrics can help draw some conclusions about the behavior of the representative elements when their periodic properties (size), first ionization energy (the energy required to remove an electron from a gaseous atom), electron affinity (the energy change involved in adding an electron to a gaseous atom) and electronegativity (a measure of the tendency of an atom to attract electron in a chemical bond) are analyzed together. In general these properties are studied separately.

We agree with Hibbert that teaching the statistics of data analysis to undergraduate students can be considered quite straightforward. For this reason this paper describes an interdisciplinary activity that targets undergraduates and involves Chemistry and Statistics according to the topics and subtopics displayed in Table 1. We must keep in mind that Statistics is a valuable tool to chemists.

Table 1. Topics and subtopics involved in this study

<table>
<thead>
<tr>
<th>Topics</th>
<th>Subtopics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periodic Table</td>
<td>Organization</td>
</tr>
<tr>
<td></td>
<td>Classification</td>
</tr>
<tr>
<td></td>
<td>Periodicity</td>
</tr>
<tr>
<td>Chemometrics</td>
<td>Basic Statistics</td>
</tr>
<tr>
<td></td>
<td>Visualization of Data</td>
</tr>
<tr>
<td></td>
<td>Principal Component Analysis (PCA)</td>
</tr>
<tr>
<td></td>
<td>Hierarchical Cluster Analysis (HCA)</td>
</tr>
</tbody>
</table>

2. Methodology
The start point in this work is the construction of a data matrix whose rows are elements and whose columns are periodic properties, as can be seen in Table 2. In this discussion the noble gases were not included since they are generally not listed in electron affinity/electronegativity tables. They have no affinity for electrons, because any additional electron must be added to the next higher electron shell.

In this work the statistical analysis was performed on the data matrix with aid of computation. The program used to obtain the results was PAST, which is a free software that includes common statistical, plotting and modeling functions. Originally PAST was aimed at paleontology, but now also popular in many other
fields. However, before running PCA and HCA programs, data were autoscaled as preprocessing, so that they could be standardized and have the same importance regarding the scale. Autoscaling a value is simply subtracting mean followed by division by standard deviation. The results are scaled variables with zero mean and unit variance. This strategy is necessary because the original data usually does not have optimal value distribution for the analysis (for example, data have different units and variances in variables), for this reason data require some pretreatment prior to multivariate analysis\textsuperscript{11}.

Afterwards PCA was used as an exploratory data analysis intended to find general relationships among data. One of the plots generated by PCA displays the scores and gives information about the elements (similarities and differences) whereas the other plot is for the loadings and shows how the properties are connected to each other and which properties are the best to describe the variance in the original data. Pearson correlation coefficient was calculated to evaluate the linear correlation involving the periodic properties studied.

The second exploratory method used was HCA. This method gives a more precise grouping of the representative elements of similar kind into respective categories (metals and non-metals). HCA is suitable for this purpose since it generates a dendrogram that makes possible the visualization of the disposition of the elements with respect to their similarities/dissimilarities (based on the periodic properties investigated). The objective of HCA was also to present the compounds distributed in natural groups and the results confirm the PCA results. When performing HCA many approaches were attempted to establish links between elements/cluster. All of them are of an agglomerative type. By this strategy each sample is first defined as its own cluster, then others are grouped together to form new clusters until all samples are part of a single cluster. For a further study of the methodology employed here and applications in Chemistry see standard literature on Chemometrics\textsuperscript{1,12-14}.

Table 2. Elements and values of the four descriptors\textsuperscript{a} (periodic properties) selected to run PCA and HCA

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radius (pm)</th>
<th>Ionization Energy (kJ.mol\textsuperscript{-1})</th>
<th>Electron Affinity\textsuperscript{b} (kJ.mol\textsuperscript{-1})</th>
<th>Electronegativity\textsuperscript{c}</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>157</td>
<td>519</td>
<td>80</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>191</td>
<td>494</td>
<td>53</td>
<td>0.93</td>
<td>1</td>
</tr>
<tr>
<td>K</td>
<td>235</td>
<td>418</td>
<td>48</td>
<td>0.82</td>
<td>1</td>
</tr>
<tr>
<td>Rb</td>
<td>250</td>
<td>402</td>
<td>47</td>
<td>0.82</td>
<td>1</td>
</tr>
<tr>
<td>Cs</td>
<td>272</td>
<td>376</td>
<td>46</td>
<td>0.79</td>
<td>1</td>
</tr>
<tr>
<td>Fr</td>
<td>270</td>
<td>400</td>
<td>44</td>
<td>0.70</td>
<td>1</td>
</tr>
<tr>
<td>Be</td>
<td>112</td>
<td>900</td>
<td>-6\textsuperscript{a}</td>
<td>1.60</td>
<td>2</td>
</tr>
<tr>
<td>Mg</td>
<td>160</td>
<td>736</td>
<td>-67\textsuperscript{a}</td>
<td>1.30</td>
<td>2</td>
</tr>
<tr>
<td>Ca</td>
<td>197</td>
<td>590</td>
<td>2</td>
<td>1.30</td>
<td>2</td>
</tr>
<tr>
<td>Sr</td>
<td>215</td>
<td>548</td>
<td>5</td>
<td>0.95</td>
<td>2</td>
</tr>
<tr>
<td>Ba</td>
<td>224</td>
<td>502</td>
<td>1</td>
<td>0.90</td>
<td>2</td>
</tr>
<tr>
<td>Ra\textsuperscript{a}</td>
<td>283</td>
<td>509</td>
<td>10</td>
<td>1.60</td>
<td>13</td>
</tr>
<tr>
<td>Al</td>
<td>143</td>
<td>577</td>
<td>43</td>
<td>1.60</td>
<td>13</td>
</tr>
<tr>
<td>Ga</td>
<td>153</td>
<td>577</td>
<td>29</td>
<td>1.60</td>
<td>13</td>
</tr>
<tr>
<td>In</td>
<td>167</td>
<td>556</td>
<td>29</td>
<td>1.80</td>
<td>13</td>
</tr>
<tr>
<td>Ti</td>
<td>171</td>
<td>590</td>
<td>19</td>
<td>2.00</td>
<td>13</td>
</tr>
<tr>
<td>Ge\textsuperscript{a}</td>
<td>122</td>
<td>784</td>
<td>116</td>
<td>2.00</td>
<td>14</td>
</tr>
<tr>
<td>Sn</td>
<td>158</td>
<td>707</td>
<td>116</td>
<td>2.00</td>
<td>14</td>
</tr>
<tr>
<td>Pb</td>
<td>175</td>
<td>716</td>
<td>35</td>
<td>2.30</td>
<td>14</td>
</tr>
<tr>
<td>Sb\textsuperscript{a}</td>
<td>141</td>
<td>834</td>
<td>103</td>
<td>2.10</td>
<td>15</td>
</tr>
<tr>
<td>Bi</td>
<td>182</td>
<td>703</td>
<td>91</td>
<td>2.00</td>
<td>15</td>
</tr>
<tr>
<td>Po\textsuperscript{a}</td>
<td>167</td>
<td>812</td>
<td>174</td>
<td>2.00</td>
<td>16</td>
</tr>
<tr>
<td>H</td>
<td>78</td>
<td>1310</td>
<td>73</td>
<td>2.20</td>
<td>-</td>
</tr>
<tr>
<td>B\textsuperscript{a}</td>
<td>88</td>
<td>799</td>
<td>27</td>
<td>2.00</td>
<td>13</td>
</tr>
<tr>
<td>C</td>
<td>77</td>
<td>1090</td>
<td>122</td>
<td>2.60</td>
<td>14</td>
</tr>
<tr>
<td>Si</td>
<td>118</td>
<td>786</td>
<td>134</td>
<td>1.90</td>
<td>14</td>
</tr>
<tr>
<td>N</td>
<td>74</td>
<td>1400</td>
<td>-7</td>
<td>3.00</td>
<td>15</td>
</tr>
<tr>
<td>P</td>
<td>110</td>
<td>1011</td>
<td>72</td>
<td>2.20</td>
<td>15</td>
</tr>
<tr>
<td>As\textsuperscript{a}</td>
<td>121</td>
<td>947</td>
<td>78</td>
<td>2.20</td>
<td>15</td>
</tr>
<tr>
<td>O</td>
<td>66</td>
<td>1310</td>
<td>141</td>
<td>3.40</td>
<td>16</td>
</tr>
<tr>
<td>S</td>
<td>104</td>
<td>1000</td>
<td>200</td>
<td>2.60</td>
<td>16</td>
</tr>
<tr>
<td>Se</td>
<td>117</td>
<td>941</td>
<td>195</td>
<td>2.60</td>
<td>16</td>
</tr>
<tr>
<td>Te\textsuperscript{a}</td>
<td>137</td>
<td>870</td>
<td>190</td>
<td>2.10</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>64</td>
<td>1680</td>
<td>328</td>
<td>4.00</td>
<td>17</td>
</tr>
<tr>
<td>Cl</td>
<td>99</td>
<td>1255</td>
<td>349</td>
<td>3.20</td>
<td>17</td>
</tr>
<tr>
<td>Br</td>
<td>114</td>
<td>1140</td>
<td>325</td>
<td>3.00</td>
<td>17</td>
</tr>
<tr>
<td>I</td>
<td>133</td>
<td>1086</td>
<td>295</td>
<td>2.70</td>
<td>17</td>
</tr>
<tr>
<td>At</td>
<td>140\textsuperscript{a}</td>
<td>1037</td>
<td>270</td>
<td>2.00</td>
<td>17</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Atkins, P.; Jones, L. Chemical Principles: the quest for insight, 5\textsuperscript{th} Ed., W. H. Freeman and Company, New York, USA, 2009\textsuperscript{a}.

\textsuperscript{b} The convention adopted in this work is that positive electron affinity corresponds to an endothermic process while negative electron affinity corresponds to an exothermic process.

\textsuperscript{c} Pauling scale.

\textsuperscript{d} Lee, J. D. Concise Inorganic Chemistry, 4\textsuperscript{th} Ed., Chapman & Hall, New York, USA, 1997\textsuperscript{d}.

\textsuperscript{e} http://www.rsc.org/periodic-table/element/86/radium\textsuperscript{e}.

\textsuperscript{f} Metalloids.

\textsuperscript{g} Zumdahl, S. S.; Zumdahl, S. A. Chemistry, 7\textsuperscript{th} Ed., Houghton Mifflin Company, Boston, USA, 2007\textsuperscript{g}.
3. Discussion
The exploratory analysis of the data set presented in this work (Table 2) can be better visualized through graphics generated by PCA and HCA, which are powerful visualization tools. In the case of PCA the main idea is to find principal components PC1, PC2, ... PCn that are linear combinations of the n original variables (periodic properties) describing each sample (element). The principal components are at right-angles to each other (orthogonal) and are selected so that the first principal component (PC1) explains most of the variation in the data set, the second (PC2), explains the next largest variation and so on. A 2D (two dimensions) plot of PCA was constructed by placing PC1 and PC2 on the axes instead of the original variables since PC1 and PC2 are the most important principal components.

In Figure 1 we see the plot of PC1-PC2 scores for the representative elements based on atomic radius, first ionization energy, electron affinity and electronegativity. By analyzing the figure we conclude that the representative elements can be classified according to PC1 values as follows: metals (PC1 < 0), metalloids (0 < PC1 < 0.7) or non-metals (PC1 > 0.7). Moreover the general tendency among elements in a group is that both PC1 and PC2 decrease when we move down a column of the periodic table. In the period, elements with greater atomic number have lower values for PC1.

It is interesting to point out that in a modern classification Ge, Sb and Po are classified as metals whereas B, Si, As and Te are classified as non-metals. However the scores plot shows that for metalloids the separation into these two groups (metals and non-metals) is not so distinct in PC1. The reason for this lies in the fact that they have characteristics similar both to metal and non-metals and these characteristics are related to the periodic properties under study. As a consequence metalloids have an ambiguity in behavior and chemists do not have the same opinion about which elements fit into metals or non-metals.

The other plot generated by PCA presents the PC1-PC2 loadings for the four properties (Figure 2). It suggests that based on the first two principal components there must be a strong correlation between the first ionization energy and the electronegativity, as also demonstrated by the Person correlation coefficient in Table 3 ($r = 0.912$). The lowest linear correlation occurs between atomic radius and electron affinity ($r = -0.421$).

<table>
<thead>
<tr>
<th>Table 3. Pearson correlation coefficient, $r$ ($p &lt; 0.05$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Radius</td>
</tr>
<tr>
<td>Ionization Energy</td>
</tr>
<tr>
<td>Electron Affinity</td>
</tr>
<tr>
<td>Electronegativity</td>
</tr>
</tbody>
</table>

According to Table 4, the three principal components PC1, PC2 and PC3 explained 79.3, 15.5 and 3.2%, respectively, of the total variance. The greatest percentage of explained variance, as expected, is associated to PC1. Interpretation of loadings plot for PC1 reveals that all periodic properties are important (have the same magnitude) to the classification of the representative elements. Then, based on PC1, the representative elements exhibit the following general trends if they are metals, i.e, to generate more negative PC1 values: greater atomic radius, but lower first ionization energy, electron affinity and electronegativity. The contrary is valid for non-metals.

<table>
<thead>
<tr>
<th>Table 4. Principal components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>Atomic Radius</td>
</tr>
<tr>
<td>Ionization Energy</td>
</tr>
<tr>
<td>Electron Affinity</td>
</tr>
<tr>
<td>Electronegativity</td>
</tr>
<tr>
<td>Eigenvalue</td>
</tr>
<tr>
<td>Explained Variance (%)</td>
</tr>
<tr>
<td>Accumulated Explained Variance (%)</td>
</tr>
</tbody>
</table>

Figure 1 Scores plot of the first two PCs for the main group elements based on atomic radius, first ionization energy, electron affinity and electronegativity. Metals are displayed on the left side, metalloids in the middle and non-metals are on the right side.
Considering the HCA results, the best approach chosen to group samples into clusters employed the Euclidean distance and Ward’s method. Euclidean distance is a common numerical measure of similarity used in multivariate analysis that is calculated through the equation 1:

$$d = \sqrt{(x_1 - y_1)^2 + (x_2 - y_2)^2 + \cdots + (x_n - y_n)^2} \quad (1)$$

where $d$ is the distance between two points in $n$ dimensional space with coordinates $(x_1, x_2, \ldots, x_n)$ and $(y_1, y_2, \ldots, y_n)$. The smaller the distance, the more similar are the samples. The Ward’s method algorithm established links between samples/cluster so that the agglomerative clustering criterion is based on the minimization of the squared Euclidean distances of individuals from the centre of gravity of the cluster to which they have been assigned. The purpose of performing HCA is also to group the elements into two main clusters: one for metals and another for non-metals.

The representation of clustering results is shown by the dendrogram in Figure 3, which depicts the similarity of the representative elements. The branches on the bottom of the dendrogram represent single elements. The length (distance) of the branches linking two clusters is related to their similarity in order that long branches suggest low similarity while short branches mean high similarity. The distances between merged clusters increase as we proceed from singleton clusters to one all-inclusive cluster. The dendrogram displays clusters for metals on the left, metalloids in the middle and non-metals on the right. As already explained, metalloids have similarities with metals and non-metals. Thus the cluster having metalloids is between those for metals and for non-metals. Groups of elements with the greatest similarities are: Fr and Cs; Rb and K; Ba and Sr; Na and Li; Bi and Sn; Tl and In; Ga and Al; Si and Ge; As and P; Se and S.

The element phosphorus (P) is wrongly labeled as metalloids. However, in the periodic table, it is localized close to metalloids: just after silicon in the third period and just above arsenic in column 15. Certainly phosphorus must have a behavior compared to that of metalloids, at least if we take into account the periodic properties employed to generate the dendrogram. In fact, the closest element to metalloids in PC1-PC2 scores (Figure 1) is phosphorus.

Finally fluorine is the element that presents the lowest similarity with other elements. This behavior is due to its great electronegativity, very small atomic radius and high ionization energy. Hydrogen, because of its small size and single electron, shows special properties not found fully in other elements. Thus depending on the property being considered the position of hydrogen in group varies in periodic tables. For example, in some periodic tables, hydrogen is put in group 1 for it has one electron that is easily lost. This group has alkaline metals, but hydrogen is not a metal at all. In other periodic tables, hydrogen is put in group 17 for it is one electron short of a noble gas configuration (He), but it is not a halogen. According to PCA and HCA the classification of hydrogen is among non-metals and close to carbon. Nevertheless it is not altogether correct to put hydrogen in the same group of carbon for there are other elements in the group with properties very different from those of hydrogen such as tin and lead, which are metals.

![Figure 2 Loadings plot of the first two PCs for the main group elements based on atomic radius, first ionization energy, electron affinity and electronegativity](image-url)
Figure 3 HCA dendrogram (Euclidian distance and Ward’s method) for the representative elements based on atomic radius, first ionization energy, electron affinity and electronegativity. In general metals are displayed on the left side, metalloids in the middle and non-metals are on the right side.

4. Conclusions

Chemometrics suggests that it is not possible to classify all the representative elements exclusively into metals and non-metals through PCA and HCA based on atomic radius, first ionization energy, electron affinity and electronegativity. Metalloids are presented as being elements with periodic properties between metals and non-metals. So metalloids must have a behavior in some aspects similar to these two classes of compounds. According to PCA, the general rule to differ a metal from a non-metal is that metals have greater atomic radius, but lower ionization energy, electron affinity and electronegativity whereas the contrary is observed for non-metals.

Some elements demonstrate a high similarity with other elements. This is a direct consequence of the fact that they have similar periodic properties. However it is important to have in mind that the behavior of the representative elements analyzed through PCA and HCA may vary significantly if other properties are taken into account, such as boiling point, melting point, density and conductivity.

By this strategy we try to encourage teachers and students to develop the application of Chemometrics to investigate not only relations in the periodic table but also in any problem of chemical interest. Certainly it is an interesting and useful way of teaching and learning in an interdisciplinary way.

References

Green Chemistry and Guided-Inquiry Approaches to the Organic Chemistry Laboratory

Elisabeth Rukmini

Department of Chemistry and Biochemistry, School of Medicine, Atma Jaya Catholic University of Indonesia, Jakarta, 14440, Indonesia elisabeth.rukmini@gmail.com

Abstract
We have introduced a green chemistry and guided-inquiry laboratory experiment into our sophomore organic chemistry laboratory course. Prior to the lab activity, students were provided an introduction to the green chemistry and the Twelve Principles of Green Chemistry to give them a glance of the significance of doing green chemistry. Students then were asked to read the main article about acetylation and to answer the questions in the Student’s guide.

Introduction
The goals of the sophomore organic chemistry laboratory course are not limited to the simple acquisition of lab skills. The course is also intended to amplify the content of the lecture. This sophomore organic course emphasizes the use of methods to determine organic structures. This course also tries to incorporate a writing component, with the intent of encouraging thoughtful engagement of the material. An additional focus of the course was the introduction of the process of “green chemistry,” a more environmentally conscious way to carry out reactions. One such experiment is acetylation of some amines using a green catalyst (Kadam and Kim, 2008).

The laboratory instructional material for this experiment was designed as a guided-inquiry approach. Students were required to read the paper by Kadam and Kim (2008) and answer the guided-questions prior to the lab activity. The experimental procedure was derived from this reference; however, the instructor did not provide detailed experimental procedure. Students were asked to write the detailed reaction conditions guided by the questions in the students’ guide. This experiment was also a combinatorial activity, in which students could choose one of the four choices of amines as the starting material (Figure 1).

Figure 1. Choices of starting amines

Learning goals for this experiment are to learn TLC through organic synthesis, to introduce GC/MS as an instrument to identify the reaction’s products, and to learn green chemistry principles. The reaction is acetylation of amines, using a heteropolyacid catalyst (phosphomolybdic acid, PMA), without heating and without solvent. The reactions were completed in about 10-20 minutes by stirring at room temperature. To monitor the reaction, students needed to perform thin layer chromatography (TLC). In the second lab session, students were provided with their GC/MS spectra and they learned how to interpret their GC/MS data.

This lab activity used a guided-inquiry approach to help students’ learning. Students were provided with the referenced article and questions to guide them through the referenced article. Through the questions, students would learn the reasons for performing the reaction, the decision in using PMA as catalyst, combinatorial chemistry, cost-efficiency process in comparing with other acetylation and some of the green chemistry principles. Students would also find the procedure through the reference by themselves.

This article describes how the guided-inquiry questions lead the students throughout the lab activity. The questions asked about the acetylation experiment, green chemistry principles, TLC, and the GC/MS spectra.

Three characteristics related to inquiry learning (Abraham, 2005) are: (i) it leans toward inductive reasoning, (ii) it shifts the teacher’s role as facilitator and (iii) it incorporates problem-solving activities including questions and answer, writing, and group discussion. Research in inquiry learning and its comparison to traditional approaches have been explored; there are substantial differences between inquiry versus traditional approaches in conceptual acquisition, process learning, motivation, and attitude (Abraham, 2005; Burke, Greenbowe, & Hand, 2006; Friel, Albaugh, & Marawi, 2005; Greenbowe, Pock, Burke, & Hand, 2007; Oliver-Hoyo, Allen, Hunt, Hutson, & Pitts, 2004; Sanger, 2007; Sanger, 2008).

The Environmental Protection Agency of the United States of America (EPA) included green chemistry as part of its negotiation in industrial impact on the environment. This action was also a response to The Pollution and Prevention Act of 1990 that urged the EPA to avoid or diminish pollution at its source (Anastas & Warner, 1998; EPA, 2010c; Woodhouse & Breyman, 2005; Woodhouse, Hess, Breyman, & Martin, 2002). This effort also pushed for new approaches to solve pollution through prevention. With this spirit, EPA developed the Green Chemistry Program. The major goal of green chemistry is to reduce hazardous substances right from the beginning of the reaction design. This is to say that if reactions were designed
without hazardous material, then the waste would not be harmful (Anastas & Warner, 1998; Cann, 2009). The Twelve Green Chemistry Principles, which for the first time were published by Anastas and Warner (1998), have been excellent sources to drive research and development in green chemistry.

To promote green chemistry to science students, chemistry education needs to incorporate green chemistry into the curriculum. Students need to be introduced to and be trained further in green chemistry reactions. In the future when these young students compete for jobs and need to design better chemical reactions or processes in industries, their education in green chemistry will be important. Several groups have implemented green chemistry into their curriculum, for example Carnegie Mellon University (Collins, 1995), Princeton University (Swan & Spiro, 1995). Through prominent chemical societies, for example the American Chemical Society (ACS) and Royal Society of Chemistry, green chemistry education has been implemented throughout their chapters to undergraduate and graduate levels.

Experimental Procedure (Kadam & Kim, 2008)

Procedures. 

Materials and instrumentation. All of the starting materials were available commercially. GC/MS data was collected on a Varian-2000 instrument.

Hazards. The organic chemicals used in this experiment should not come in contact with skin. Acetic anhydride is corrosive and a lachrymator. It can cause severe irritation and burns skin and eyes and may cause a skin allergy. Safety goggles and gloves should be worn at all times. Further health and safety notes may be found in the Supplemental Material.

The Guided-Inquiry Material (Student’s Guide)

The student’s guide incorporated guidelines and questions to be answered by the student. In the introduction to the experiment, we introduced briefly what students needed to do prior to the experimental section (see Appendix: Supplemental material: students’ guide). Students were asked to submit their answer on number 3 prior to the experiment. This step was intended to help students reading and writing their experiment method before the lab work. The final report (acetylation writeup) would have the rest of the answers and the GC/MS spectra.

Understanding Acetylation Process. From student’s guide: question number 1 in the student’s guide asked about what the word “acetylation” means. Students were asked to draw the functional group that should be attached to alcohols or amines as the acetylation was completed. This question addressed students’ prior knowledge about functional groups. Through questions number 2 and 3 in the student’s guide, the students were required to read the abstract and experimental sections of the cited reference. Question number 2 aimed to introduce students to the acetylation lab that they were about to perform. The abstract section in a scientific publication gives significant information to the readers. Students should be able to answer question number 2 by reading the abstract of the cited reference. Question number 3 asked about the procedure to perform acetylation. This question has five sub-questions which were intended to guide the students through how to calculate their starting amines, acetic anhydride and catalyst (PMA) amounts.

Background Information of Acetylation, TLC and Green Chemistry. Questions number 4 to 8 required students to read through the main reference and possibly to search through other references to answer the background information about acetylation. These questions lead to the application, the reaction, and the chosen catalyst in this lab activity. Questions 4 to 10 required students to understand the TLC and green chemistry principles.

TLC is a simple procedure to monitor an organic reaction. In question number 10, students were required to describe how TLC works and why they need to perform TLC in this reaction. Before this lab activity, students had had experience in applying TLC directly on the organic reaction mixture.

Prior to the lab activity, the students were introduced to the Twelve Principles of Green Chemistry (Anastas & warner, 1998). In the guided-inquiry questions, students were asked about the green catalyst and the green chemistry principles involved in the acetylation reaction. Students were expected to answer by learning through doing this experiment.

GC/MS spectra. On the second week, students were provided with their GC/MS spectra of their starting amines and products. Question number 11 addressed the spectra. It asked the reason why GC/MS was performed. It also required the students to assign the peaks on their provided spectra as reactants or products. Students needed to explain briefly why they decided to assign the specific peak. By assigning the spectra, the instructor may identify common misconceptions that students made in identifying GC/MS data. In the final question (number 12), students were asked about their opinion
whether TLC and GC/MS were interchangeable. This question was intended to evaluate two different methods to identify products in organic reactions.

Results and Discussion
The guided-inquiry material in this experiment forced students to learn how scientific information could be found in the published paper. This way led students to read through the abstract, experimental method, and introduction of the published article. By providing answers to the questions, students were led to understand and carefully design what they needed to perform the same reactions.

Experimental procedure was not provided by the instructor, so students needed to write down by themselves. To help students, the guided material asked questions in details what students need to prepare, the calculation and the procedure itself. Question number 3 in the material was important and part of the assessment from the teaching assistants (TA). TAs also performed a mentor role by helping students formulate the answer and monitor how students write the procedure. This activity was performed prior the experiment. Therefore, there was scaffolding from TAs to students, from the advanced learners to the first learners (Vygotski & Cole, 1978).

Question number 4 to 7 introduced students about the nature of the experiment. Again, students were asked to find the answers within the referred article. By answering the significance of acetylation, students learn that the process would resulted in a precursor for other organic synthesis since the acetyl group is easily to be attached as well as to be removed, by mild alkaline hydrolysis, and that the group is stable under acidic conditions. Acetyl group is also significant for protecting alcohol and phenol groups. Students also learned that there were some problems in acetylation in which it needed special and expensive yet non-environmentally friendly catalysts. Acetylation used to be a long time reaction and thus it consumed a lot of energy and again it was non-environmentally friendly reaction. By answering the questions, students were also guided to learn about heteropolyacid (HPA) in the reaction. HPA is economically efficient, environmentally friendly, stronger acid when compared to conventional acid. HPA can be incorporated in the reaction with low concentration at ambient temperature, thus HPA could be classified as an environmentally friendly. Phosphomolybdic acid (PMA) is an example of HPA. It is stronger than sulfuric acid but it can work at ambient temperature. PMA has been used in some important reactions for example in Friedel-Craft acylation of phenol, Fries rearrangement of phenyl acetate, the oxidation of hydroxyl group, the regioselective opening of N-tosylaziridine and in the deprotection of tert-butyldimethylsilyl ethers (Kadam & Kim, 2008).

Results on students’ learning could be implied from students’ reflection about the lab activity. Students responded that the acetylation lab has taught them about green chemistry.

I feel that the concepts we learned in our first Green Chemistry lab are extremely practical. Instead of doing labs where we add an excess of one reagent, heat it up for long periods of time, and create a hazardous waste as a by-product, we can be more environmentally conscious. We can only use the amounts we need. This can best be done by performing calculations before the lab, figuring out how much product we want, calculating yields, and

Figure 2. GC chromatogram for: Aniline starting material (top) and the product of acetylation of aniline (acetanilide) (bottom)

Figure 2. MS Spectra for aniline as starting material (top) and the product of acetylation of aniline (bottom).
determining what starting amounts will give the results that we are looking for. F09-PP2-1_Essay 1

In this Acetylation Lab, the most important principle I found was using the most appropriate catalyst, because it is not only beneficial itself by minimizing waste, but fulfills many other principles. Using PMA as the catalyst for this reaction prevents disposal problems because they are active in low concentration and noncorrosive and increases energy efficiency because the reaction happens at room temperature. It also makes the chemical sythese not hazardous because none of the chemicals has high toxicity. So this principle—using appropriate catalysts—was the most essential one for the “greenness” of this experiment. S09_RX_Essay 1

The guiding questions had helped students in preparing the lab also to understand about the acetylation.
The guiding questions were useful for me to learn this lab. They helped me learn the reactions involved in this experiment, which were the most important part for me to understand this lab. The questions also guide me to grasp the essence of the reference and design procedures for the lab in the process of finding answers. Most importantly, they led me to think about the green chemistry principles and how they were important to chemistry lab. S09_RX_Essay 1

As the students learned about the chemistry, they also learned about the connection between chemistry and the society through green chemistry.
The green chemistry experiments helped me learn more about why the experiments we did were important in society. There was usually very little background about the regular experiments. It was not as easy to see the significance that those experiments held in society. I liked reading about how the green chemistry reactions were used in pharmaceuticals, because then I can relate it to my life. F09-PP2-13_Essay 3

Conclusion
Students have had new experience in guided-inquiry and found that the questions were thought-provoking. They encouraged the incorporation of more green chemistry experimentation in the organic lab course.

Acknowledgement
The authors would like to thank Summer and Fall 2009, CHM 244 Organic chemistry students for doing this lab activity. The authors would also like to thank Dr. Richard P. Hotz and Dr. Richard T. Taylor for facilitating this activity in their Summer 2009 and Fall 2009 classes.

Supplemental Material
Students’ guide, which include guided-inquiry questions and safety information are available.

References


Appendix 1: Supplementary information

Students’ guide

Acetylation, TLC and GC/MS

Before this meeting, you have already decided what starting material you are going to use in this reaction. They are basically amines.

Choose one of these amines as your starting material:

![Chemical structures of amines]

The reaction you are going to perform is based on the reference below:


Pull out the paper from the Blackboard. Please follow the questions and read the paragraph below in each step while performing the reactions. You may find the answers from the cited reference. Write your answers in your hand-in papers. Before leaving the lab, please ask an approval signature on your paper, from your TA.

Answer for question #3 due before the start of the lab class. The rest of the questions (Acetylation write-up) due to one week later; hand in your paper with your GC/MS spectra.

1. You are going to perform an acetylation of alcohol or amine. Briefly explain with your common sense what is acetylation of alcohol or amine? (What functional group are you going to “attach” to your alcohol or amine? Draw this group or you may draw the reaction. Just use your prior knowledge and give a brief reason by doing that). [2 points]

2. Now, read the abstract of the cited reference and answer the following:
   a. What will you use to introduce acetyl group into your amines? [2 points]
   b. What catalyst will you use in this reaction? [2 points]
   c. What is the meaning of acetic anhydride (1.0 equiv) and catalytic amount (0.2%) of PMA? [2 points]
   d. Based on the abstract, do you think you are going to perform this reaction by heating? Give the reason. [2 points]

3. Read the first couple sentences under the subtitles “Acetylation of Alcohols, Phenols, and Amines; General Procedure” on page 269. Find your starting material in Table 1 (p. 268-269). Write down your schema or simple notes to perform your reaction. Whenever you are ready, try to perform this reaction. The following statements may help you to discover your own reaction condition. [same as lab note’s total points = 10 points]
   a. Write down your amine (structure and formula). Suppose you want to use 1 mmol of your starting material (amine).
   b. Write down the acetic anhydride (structure and formula). If the reaction is 1:1 equiv, you may want to calculate how many your acetic anhydride is.
   c. Write down the catalytic amount of the catalyst.
   d. Draw your own schema or write your own procedure with actual reaction time you need (consult Table 1 on p. 268-269 of the reference). You don’t need to do column chromatography.
   e. Read the safety precaution about your material before performing the reaction.

While waiting for the reaction, please go through the following questions and answer them based on the reference.

4. Why do people want to introduce acetyl group into alcohols, phenols and amines? [4 points]
5. The reference indicates some problems in acetylation. List here what are the problems. [5 points]

6. How do the authors suggest solving those problems? [2 points]

7. The catalyst you are using in this reaction is categorized as heteropolyacid (HPA). According to the reference, what are the significances in using HPA? [5 points]

8. The authors compare the use of PMA versus sulfuric acid. In your own words, what makes PMA a better choice than sulfuric acid? [5 points]

9. In the key words, the authors list green catalysis. Why? By performing this reaction, do you find any green chemistry principles? What are they and why do you say so? [2 + 3 points]

10. Thin layer chromatography (TLC).
   a. Based on your knowledge, how TLC works? [3 points]
   b. Why do we need to do TLC in this reaction? [2 points]

Second week

11. GC/MS. You are provided with your own GC/MS spectrum
   a. Why do we need GC/MS spectrum? [2 points]
   b. Assign your spectrum by drawing your product and or reactant in your spectrum sheet. How do you decide that? [3 points]

Appendix 1: Supplementary information

Safety and hazard
Reagents that will be used in the acetylation:

<table>
<thead>
<tr>
<th>Reagents</th>
<th>CAS number</th>
<th>Warnings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>62-53-3</td>
<td>Aniline is toxic by inhalation and in contact with skin. Harmful if swallowed</td>
</tr>
<tr>
<td>Phenylmethanamine</td>
<td>100-46-9</td>
<td>Corrosive and flammable. Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation (lung irritant).</td>
</tr>
<tr>
<td>Cyclohexanamine</td>
<td>108-91-8</td>
<td>It is flammable and reacts violently with water. Avoid inhalation and contact with skin. Harmful by inhalation. Harmful in contact with skin.</td>
</tr>
<tr>
<td>Octylamine</td>
<td>111-86-4</td>
<td>Corrosive and irritant. Harmful in contact with skin and by inhalation. It can cause severe burns.</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>75-64-9</td>
<td>Highly flammable and corrosive. Contact with water liberates extremely flammable gases.</td>
</tr>
<tr>
<td>Phosphomolybdic acid</td>
<td>51429-74-4</td>
<td>Highly flammable and corrosive.</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>108-24-7</td>
<td>It is corrosive and a lachrymator. It can cause severe irritation and burns skin and eyes and may cause a skin allergy.</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>144-55-8</td>
<td>Relatively non-toxic.</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>8032-32-4</td>
<td>Flammable and may cause lung damage if swallowed. Irritating to eyes, respiratory system and skin.</td>
</tr>
</tbody>
</table>

The organic chemicals used in this experiment should not come in contact with skin. Wash affected areas thoroughly with water and soap. Safety goggles and gloves should be worn at all times.

Reagents’ Specification

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Formula</th>
<th>MW (g/mol)</th>
<th>d (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>C₆H₇N</td>
<td>93.13</td>
<td>1.0217</td>
</tr>
<tr>
<td>Phenylmethanamine</td>
<td>C₆H₅CH₂NH₂</td>
<td>107.15</td>
<td>0.981</td>
</tr>
<tr>
<td>Cyclohexanamine</td>
<td>C₆H₁₁NH₂</td>
<td>99.17</td>
<td>0.867</td>
</tr>
<tr>
<td>Octylamine</td>
<td>C₈H₁₇NH₂</td>
<td>129.24</td>
<td>0.782</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>(CH₃)₃CNH₂</td>
<td>73.14</td>
<td>0.696</td>
</tr>
<tr>
<td>Phosphomolybdic acid</td>
<td>H₃[P(MoO₄)₁₀₉₄]·xH₂O</td>
<td>1825.25</td>
<td>1.62</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>(CH₃CO)₂O</td>
<td>102.09</td>
<td>1.08</td>
</tr>
</tbody>
</table>
Insights Gained from an Initial Trial of a Student-Centred Approach in an Introductory Chemistry Unit

Allan R. Knight and Catherine C. Rowen

School of Engineering & Information Technology, Murdoch University, Perth, Western Australia 6150, Australia, k.rowen@murdoch.edu.au

Abstract
A student-centred approach based on principles of Process-Oriented Guided Inquiry Learning (POGIL) was trialled with a group of students in an introductory chemistry unit for one semester. Traditional didactic lectures were used for one group of students (PEC140) and the student-centred approach implemented for a second group (TPEC140). Other learning activities, assessments and additional learning materials were the same for both groups. Unit survey data indicated a positive experience for students who participated in the student-centred approach, but also identified limitations. No significant difference in levels of achievement or engagement was observed between the two groups.

Introduction
With the increasing provision of learning experiences to Australian university students through online platforms it is not surprising that, given the opportunity for more flexible ways to meet their learning needs, many students are opting for reduced face-to-face interaction with teaching staff and their peers. Provision of online resources, such as lecture slides and their audio recordings, may contribute to disengagement from lectures and tutorials. Student satisfaction and success are usually linked to engagement with teaching staff and other students, who comprise the learning community. Murdoch University offers a bridging chemistry unit (PEC140 Introduction to Chemistry) for students who require various levels of chemistry knowledge for their degree programme, but did not take it at high school. Students in the unit come from a wide range of backgrounds including recent high school graduates, mature-aged students, international and migrant students with English as a second language, as well as many first-generation university students. Lectures are the main vehicle for content delivery in this unit and a lack of student engagement with them, the interaction with staff and fellow students that is lost as a consequence, and the possible impact on student achievement are concerning.

A trial was undertaken to deliver lectures in this unit using the principles of Process-Oriented Guided-Inquiry Learning (POGIL) to assess its effect on attendance, engagement and achievement. POGIL is a learning and teaching strategy based on an understanding that people learn by:4

- Building understanding based on prior knowledge, experiences, skills, attitudes and beliefs
- Following a learning cycle of exploration, concept formation and application
- Making connections between multiple concepts and representations
- Discussing and interacting with others (i.e. learning is social)
- Evaluating their progress and performance
- Interconnecting conceptual and procedural knowledge in large mental structures.

The student-centred POGIL methodology uses activities based upon the exploration, concept development and application phases of the learning cycle to actively engage students in understanding concepts whilst developing valuable learning skills by working in groups.2 Studies have shown that students learning using this cycle have better attitudes, higher achievements, greater understanding and retention of concepts and develop learning process skills.6-10 POGIL style teaching has been successful in improving both retention rates and student achievement. Introduction of POGIL at Franklin and Marshall College in the U.S.A. in general first year chemistry decreased attrition from 22% (traditional) to 10% (POGIL) and was accompanied by improved performance by the students taught in the POGIL style.11 In a large study covering seven institutions in the U.S.A., POGIL was more effective than lecture instruction for organic chemistry in terms of both student achievement in standardised exams and student perceptions of their learning.12 Another study involving general chemistry students found that those who experienced POGIL achieved higher scores in exam questions requiring higher-order skills that are specifically developed using this type of instruction.13 The same study showed that POGIL students achieved higher than the national average on standardised exams.13

The aim of this study was to compare the effectiveness of teaching a bridging chemistry unit using a student-centred approach incorporating principles of POGIL, to teaching it in the traditional mode. The effectiveness was assessed in terms of student engagement, level of achievement and retention. The study also provided the opportunity to gather information about the applicability and viability of the student-centred approach for our students and circumstances.

Methodology
Upon enrolment in PEC140 for Semester 2 2011, 75 students were randomly allocated to a cohort (TPEC140) to whom ‘lectures’ in the unit would be delivered using a student-centred approach based on the principles of POGIL. Students in PEC140 would experience traditional didactic lectures. A requirement of the University’s ethics approval for this pilot program was that students be given the opportunity to
transfer between groups, so up to the end of Week 2 students could transfer from TPEC140 to PEC140 or, without exceeding the limit of 75, from PEC140 to TPEC140. There were 11 students who transferred from TPEC140 to PEC140 and 8 students from PEC140 to TPEC140. The bulk of students in TPEC140 were those randomly selected at the start of the semester. At the end of the semester enrolment in PEC140 was 129 students and in TPEC140 48 students.

PEC140 lectures consisted of the traditional lecture style with the lecturer using PowerPoint presentation, overhead projection (light or video), or a combination of these, and speaking at the front of a lecture theatre. For TPEC140 ‘lectures’ content was delivered using POGIL principles. The ‘Basic POGIL Classroom Implementation’ document outlines these principles, which are as follows:

1. Students are expected to work cooperatively in groups of 3 or 4.
2. Students work on activities that are designed specifically for POGIL implementation.
3. Students work on the activities during class time with a facilitator present.
4. The dominant mode of instruction is not lecture or instructor-centred, the instructor facilitates student learning.
5. Students have assigned roles within their group.
6. The activity is designed to be the first introduction to a topic or specific content.
7. Students are not expected to have worked on the activities prior to classes.
8. Groups are expected to complete particular questions/exercises during classes and there are additional questions for after class.

These principles were not applied to the full extent in this trial. Students were expected to work in groups, but were not assigned roles. The activities were made available to students before classes using the University’s online Learning Management System (LMS) for the unit. Students therefore had the opportunity to work on the learning activities before the classes, but were not expected to have done so. Students were expected to work through any activities not completed during class in their own study time. The learning activities were designed so students could work on them independently if they chose to do so and this is in keeping with the flexible access ethos of this institution. Some activity sheets were adapted from existing POGIL activities and others developed by the authors. For TPEC140 the lecturer, although sometimes speaking to or working through exercises with the whole class, usually spent the 50 minutes interacting with students in their groups as they worked through learning activities. One of the lecturers has a formal qualification in education and experience working with small groups in guided enquiry-type learning activities. Neither lecturer had specific professional development in the implementation of POGIL.

TPEC140 lectures also incorporated an audience response system enabling students to respond to questions during lectures and giving lecturers the opportunity to review and reinforce concepts should the need arise. Audio and screen capture recordings of lectures were made in both PEC140 and TPEC140. These were available to students through the LMS, where use of recordings could be tracked. There were separate LMS sites for PEC140 and TPEC140, so students had access only to recordings for the unit in which they were enrolled. There were four 50 minute lectures per week (over the 12 teaching weeks of the semester) for each group which were run at the same time with different lecturers. All students were provided with the same laboratory (five 3-hour laboratory activities) and tutorial experiences (one hour per week). Assessment items were the same for both cohorts and were jointly designed by PEC140 and TPEC140 lecturers. Assessment consisted of two one-hour in-semester tests (25%), five online assignments (10%), laboratory assessments (15%) and a two-hour examination (50%) at the end of the teaching period. The assignments and laboratory exercises were formative assessment providing feedback to support learning whilst the final examination was summative. Test and examination questions ranged from those designed to probe knowledge recall to those designed to probe critical thinking/problem solving skills.

Student engagement was assessed through comparison of attendance at lectures and tutorials, assignment completion, and student impressions gathered from survey responses. Attendance at lectures and tutorials was monitored by the lecturer/tutor manually counting the number of students in the room at the commencement of the class. The average attendance each week was calculated as a percentage of the number of students who remained enrolled at the beginning of the week. Assignment completion could be tracked using the LMS where these assessments were administered. The standard Murdoch University student survey of units was modified to obtain information about student impressions, attitudes and experiences. Unit surveys were administered online and students offered the opportunity to enter a draw for an iPad at the end of the survey. The survey was anonymous and the entry form for the prize was not linked to the survey. The survey questions for PEC140 and TPEC140 students are shown in the Appendix.

Student achievement was assessed by comparison of results on all assessment components, overall pass rates, and spread of grades. The effect of the traditional versus student-centred inquiry based style lectures on retention was assessed by comparing the number of withdrawals and the number of DNS grades (the student failed to participate in assessment components that had a combined weighting of 50% or more of the final mark). Quantitative data (scores on tests, assignments, laboratory mark and examination) were subjected to t-tests and means were considered to be statistically different at \( p = 0.05 \). Assignment completion rates were subjected to a two proportion test.
Results and Discussion

Attendance at lectures and tutorials is not mandatory in this unit and many students do not engage in these on-campus learning activities, preferring to access the extensive online materials and lecture recordings outside of scheduled class times. This flexible approach to student learning is strongly advocated by Murdoch University and the majority of Australian Universities. Declining attendance at lectures and tutorials, that have no associated credit for participation, is widely discussed by academic staff. Research carried out at two Australian Universities explored reasons for non-attendance. Access to learning materials outside formal classes is just one factor affecting attendance rates. Another study led to the conclusion that students support the principle of flexible access to learning materials, but lack the preparedness required to take responsibility for their learning. Implementation of a student-centred approach in our introductory chemistry unit did not overcome this culture and attendance at classes was poor. It seems that the success of this methodology does require students to be in the classroom and a comparison of achievement in the two cohorts of students in the trial will be discussed later. This section will focus on the impressions of TPEC140 students who completed the survey at the end of semester, and the level of engagement with the lectures in both groups.

Student Impressions and Engagement

The written comments in the TPEC140 survey gave the impression that students who engaged with the learning activities had a generally positive experience. The majority of responses (9/15) to Question 27 (Describe one or two aspects of the learning activities in this unit that were most helpful) identified the activity sheets developed for use in lectures as an effective tool. Some students were specific about the benefits of the lecture worksheets, stating that they provided an opportunity to apply new knowledge immediately.

- I think the activities provided during the lectures were useful as we are able to apply our knowledge straight away when we learn it as it is still fresh.
- I found the activities to be very useful. The activities allow one to concrete a concept by doing rather than trying to read about a concept. It is also useful to have other students and the lecturer to learn from.

It was obvious from some student responses that students who were repeating PEC140 in the TPEC140 group found the alternative lecture format helpful. A comparison of the pass rates for repeating students in both groups is discussed later.

- I started PEC140 last semester but decided to drop out because I just couldn't follow the lectures etc. and found myself failing miserably. TPEC140 is the complete opposite – the way the information is presented and the opportunity to work through the concepts immediately with peers made the content so much more accessible. I'm now achieving reasonable marks and I enjoy chemistry now! Big thumbs up!
- This unit has been SO much more helpful than PEC140 and I really really hope it is continued to be offered, I'm not sure if I would have been doing so well at chemistry if I had been taking PEC140 again.
- I found it a lot better than PEC140 as the interactions helped me to learn a lot faster and ask questions more regularly.

Students who were not able to attend all the lectures recognised the worksheets as the cornerstone for learning the unit material and they engaged with those as a study tool.

- The interactive group work was helpful at times when we were able to bounce things off each other and ask the lecturer questions. If I had to miss a lecture it was useful to have the activities to do at home alone also.
- The worksheets we were given in class were really helpful when studying for the tests. I went through them, made sure I could do everything on my own, and studied hard and I received a distinction on the first test and a high distinction on the second. They were a really great studying tool. They covered everything which was necessary to learn for the tests (probably a little bit harder too) so that when I got into the test it was easy.

It was anticipated that student-centred lectures implemented in TPEC140 for this trial would not be amenable to recording, but the lectures were recorded in accordance with the flexible access approach of this institution. It was further predicted that students would recognise the limitations of the lecture recordings and that the interactive nature of the student-centred lectures would engage students and encourage attendance. The importance of attending the TPEC140 lectures and the limitations of their recordings were articulated by one student in a response to a survey question.

- At various times throughout the semester I was unable to attend the lectures due to work commitments. While the activity sheets were very useful, it felt that the lecture slides and Lectopia recordings were not as much of a useful tool as they would be if the unit was presented in the traditional way. This lecture format seems to depend heavily on student attendance, this is not a bad thing per se, however, it does feel more difficult at times when lecture attendance is not possible.

Comparison of lecture attendance between the two groups of students showed that the lecture format had no influence on attendance (Figure 1). The percentage of students attending lectures in the two groups was comparable, starting with 40% of students attending in Week 1 and declining throughout the semester to 19% of PEC140 students and 18% of TPEC140 students attending in the final teaching week. The use of audience response questions in the TPEC140 lectures was reduced dramatically as the semester progressed. Students did not tend to respond to the questions because, with so few people in the room, some of the anonymity associated with using such a system was lost.
Comparison of tutorial attendance and assignment completion rates also showed no difference between the two groups.

Figure 1. Attendance in the traditional (●) and student-centred (■) lectures as a percentage of the number of students enrolled each week.

While the physical attendance at lectures was comparable between the two groups of students, there was a marked difference in the usage of lecture recordings and this added weight to the view that the TPEC140 lectures were not amenable to recording and less useful than recordings of traditional lectures. The percentage of students who accessed lecture recordings was the same for each group (58%), 75/129 PEC140 students and 28/48 TPEC140 students. However, the ratio of total number of hits on lecture recordings to students accessing recordings tells a different story. For PEC140 the number of hits to students using recordings was 1556:75 (21:1) and for TPEC140 315:28 (11:1). Students using recordings of PEC140 lectures did so at nearly twice the rate of TPEC140 students. Closer analysis showed that 54% of TPEC140 students accessing recordings did so five or fewer times and 25% only accessed a single recording. This is in contrast to the PEC140 students accessing recordings, where 28% accessed recordings five or fewer times and only 9% were single users. The conclusion drawn from this analysis was that the student-centred lecture recordings were not an effective tool for students, but this did not motivate students to attend the lectures as predicted.

Responses of TPEC140 students to Question 28 (Describe one or two aspects of the learning activities in this unit that were least helpful) revealed some areas where there was difficulty with the student-centred guided inquiry style. Lack of attendance made the allocation of students to specific groups redundant. Students who attended formed ad hoc groups for each lecture. Some responses about the least helpful aspects of TPEC140 are shown below.

- The attendance for lectures was pretty poor most days, which made working in groups difficult at times. I was lucky to have a group that almost always turned up.
- I actually found the group work in class really unhelpful. At the beginning of the semester, I was attending every lecture. One person transferred into the normal PEC140 from my group, and the other two after a week or so stopped turning up. This really got me off to a rocky start because there was no consistency in the group work. Eventually, I began to talk to other groups etc. I spent so long being confused, trying to figure out what others were talking about that it became obvious that I needed to do the readings for the week before the first lecture to gain an understanding just so that I could get through the work sheets. Everyone in the groups had no idea what they were doing, and spent so much time confused and doing the wrong thing that I stopped going to the lectures and started doing the work on my own. It was much more efficient, with much less confusion - but I was still using the worksheets. As a result of stopping going to the lectures, I actually did better on the second test than I did on the first!
- If I/my group were finding something particularly difficult and the lecturer was busy with another student then the whole lecture could be wasted while waiting, stuck on a question, for the lecturer to be available to help clarify things
- Some activities were too long to cover during lecture times.
- Group work. Rushed and brief lectures.
- I thought more explanation of a number of subjects was warranted. At times it felt as if the subjects were not adequately explained before we started on the worksheets.
- Quite often I found it more difficult to concentrate during the lectures with the constant chat, it can be very distracting. I try to work through the worksheets before going to the lecture so I could concentrate. When it came to certain topics that I didn't understand, I found it really difficult that no demonstration of the solution was given, so I could see how it was supposed to be worked out. For example Stoichiometry, I didn't understand the written (wordy) explanation given in the worksheet, and only one example in one area was given during the entire study block. This was deeply frustrating, and I still have not mastered this subject. When I asked questions, I still did not get a demonstration, so I am still a bit baffled!
- It is hard to pair up with students who don’t turn up for all lectures.

Other survey comments (Question 29 Any other comments about your experiences in this unit?) show that students appreciated the POGIL style learning activities, but would perhaps prefer them to complement the traditional lecture format.

- This lecture format seems to be an effective way of learning the unit material. If lectures are attended I feel it results in less time required studying outside of lecture times. To counter balance the problem of attendance I think also providing the traditional PEC140 lecture slides and recordings might go a long way to fill the gap. There were times when I was working through the material at home having missed the lectures that I felt such material would be very useful. The activity sheets were still a very powerful tool in these cases.
At the end of the day, I still believe that the structure of TPEC140 was better than that of PEC140. I am not repeating the unit, I don’t know what the original lectures were like, but compared to other units, engaging in the worksheets was much better than just listening to a lecturer speak for 50 minutes. I would suggest perhaps moulding the two units together - Giving both the lectures and the activity sheets to the students in PEC140?

I hope you continue to use this learning style. It might need some refinement but I think it’s an improvement over the traditional lecture style.

Responses to survey questions indicated a different experience between the two groups of students, but a detailed comparison of survey responses was not possible. The online unit survey was completed by 64/178 (36%) of PEC140 students and 20/48 (42%) of TPEC140 students. Note that the total number of students indicated for PEC140 (178) is greater than the number of students who completed the unit as part of this trial (129). This is because the unit survey for PEC140 was also available to students who completed PEC140 externally (distance education) in the same semester as this trial (the number of on-campus students in PEC140 was 129). Due to the anonymity of the survey, responses of external students could not be identified or excluded and this is a limitation of the survey data. The proportion of PEC140 students who participated in the trial and completed the survey is not known. Despite the inability to compare survey responses between the two groups, a high rate of overall agree responses from TPEC140 students to particular questions was encouraging and provided information to guide changes in our teaching practices.

Survey questions 9 – 15 related to the teaching activities in the unit and Table 1 shows the percentage of overall agree (Strongly Agree, Agree, Slightly Agree) responses of TPEC140 students. The low rate of agreement (47%) with Question 11 is consistent with the learning activities that this group of students was exposed to, small group work rather than lecture presentations. For the other questions related to the learning activities the rate of agreement with the statements was 90% or greater. The response to Question 9 was particularly pleasing; with 50% strongly agree responses. These survey responses provide a strong impetus for incorporating guided inquiry learning activities into our introductory chemistry unit. Engendering a positive attitude towards learning chemistry (Question 9) and peer/group learning (Questions 12, 13 & 14), along with the recognition of enhanced problem solving skills (Question 15) are very important for students’ academic development.

It is worth noting that TPEC140 students who responded positively to the questions about the learning activities in the survey may have attended or accessed the learning activities through the LMS, but it was concluded that the majority of students responding to the survey attended the lectures regularly. One limitation of this study is that is did not track the attendance of individual students and compare that with their level of achievement. It may have been the case that the positive attitudes of TPEC140 students conveyed in survey responses resulted in a better academic performance for those who attended regularly, but it is not possible to conclude this due to the nature of the study and the focus on overall level of achievement of the two groups of students.

Students have identified positive and negative aspects of the student-centred guided inquiry approach for this unit. It seems clear from the written survey responses that students who engaged with the guided inquiry learning activities in the lectures had a good experience. Students have also identified limitations and their comments indicate that a combination of traditional delivery incorporating guided inquiry learning activities and provision of the activities with the online learning materials may be the way forward for our students and circumstances.

Table 1: Percentage overall agree (Strongly Agree, Agree, Slightly Agree) responses of TPEC140 survey respondents to Questions 9 – 15.

<table>
<thead>
<tr>
<th>Question number</th>
<th>Question text</th>
<th>TPEC140 Overall Agree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>I have a more positive attitude about learning chemistry now compared to when I started the unit.</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>The teaching in this unit helped me improve my understanding of chemistry.</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>I learn better from lecture presentations than small group work.</td>
<td>47</td>
</tr>
<tr>
<td>12</td>
<td>Solving problems in a group is an effective way to learn chemistry.</td>
<td>95</td>
</tr>
<tr>
<td>13</td>
<td>I have a more positive attitude about learning with my peers.</td>
<td>90</td>
</tr>
<tr>
<td>14</td>
<td>My experiences in this unit have improved my view of group learning.</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>The learning activities helped me develop my thinking skills (e.g. problem solving, analysis).</td>
<td>95</td>
</tr>
</tbody>
</table>

Student Achievement and Retention

Comparison of average mark, pass rate and distribution of grades for students in the two cohorts showed no statistical difference (at $p = 0.05$) (Table 2). The average mark for PEC140 students (53.2%) and TPEC140 students (53.5%) as well as individual assessment component marks (in-semester tests, online assignments, laboratory and final exam) showed no statistical difference between the two groups. This result was disconcerting, but not unprecedented. In a similarly designed study, Murphy et al. found that students in two cohorts using POGIL learning activities (either 100% or 1/3 of the lecture time) did not achieve on average to the same level as those in a group using traditional didactic lectures. In that study, student achievement improved with an adaptation incorporating ‘mini lectures’ of a few minutes duration into the classes based on POGIL learning activities. Qualitative data from student surveys in the study reported here indicate that this combination of brief lectures and student-centred guided inquiry learning activities may be preferred by students and this will be expanded upon later.
There was also no significant difference between the percentage of students who achieved a pass overall, 65% of PEC140 and 63% of TPEC140 students. The major difference between the two groups of students is in the level of achievement in the Distinction (D, 70 – 79%) and High Distinction (HD, > 80%) grades. If these grades are considered together, the number of students achieving in this range was comparable between the two groups (PEC140 24%, TPEC140 27%), but only 2% of TPEC140 students achieved a HD, compared with 12% of PEC140 students.

### Table 2: Average mark, pass rate and distribution of grades for PEC140 and TPEC140.

<table>
<thead>
<tr>
<th>Grade</th>
<th>PEC140 (%)</th>
<th>TPEC140 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average mark</td>
<td>53.2</td>
<td>53.5</td>
</tr>
<tr>
<td>Pass rate</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>High Distinction (≥ 80%)</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>Distinction (70 – 79%)</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>Credit (60 – 69%)</td>
<td>22</td>
<td>19</td>
</tr>
<tr>
<td>Pass (50 – 59%)</td>
<td>19</td>
<td>17</td>
</tr>
</tbody>
</table>

A comparison of withdrawal rates from the two offerings of the unit was also carried out to assess the impact of the student-centred approach on retention. There are two deadlines for students to withdraw from a unit. Withdrawal by the end of the 4th week of semester incurs no financial or academic penalty whilst withdrawal between the end of the 4th and 10th weeks of semester students pay fees for the unit but no academic penalty is recorded. Implementation of active learning strategies seemed to improve student retention in a previous study, but there was no difference in rates of withdrawal from either cohort in this trial (Table 4). There was also no influence on the number of DNS grades between the two groups of students (PEC140 9.4%, TPEC140 10.4%). Students who obtain this grade stopped participating in the unit at some point, but did not formally withdraw.

### Table 4: Withdrawal rates from PEC140 and TPEC140.

<table>
<thead>
<tr>
<th>Timing of withdrawal</th>
<th>PEC140 (%)</th>
<th>TPEC140 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before the end of Week 4</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>After Week 4 and before the end of Week 10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

A comparison of achievement by repeating students in PEC140 and TPEC140 showed the pass rate for repeaters in PEC140 was actually better than TPEC140.

It is important to reiterate that the study compared overall achievement in the unit between the two groups and did not track the engagement and performance of individual students in the TPEC140 group. The participation in the TPEC140 lecture activities was such that only a handful of students (as low as 8 – 9 students in the final 4 weeks of semester) actually experienced the different method of instruction. This level of participation was not sufficient to impact the overall results of the group.

### Table 3: Grade distribution for PEC140 and TPEC140 as a percentage of overall pass rate.

<table>
<thead>
<tr>
<th>Grade</th>
<th>PEC140 (%)</th>
<th>TPEC140 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Distinction (≥ 80%)</td>
<td>18.5</td>
<td>3</td>
</tr>
<tr>
<td>Distinction (70 – 79%)</td>
<td>18.5</td>
<td>40</td>
</tr>
<tr>
<td>Credit (60 – 69%)</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>Pass (50 – 59%)</td>
<td>29</td>
<td>27</td>
</tr>
</tbody>
</table>

A comparison of withdrawal rates from the two offerings of the unit was also carried out to assess the impact of the student-centred approach on retention. There are two deadlines for students to withdraw from a unit. Withdrawal by the end of the 4th week of semester incurs no financial or academic penalty whilst withdrawal between the end of the 4th and 10th weeks of semester students pay fees for the unit but no academic penalty is recorded. Implementation of active learning strategies seemed to improve student retention in a previous study, but there was no difference in rates of withdrawal from either cohort in this trial (Table 4). There was also no influence on the number of DNS grades between the two groups of students (PEC140 9.4%, TPEC140 10.4%). Students who obtain this grade stopped participating in the unit at some point, but did not formally withdraw.

These results show that this initial application of a student-centred approach had no impact on the level of student achievement or retention for TPEC140 students in the introductory chemistry unit. This is consistent with the contention of Kirschner et al. that forms of instruction using minimal guidance are actually ineffective, particularly for novice learners. However, the lack of improved outcomes for students in the TPEC140 group may be linked to a lack of engagement with the approach, rather than the approach itself. Note that PEC140 students and TPEC140 students had the same level of engagement in learning activities (lectures, tutorials, online assignments), but TPEC140 students made less use of lecture recordings. Despite the lack of participation in the TPEC140 group lectures and the limitations of their lecture recordings, the learning activities made available engaged them to the extent that they achieved to the same level as students in the traditional PEC140 group.

### Conclusions

While there was no improvement in attendance and achievement, the positive feedback from students who engaged with the student-centred guided inquiry learning activities encouraged us to gradually
incorporate more active learning into the traditional PEC140 lectures. These activities are made available online to all students enrolled in the unit to use as tools in their overall study plan. Students who attend lectures bring them along and use them at the appropriate time. PEC140 lectures are now punctuated with time for students to work on activities and recording of the lecture can be paused during this time. When the lecturer resumes to work through an activity with the whole group, the recording is resumed and any working the lecturer does by hand is captured using an overhead digital video camera. Students using the lecture recordings can participate in essentially the same way as students in the lecture theatre, they just don’t get an immediate answer to any questions they might have.

Student survey responses from the teaching periods where this has been implemented cannot be reported here as ethics approval only applied to the one-semester trial. However, the general theme of student feedback obtained from these surveys, as well as positive face-to-face feedback obtained in interactions with students, has further encouraged us to continue with this approach. Improvement in student attitudes and outlook to studying introductory chemistry for their degree is a positive short-term outcome, even though there has been no improvement in the average level of achievement to date. Improvements in student outcomes will not become evident until the best approach for our particular group of students, and the current cultural context of our university, is developed.

Acknowledgements

The authors gratefully acknowledge the Murdoch University Office of Student Life & Learning for funding support and Luke Reagan, Research Officer Murdoch University Educational Development Unit, for preparation of the online survey. This study was approved by the Murdoch University Human Research Ethics Committee (Approval 2011/076).

References

Appendix. Survey Questions for PEC140 and TPEC140 Students.

Rating scale for all rating questions (excludes Q16 & 22):

<table>
<thead>
<tr>
<th></th>
<th>Strongly Agree</th>
<th>Agree</th>
<th>Slightly Agree</th>
<th>Slightly Disagree</th>
<th>Disagree</th>
<th>Strongly Disagree</th>
<th>Unable to judge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Standard Ratings Questions
1. It was clear what I was expected to learn in this unit.
2. The assessment tasks were appropriate to the learning objectives.
3. The feedback on my marked work was useful for my learning in this unit.
4. The assessment tasks tested my understanding of the subject area, rather than just memory.
5. Activities in this unit helped me achieve the learning objectives.
6. The unit resources were useful for my learning in this unit.
7. I was satisfied with the level of support from staff in this unit.
8. Overall, I was satisfied with the quality of this unit.
9. I have a more positive attitude about learning chemistry now compared to when I started the unit.
10. The teaching in this unit helped me improve my understanding of chemistry.
11. I learn better from lecture presentations than small group work.
12. Solving problems in a group is an effective way to learn chemistry.
13. I have a positive attitude about learning with my peers.
14. My experiences in this unit has improved my view of group learning.
15. The learning activities helped me develop my thinking skills (e.g. problem solving, analysis).

Attendance at Lectures
16. During semester I attended lectures on average:
   (Please select one answer which best represents your attendance in this unit).
   - Irregularly
   - 1 - 2 times per week
   - 2 - 3 times per week
   - 3 - 4 times per week
   - I listened to the recordings on Lectopia instead
   - Not applicable - didn't attend any lectures

Please indicate to what extent you agree with the following statements.

I attended lectures because:
17. I found them engaging and interesting.
18. I didn't find the recordings (Lectopia) useful.
19. There are opportunities to interact with other students.
20. There are opportunities to interact with the lecturers.
21. There are opportunities to ask questions.

Attendance at Tutorials
22. During semester I attended tutorials:
   (Please select one answer which best represents your attendance in this unit).
   - 1 - 4 times
   - 4 - 8 times
   - 8 - 12 times
   - Not applicable - didn't attend any tutorials

Please indicate to what extent you agree with the following statements.

I attended tutorials because:
23. I found them engaging and interesting.
24. There are opportunities to interact with other students.
25. There are opportunities to interact with the tutor’s.
26. There are opportunities to ask questions.

Comments:
27. Describe one or two aspects of the learning activities in this unit that were most helpful.
28. Describe one or two aspects of the learning activities in this unit that were least helpful.
29. Any other comments about your experiences in this unit!!
A Tactile Limiting Reagent Exercise: Toys in the Classroom

Tenaya L. Newkirk

Science Department, Red Rocks Community College, Lakewood, CO, USA; Email: Tenaya.Newkirk@colostate.edu

Abstract
The following is a description of a classroom activity in which students learn the concepts of limiting reagents and theoretical yield. Students assemble Mr. Potato Head toy sets from kits distributed to them and determine the "limiting reagent" from the pieces available. Once the students are more practiced in the application of these concepts, more detailed discussions can take place in the lecture.

Background
As all chemistry teachers well know, the concepts of limiting reagents and theoretical yield can be difficult for beginning chemistry students. In particular, those instances in which reagents are not combined in a 1:1 ratio or more than two reagents are involved present a significant challenge for students. Furthermore, the students are often tempted to decide which reagent is limiting on the basis of mass as opposed to looking at the stoichiometry of a balanced equation. Although perhaps every teacher has their favorite method to present this information, it appears that physical demonstrations of this idea are most helpful to students; specifically, tactile demonstrations seem to be the best option.

To address the issues mentioned above, we have developed an activity for use in our introductory chemistry courses. The activity has also successfully been used in our first year General Chemistry course, and could easily be used in high school level classes as well. In a setting with smaller class sizes, this activity can be used as part of the regular class period. However, in those cases where class size is too large to permit this approach, this activity could be included as part of a smaller recitation or lab session. The example described below is only one of many possibilities, and could easily be modified.

Activity
By using familiar materials in a more casual atmosphere than a lecture usually allows we sought to create an activity memorable enough to enhance the students’ understanding of the limiting reagent concept. As described in further detail below, we use Mr. Potato Head toys to aid in demonstrating these ideas. After providing the students with the definition of limiting reagents and theoretical yield, the class then has a chance to recognize the concepts for themselves prior to returning to a more in-depth discussion in the lecture.

For our classes of 28 students, we purchased fifteen Mr. Potato Head toys. These toys were found at local toy stores for between eight and twelve dollars apiece. The initial outlay of roughly $US 150 has the advantage of being a one-time expense in that the toys are easily saved and stored from semester to semester. The activity could also be modified over time by purchasing further sets or extra parts as desired.

Prior to conducting the activity, the toy sets were divided into seven kits as described below (the "limiting reagent" for each kit is shown in bold). This allows each group of students to have a different set of "reagents". Each kit is assigned to a group of four students who must follow the balanced equation shown below to design their Mr. Potato Heads:

\[
\text{Kit 1: } \text{1 body+1 pair of eyes+2 ears+2 arms+1 pair of feet+3 accessories} \rightarrow \text{Mr. Potato Head}
\]

Kit 1: 3 bodies, 2 pairs of eyes, 7 ears, 4 mouths, 6 arms, 3 pairs of feet, 10 accessories

Kit 2: 2 bodies, 4 pairs of eyes, 4 ears, 2 mouths, 3 arms, 2 pairs of feet, 8 accessories

Kit 3: 1 body, 1 pair of eyes, 3 ears, 2 mouths, 2 arms, 1 pair of feet, 2 accessories

Kit 4: 2 bodies, 3 pairs of eyes, 4 ears, 3 mouths, 4 arms, 3 pairs of feet, 7 accessories

Kit 5: 2 bodies, 2 pairs of eyes, 5 ears, 2 mouths, 4 arms, 1 pair of feet, 8 accessories

Kit 6: 1 body, 1 pair of eyes, 1 ear, 1 mouth, 2 arms, 2 pairs of feet, 3 accessories

Kit 7: 2 bodies, 2 pairs of eyes, 6 ears, 1 mouth, 5 arms, 3 pairs of feet, 7 accessories

Each group then works together to find: a) the limiting "reagent" for their set of reagents; b) the "theoretical yield" (number of complete figures); and c) amount of excess "reagents" (see Appendix for a sample worksheet to accompany the activity). While the students complete the activity, a table showing the contents of each kit can be written on the board or provided to the students on a worksheet. This enables the students to confirm their understanding of the ideas by ensuring that they can determine the limiting reagents in other groups’ sets of reagents. To provide further practice, the students can be asked which reagent(s) from a given kit was present in the largest excess and how much of a given reagent remained.

Once the activity has been completed, the instructor can return to the definition of limiting reagents and theoretical yield, and perhaps provide further examples. One advantage to using this particular toy is that the analogy can be extended to include bimolecular species – another point of significant difficulty for many beginning students. As both the eyes and feet come in pairs in these toy sets, they can be used as easily comprehensible stand-ins for any bimolecular species. One example that we have found to be helpful is the analogy...
formation of water from two bimolecular species (H₂ and O₂). When explained to the students as being a similar calculation to that used to determine how many noses and pairs of feet required for their toys, the students’ performance on questions of this type appeared to improve. A further analogy can be drawn using the masses of different pieces in the kits. Although, for example, an ear may have less mass than a body, this does not automatically make the ear the limiting reagent.

Overall, we have found this classroom exercise to be both enjoyable and beneficial for our students to enhance their understanding of these difficult concepts.

Notes
The author declares no competing financial interest. The author’s affiliation is currently as follows: Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

Acknowledgment
Thank you to Gayle Crane and Lydia Walsh for help in testing this activity in their classrooms, and to Scott Newkirk for assistance in creating the kits.

References

Appendix: Sample worksheet

1. Given the following, select the limiting reagent for each Mr. Potato Head.

<table>
<thead>
<tr>
<th>Set #</th>
<th>Bodies</th>
<th>Eyes (pairs)</th>
<th>Ears</th>
<th>Mouth</th>
<th>Arms</th>
<th>Feet (pairs)</th>
<th>Accessories</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>2</td>
<td>7</td>
<td>4</td>
<td>6</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>5</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

2. In Set #7, which “reagent” is present in the greatest excess, and how much would be left over?

3. How many pairs of eyes would be needed to complete 3 Mr. Potato Heads?

4. How many individual eyes would this be?

5. If you have 2 moles of H₂, how many moles of H atoms do you have?

6. If you have two mouths and two pair of eyes, how many Mr. Potato Heads could you make? (Assume that you have all other necessary pieces.)

7. If you have two moles of Mg and two moles of Cl₂, how many moles of MgCl₂ could you make?

8. What would the theoretical yield of MgCl₂ be in grams? (Use your answer from #7.)
**Determination of lifetime of α-chlorobenzyl cation in water by “Chloride Clock”: A competition kinetic experiment**

R. Sanjeev₁*, V. Jagannadham², Adam A Skelton¹ R. Veda Vrath³

₁Department of Pharmacy, School of Health Science, University of KwaZulu-Natal, Durban, South Africa
²Department of Chemistry, Osmania University, Hyderabad-500007, India; ³Department of Chemistry, L N Gupta Evening College, Hyderabad-500002, India, email: rachuru1sanjeev1@rediffmail.com

**Abstract**

In this article, we describe an experiment in UV-spectroscopy as part of a 'Discovery Chemistry' curriculum. Discovery Chemistry is a pedagogical philosophy that makes the laboratory the key centre of learning for students in their first two years of undergraduate instruction (Ricci & Ditzler, 1991). Questions are posed in the pre-laboratory discussion and assessed using pooled student data. Results of experiments are then used in lectures to discover chemical principles. This pedagogical philosophy has been adopted in some American universities; but the same pedagogy philosophy can be extrapolated to graduate or senior undergraduate students and incorporated in the curricula of other universities all over the world. This particular experiment enables the students to record the time-dependent spectra and astute application of steady state principle to enable the student to find the lifetime of the intermediate α-chlorobenzyl carbocation. Furthermore, it is a prelude to the honing of student research skills through searching for the answers to most of the set questions (both prior to performing the experiment in the laboratory and after performing the experiment in the laboratory) in the references listed in research articles.

**Keywords**: Graduate students; senior undergraduate students; UV spectroscopy; intermediate carbocation, discovery learning.

**Introduction**

In the following experiment we explain how the lifetime of the intermediate α-chlorobenzyl carbocation can be determined by the astute application of steady state principle (Sanjeev et al, 2012). This experiment does not involve any advanced instrument for the determination of lifetime of short lived carbocations, other than a double beam spectrophotometer of the type UVIKON-923 (from Milan) which is normally available in any Graduate analytical or physical chemistry laboratory; hence very simple for the Graduate students to carry out this experiment. The experiment is followed by some pertinent questions, the answers of which lead to the conceptual comprehension of many aspects of chemistry such as thermodynamic and kinetic reactivity of intermediate benzyl carbocations, relative stability of benzylic carbocations and some insight into the application of Hammett relation etc.

**Questions prior to performing the experiment in the laboratory**

1. What do you mean by solvolysis reaction? Give an example of solvolysis reaction wherein a benzyl α-azidocarbocation is formed (Richard et al 1995)?
2. Explain the steady state approximation. Apply this approximation for the determination of lifetime of α-azidobenzyl-carbocation formed in the foregoing question (Richard et al 1995)? In case the students are not able to answer this question prior to performing the experiment, they can attempt to answer this question after carrying out the experiment.
3. How can you say with certainty that the order of solvolysis reaction of the type mentioned in question 1, is pseudo first order?
4. Consider the following solvolysis reaction:

   \[ A{-}Lg \xrightleftharpoons[\text{k_{solv}}]{\text{k_{diss}[Lg]}} A^{+} + Lg^{-} \]

   where Lg is a leaving group (say chloride ion) and A⁺ is the carbocation [say C₆H₅C⁺(HCl)]. If A⁺ reacts with water with a rate constant of 1 x 10⁶ s⁻¹, what exactly would the reciprocal of this rate constant yield?

   There is a misbelief among the students that if one has to determine the lifetimes of intermediates of the order nanoseconds, usually sophisticated techniques such as Flash photolysis technique, Time resolved spectroscopy etc have to be used. After carrying out the following experiment, students would realize that their belief is definitely inappropriate. Once the students answer the above set of questions, they have braced themselves to comprehend and discover the simple and smart method (of course the method has already been established) for the determination of lifetime of α-chlorobenzyl cation (of the order of nanoseconds) in water.

**Chemicals and equipment required:** Benzyl-gem-dichloride, HPLC grade acetonitrile, Millipore distilled water, micro pipette, double beam spectrophotometer of the type UVIKON-923 (from Milan).

**The experiment**

A stock solution of benzyl-gem-dichloride of concentration 1 x 10⁻² M was prepared in HPLC grade acetonitrile. From this stock solution 30µL of the compound was taken and injected into 3 mL of water, contained in a spectrophotometric cell. The lid of the cell was placed and the solution was shaken well. Immediately after this, the spectrophotometric cell was placed in the spectrophotometer and the time-dependent spectrum recorded. The spectrum as shown in Figure 1 was obtained.
A plausible mechanism of this solvolysis is depicted in Scheme 1.

Scheme 1.

The first step in scheme 1 is the solvolysis of benzyl-gem-dichloride to yield α-chlorobenzyl cation (by the removal of chloride ion). This is the equilibrium step. Then the generated carbocation competes for the reaction between available acetonitrile i.e. the Ritter reaction and the excess water molecules. The carbocation reacts with water to yield chlorohydrin, which further reacts with water to yield gem-diol. The gem-diol finally yields the product benzaldehyde. The elaborated mechanism of the solvolysis is depicted in Scheme 2.

Scheme 2.

From the time dependent spectra the $\lambda_{\text{max}}$ of the reactant and the product are obtainable. After the $\lambda_{\text{max}}$ of the reactant and product are obtained, the reaction can be followed either by following the depletion of the [reactant] or build-up of the [product] (Figure 2). The rate constant thus obtained, is termed as $k_{\text{solv}}$.

Then applying the steady state principle to the intermediate α-chlorobenzyl carbocation (Sanjeev et al., 2012) the following relation was obtained.

$$ \frac{k_{\text{solv}}}{k_{\text{obs}}} = 1 + \left(\frac{k_{\text{Cl}}}{k_{\text{solv}}}\right)[\text{Cl}^-] \quad (1) $$

From the slope of the line of the plot (Figure 3) of $k_{\text{solv}}/k_{\text{obs}}$ vs [Cl$^-$], $k_s$ was found to be $7.49 \times 10^9$ s$^{-1}$ using a value of $k_{\text{Cl}}$ as $5 \times 10^9$ M$^{-1}$s$^{-1}$ (for the explanation about the rate constant of chloride ion with the cation i.e. $k_{\text{Cl}} = 5 \times 10^9$ M$^{-1}$ sec$^{-1}$, please refer to the appendix at the end of this article).
intermediate carbocation, which turned out to be 0.13 ns. Thus this simple experiment for the determination of lifetime of carbocation can be incorporated in the syllabus for Graduate students. Analogous to the determination of lifetime of α-chlorobenzyl carbocation, the students can perform the experiment for the determination of lifetime of α-azidobenzyl carbocation (Richard et al 1995).

**Educational outcomes**

Some questions which would aid the understanding of the intricacies of the experiment and some related basic concepts of chemistry are given below. In their answers, the students are expected to refer to the references provided in the questions. We consider that this exercise of extracting answers from the references is a good prelude to formal training in research. The students have a misconception that, a reaction series will either have only a positive Hammett’s ρ value or a negative Hammett’s ρ value. After carrying out this experiment and being able to answer question 1, they will come to a conclusion that their misconception is unmerited. After answering some of the following questions (4, 5, 6) the students will have a far improved conceptual comprehension of the axiom in organic chemistry “Intermediates that are stable in Thermodynamic sense are reactive in Kinetic sense”. Benzyl-gem-diacetate does not undergo solvolysis; after answering question 9, students can infer its inertness in undergoing spontaneous cleavage in aqueous solution, from standpoint of semi-empirical methods, such as MNDO (modified neglect of differential overlap), AM1 (Austin model 1), PM3 (parametrization method 3) and ZINDO (Zerner’s intermediate neglect of differential overlap) belonging to ZDO (zero differential overlap) to determine the stabilities of benzyl-gem-diadducts.

The questions we posed are:

1. Describe the plausible mechanisms wherein one can examine the simultaneous negative and positive Hammett’s ρ values in a solitary reaction (Sanjeev & Jagannadham, 2002a 2002c, Richard et al., 1995).
2. How do you explain the fact that α-halobenzyl carbocations are more reactive towards water than the corresponding α-azidobenzyl carbocations (Sanjeev & Jagannadham, 2002b, Hoz and Wolk, 1990)?
3. α-azidobenzyl carbocations are less reactive towards water than the corresponding α-halobenzyl carbocations, with the exception of α-azido-4-nitrobenzyl carbocation. How is this exceptionally high reactivity of the reaction of α-azido-4-nitrobenzyl carbocation with water explained (Sanjeev & Jagannadham 2002b)?
4. It is axiomatic in organic chemistry that intermediates that are stable in thermodynamic sense are reactive in kinetic sense. Give examples and explain the conformity to this axiom (Sanjeev & Jagannadham 2002d).
5. Azido group is supposed to be a better leaving group than chloro and bromo groups, hence the \( k_{solv} \) value for benzyl-gem-diazide is less than that of benzyl-gem-dichloride and benzyl-gem-dibromide. How can one say with certainty that in the solvolysis of 4-methoxy, 4-methyl, 4-F and 4-H benzyl-gem-dichlorides, the negative sign of \( \Delta S^{solv} \) (entropy of activations) was observed. How do you account for the negative entropy of activation for the solvolysis step (Sanjeev & Jagannadham 2002a, McManus & Pittman 1973)?
6. How can one say with certainty that in the solvolysis of benzyl-gem-dichloride α-chlorobenzyl carbocation intermediate is formed (Sanjeev & Jagannadham, 2002b).?
7. The time-dependent spectra of benzyl-gem-dichloride (Sanjeev & Jagannadham, 2002a 2002b) and benzyl-gem-dibromide (Sanjeev & Jagannadham, 2002c) were observed in water, but when the time dependent spectra of benzyl-gem-diacetate in water was attempted, the solvolysis did not take place at all. What are plausible reasons for benzyl-gem-diacetate, not undergoing solvolysis in water (Jagannadham, et al., 2009)?
8. What is the plausible mechanism of the reaction between the intermediate carbocation and acetonitrile (1% acetonitrile is present in our system)? How is this plausible mechanism ruled out (Sanjeev & Jagannadham, 2002a, 2002b, Richard et al., 1995)?
9. Students can be divided into several groups and each group can estimate the lifetime of a para-substituted α-azidobenzyl carbocation and para substituted α-chlorobenzyl carbocation and asked to conclude about the effect of para-substituent on the lifetime of the corresponding intermediate carbocations.

**Appendix**

The first systematic studies on the kinetics of the reactions of carbocations with nucleophiles were performed by Ritchie (Calvin D Ritchie, 1972a, 1986b) who investigated the reactions of highly stable carbocations, such as tritylum and tropylium ions with anions and amines. This work was extended by Jencks (Richard and Jencks 1982) by introducing the “azide clock” method. This method was based on the fact that many carbocations react with the azide ion with a known diffusion-controlled rate constant of \( 5 \times 10^9 \) M\(^{-1}\)s\(^{-1}\). The method of laser flash photolytic generation of carbocations was carried out by Stenken (Stenken et al, 1991) in the presence of various nucleophiles. In his experiment Stenken gave the direct determination of the rate constant, for the reaction between carbocation and...
the nucleophile. The rate constant which turned out to be roughly between $10^6 \text{M}^{-1}\text{s}^{-1}$ and the diffusion limited value is close to $5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, was a major breakthrough in the investigation of the intermediates. Among the various nucleophiles studied, the azide ion ($\text{N}_3^-$) was found to be the most reactive. It reacted with most of the carbocations (with some exceptions like highly stabilized tri-$p$-anisylmethyl cation ($p$-$\text{MeOC}_6\text{H}_4$)$_3\text{C}^+$ with a rate constant of $5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$). These second order rate constants together with the (pseudo) first order rate constants ($k_{\text{app}}$) can be utilised for the determination of the lifetime of the intermediate carbocations.

The foregoing two paragraphs, justify the value of $5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ for the reaction of chloride ion with any cation (two oppositely charged ions generally react with a rate constant close to diffusion limit i.e. $5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$).

References


SUPPLEMENTARY MATERIAL FOR INSTRUCTORS
J. R. Jensen, H. M. Wilson and D. P. Arnold

1. Substances used in the exercise.

<table>
<thead>
<tr>
<th>Compound:</th>
<th>Step(s):</th>
<th>CA Registry number</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetocetate</td>
<td>1</td>
<td>141-97-9</td>
</tr>
<tr>
<td>ethane-1,2-diol</td>
<td>1</td>
<td>107-21-1</td>
</tr>
<tr>
<td>p-toluene sulfonic acid</td>
<td>1</td>
<td>104-15-4</td>
</tr>
<tr>
<td>toluene</td>
<td>1</td>
<td>108-88-3</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>1</td>
<td>1310-73-2</td>
</tr>
<tr>
<td>anhydrous sodium sulfate</td>
<td>1, 2, 3, 4a, 4b</td>
<td>7757-82-6</td>
</tr>
<tr>
<td>silicone grease</td>
<td>2</td>
<td>N/A</td>
</tr>
<tr>
<td>magnesium turnings</td>
<td>2</td>
<td>7438-96-4</td>
</tr>
<tr>
<td>diehydride ether</td>
<td>2, 3, 4a, 4b</td>
<td>60-29-7</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>2</td>
<td>108-88-1</td>
</tr>
<tr>
<td>iodine</td>
<td>2</td>
<td>7553-56-2</td>
</tr>
<tr>
<td>ammonium chloride solution</td>
<td>2</td>
<td>12125-02-9</td>
</tr>
<tr>
<td>methanol</td>
<td>2</td>
<td>67-56-1</td>
</tr>
<tr>
<td>dry ice</td>
<td>2</td>
<td>124-36-5</td>
</tr>
<tr>
<td>acetic acid</td>
<td>3, 4b</td>
<td>67-64-1</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>3, 4b</td>
<td>7647-01-0, 7732-18-5</td>
</tr>
<tr>
<td>sat. sodium bicarbonate solution</td>
<td>3, 4b</td>
<td>144-55-8, 7732-18-5</td>
</tr>
<tr>
<td>sat. sodium chloride solution</td>
<td>3, 4a</td>
<td>7647-14-5, 7732-18-5</td>
</tr>
<tr>
<td>hexane</td>
<td>3</td>
<td>110-54-3</td>
</tr>
<tr>
<td>ethane</td>
<td>2, 4a</td>
<td>64-17-5</td>
</tr>
<tr>
<td>sodium borohydride</td>
<td>4a</td>
<td>16940-66-2</td>
</tr>
<tr>
<td>petroleum ether</td>
<td>4a, 4b</td>
<td>8032-32-4</td>
</tr>
<tr>
<td>silica gel</td>
<td>4b</td>
<td>7699-41-4</td>
</tr>
</tbody>
</table>

2. Hints and extra information for instructors.

Depending on the levels and laboratory skills of your students, and the technical facilities you have at your disposal, parts of the sequence could be presented separately, or more parts could be added (see below). More or less help with the spectra could be offered, and the three particular examples noted in the main text (1H NMR of [B] and [D], 13C NMR of [E]) could be presented in an NMR course as illustrative examples of particular NMR phenomena and the influence of three-dimensional structure. We find that the best approach is to combine the synthesis with the discovery aspects of the spectra. The use of the X-ray crystallography results is optional, but has proved very useful in our classes, especially for interpretation of the IR spectra.

In the azeotropic distillation of step 1, we made no attempts to dry the ethane-1,2-diol, as this is difficult in our humid climate. If the water collection is carried out for the suggested 90 minutes, about 4 mL is obtained, more than the theoretical 2.6 mL, indicating that we are also drying the diol anyway. The Grignard reagent usually starts well, but sometimes may take 30 minutes, with encouragement by vigorous stirring, addition of more iodine, gentle warming, or sonication. We regularly get 12-15 students successfully started even on a typical humid Brisbane summer’s day, and in some years, it has been raining heavily on the day. The ether (bought as “anhydrous”) can be dried by standing over sodium for a week, but a simpler approach is to stand the ether over 250°C-activated 3 Å molecular sieves for a few days.

There may be other/better ways to purify some of the products, but we have found that using the three different approaches to “recrystallisation” is very instructive, even if the yields may be less than optimum. The only problematic step using our procedure is the conversion of [A] to [B], in which magnetic stirring is inadequate to homogenise the suspension during the Grignard addition. We are also restricted by having four-hour sessions; if you had longer, this step could be improved. A crude yield of about 11 g of yellow, viscous oil is usually obtained, which translates to 4 – 5 g of pale cream crystals in two crops by the dry-ice crystallisation. We have never studied by chromatography what other products are present, nor how much starting [A] remains in the crude product. These aspects could be investigated in a discovery-based program. Others have tried to optimise this step and analyze the crude product, see Alber, DeGrand and Cermak (2011). Our yields for this step are comparable with theirs.

The classical crystallisation of [C] from hexane is striking when done well – the long needles form at remarkable rate once seeds appear on the glass. Often only one or two of these will appear, then the crystals grow like moulds or bacteria in mushroom-shaped “colonies”. Most students find this fascinating, and I suggest that they calculate how many molecules are arranging themselves in the growing crystals per second, in the rapid phase of this crystallisation. It would make a good video for lectures. Curiously, having said this, every couple of years, one or two students will get another crystalline phase of [C], in the form of sugar-like cubes (from which we obtained the X-ray structure). Presumably, this is due to a particular temperature/concentration combination.

The crystallisation of [D] on such a small scale is difficult. The crude product (virtually pure), is obtained as a slightly yellow gum. If 5 mL of low-boiling petroleum ether is added, and the flask left stopped for a week, often ONE crystal will grow, to a size of ~5 x 5 x 2 mm! Unfortunately, the tiny amounts of yellowish impurities always occlude into this crystal, meaning it looks worse than the pure-white powder that results from the trituration of the gum.

Product [E] was reported by Paulson et al. and has been mentioned in the research literature many times, mostly without characterisation. Recently, Rosa and Orellano published 400 MHz NMR data (Org. Lett., 2011, 13, 3648). Their integrals appear to be incorrect, as the phenyl protons are described as 2H, 6H, 2H, whereas we find, as noted in the main text, that it is 3H, 5H, 2H.

Our results are confirmed by Shchukin and Vasilyev at Appl. Catal. A, 2008, 336, 140. The 13C chemical shifts have been reported by Rosa and Orellano, and Tani, Sakaguchi and Ishii (J. Org. Chem, 2004, 69, 1221). The latter group agrees with our value, while the former places the –CH2 carbon at 125.0 ppm. We have been unable to find a boiling point for this compound in the literature, and it is used on such small scale here that we have never tried to measure it.

3. IR and NMR spectra of [A] to [E].

**IR Spectra** (neat liquids or pure solids, ATR with intensity correction to simulate transmission spectra).

[A]: ethyl 3-oxobutanoate ethylene ketal

[B]: 2-(2-methyl-1,3-dioxolan-2-yl)-1,1-diphenylethanol
[C]: 4-hydroxy-4,4-diphenylbutan-2-one

[D]: 1,1-diphenylbutan-1,3-diol
[E]: 4,4-diphenyl-but-3-en-2-one
NMR Spectra (400 MHz, in CDCl$_3$ solutions, ca. 5 mg mL$^{-1}$ for $^1$H, ca. 20 mg mL$^{-1}$ for $^{13}$C).
[A]: ethyl 3-oxobutanoate ethylene ketal

[B]: 2-(2-methyl-1,3-dioxolan-2-yl)-1,1-diphenylethanol
[C]: 4-hydroxy-4-diphenylbutan-2-one
[D]: 1,1-diphenylbutan-1,3-diol

[E]: 4,4-diphenyl-but-3-en-2-one

$^1H$
4. Minimum energy conformation for [E].

Calculated by Spartan 10™ (Hartree-Fock, 6-31G).