Name:

Department of Chemistry, Universiti Malaya, 50603 Kuala Lumpur, Malaysia
UM/CHEM/org-chem1/Aug23

Chemistry Laboratory Safety Agreement

In the interest of safety and accident-prevention, there are regulations to be followed by all credit students in designated Chemistry Laboratory at Department of Chemistry, Faculty of Science, Universiti Malaya. Faculty and staff members are authorized to deny the use of any laboratory to students who do not adhere to the regulations mentioned below or in instances when the safety of any of the student, staff or faculty member in the laboratory might be jeopardized.

Regulations for all Chemistry Laboratories are as follows:

1. Proper attire must be worn at all times in all laboratories, including shoes that completely cover the foot (no high-heeled shoes), and a shirt that covers the entire upper torso, including the stomach and the back. Lab coats must be worn in the laboratory at all time. Long hair must be tied back. No loose or baggy clothes and dangling jewelry is allowed.
2. Safety eyewear must be worn at all times during laboratory sessions.
3. Food, drinks, chewing gum, tobacco products, and applying cosmetics are prohibited in the laboratories. Hands, pencils, pens, etc. must be kept away from the eyes, nose, and mouth in order to avoid contamination.
4. Fume hood sashes are not to be opened beyond the 18'' mark when in use. (Never put your head into the hood.)
5. Be organized. Maintain a clean, open work area free of anything except materials directly required for the exercise. Keep laboratory material/equipment away from edges of work surfaces and electrical cords from hanging below the surface of tables.
6. Equipment and/or chemicals should never be taken out of the lab unless authorized by the instructor or laboratory staff.
7. Many of the lab activities have students moving around the lab or involve moving objects. Be alert and aware of what's going on around you.
8. Be familiar with the location and the use of the following in your laboratory: e.g. broken glass receptacle, first-aid kit, emergency gas shut-off valves, closest fire alarm, fire extinguisher, eye wash, safety shower, and emergency exits and routes.
9. It is of utmost importance to know the rooms that are off-limits to the students. The students should not enter those prohibited areas.
10. Be prepared. Study the assigned experiment before you come to lab. Being familiar with the lab exercise to prevent confusion and accidents. No unauthorized experiments are to be performed. Students must follow the procedural instructions in the lab handout/manual unless modifications to the procedures have been announced by the laboratory supervisor, in which case the student must follow the supervisor's procedural instructions.

11. NEVER TOUCH ANY FORM OF BROKEN GLASS. Broken glass should be disposed of only by laboratory staff.

12. Unused reagents should not be returned to the reagent stock bottle. One should make sure to take only what is actually needed out of the regent bottle. Reagents must not be contaminated.

13. CONTACT LENSES should not be worn in the lab as chemicals can get between the eye and the lens.

14. Lab experiments have been designed to minimize unnecessary exposure to any hazardous substances; however, it is not advisable for pregnant women or those with certain medical conditions to be exposed to any chemicals. We cannot insure that a pregnant student will not be exposed to chemicals that might be unhealthy for her or her fetus. In addition, we cannot know the level of exposure, the length of exposure or the number of encounters that might occur with any chemical during a semester. By maintaining the safety rules, we expect that all students, including a pregnant student, should be able to carry out lab procedures safely. However, it is the Department's professional advice that pregnant students should be advised NOT to take a lab course unless she is willing to understand and assume the risks. She should certainly be seeking and following proper medical advice from her physician.

15. If you are pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have any medical condition or concern, including but not limited to the following, immunocompromised system, seizures, epilepsy, severe allergies, it is your, the student's, responsibility to consult with your medical care provider regarding any medical issue associated with taking this lab. Students are encouraged to provide their physician with a list of the chemicals that they might be exposed to while in lab. They should also check the MSDS sheets to be aware of the hazards of the chemicals.

SAFETY INFORMATION ACKNOWLEDGEMENT
INFORMED CONSENT

(Sign and keep for your record)

I acknowledge receipt and that I have read and understand the lab safety regulations and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

Further, I accept any and all risk associated with the use of the Chemistry laboratory(s) and the equipment contained therein. I also understand that I am responsible for my personal property at all times. By signing this agreement, I fully understand and consider it my responsibility to comply with the safety regulations outlined above. I hereby agree for myself, my family, successors, and assigns to hold harmless the Universiti Malaya (UM), Department of Chemistry of the Universiti Malaya, Faculty of Science of the Universiti Malaya, Lecturers, Laboratory Staff and assigns from any and all claims, causes of action, suits, liabilities, damages, losses, demands, costs, expenses or judgments for damages or injuries to myself or others arising from my participation in the lab, whether or not I consulted a medical provider as delineated above.

Signature of the student: _____ Course: _____

Name: _____ Lecturer: _____

Matric number: _____ Session: _____

IC number: _____ Semester: _____

Date: _____

Provide the name and telephone number of two "Emergency Contacts" that can be reached during lab class times. Please note that your medical or physical condition may be released to the contact person at the time of the emergency call.
Indicate the relationship to the person and also the telephone location (office, home or cellular). Please print clearly.

_____	_____	_____
Emergency Contact (Name)	Relationship	Phone
_____	_____	_____
Emergency Contact (Name)	Relationship	Phone

Student's copy

SAFETY INFORMATION ACKNOWLEDGEMENT
INFORMED CONSENT

(Return this signed page to your lecturer)

I acknowledge receipt and that I have read and understand the lab safety regulations and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

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Signature of the student: _____ Course: _____

Name: _____ Lecturer: _____

Matric number: _____ Session: _____

IC number: _____ Semester: _____

Date: _____

Provide the name and telephone number of two "Emergency Contacts" that can be reached during lab class times. Please note that your medical or physical condition may be released to the contact person at the time of the emergency call.
Indicate the relationship to the person and also the telephone location (office, home or cellular). Please print clearly.

_____	_____	_____
Emergency Contact (Name)	Relationship	Phone
_____	_____	_____
Emergency Contact (Name)	Relationship	Phone

Department's copy

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Safety in the First Year Laboratory

Further information in the details of the safety and health practice in the Universiti Malaya can be found at:

Occupational Safety & Health and Environment (OSHREC), Universiti Malaya	Universiti Malaya Safety Handbook	Manual Keselamatan & Kesihatan Pekerjaan dan Alam Sekitar, Universiti Malaya

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarize yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers:

- National Emergency Number — 999 (Mobile phone, dial 112)
- Universiti Malaya Security Office — +603 7967 7070
- Universiti Malaya Medical Centre (UMMC) Emergency Department — +603 7949 2500
- Universiti Malaya Students' Health Clinic — +603 7967 6445
- Occupational Safety & Health, Risk and Environment Centre (OSHREC) — +603 7967 6597
- Radiation Protection Service Unit (UPPS) — +603 7967 6962/6963
- Department of Chemistry Office — +603 7967 4204
- Pantai Fire Station (Jalan Pantai Baru) — +603 2282 4444
- Pantai Police Station (Jalan Pantai Baru) — +603 2282 2222

(The numbers given above are working telephone numbers, as of 28th August 2023)

Safety is the primary concern in any chemical laboratory. Chemicals, particularly organic chemicals, are almost all potentially hazardous. Fortunately, with sensible and correct

precautions, the risks can be minimized if basic safety practices are followed. The responsibility for laboratory safety lies with everyone working in the laboratory. Sensible laboratory conduct does not mean memorizing a list of rules! The true test is the actual conduct in the laboratory and safety rules apply to all laboratory activities. Individual safety is affected by the action of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safety work practices.

General Safety Rules for the Undergraduate Laboratories

The guidelines below are recommended for working safely in the laboratory.

- No work is to be carried out unless a member of staff is present.
- Plan your work. Follow instructions. If you do not know how to do the experiment safely, ask the lecturer or demonstrator.
- Know the location of all exits for the laboratory and the building. There are two exits in the 1st year organic lab.
- Know the location of the alarm and fire extinguishers and how to operate them. There are two fire extinguishers located at the two sides in the lab.
- Know the location and use of safety showers, eye-washers and safety aid boxes. The safety shower and eye washer are located right next to the exit of the First Year Organic Lab.

The fire extinguisher, eye wash and safety shower in the First Year Organic Laboratory.

- Know the location of the nearest telephone that can be used during an emergency.
- All persons in laboratories (whether or not they are actually doing practical work)

must wear safety spectacles or goggles and laboratory coats. You might find them a nuisance to wear, but your eyes are very precious. You are not allowed to wear contact lenses in the laboratory. Hair should be secured so that it does not hang below the neck. Other articles of clothing that may become entangled should also be secured. It is important to wear suitable clothing, and your footwear must incorporate flat heels, slip-resistant soles and uppers fully enclosing the foot.

- No food, drink (including drinking water!), cigarettes and cosmetics are allowed to be taken into the laboratory or storage place for chemicals.
- Do not smell or taste chemicals.
- Know the potential hazards of the materials and equipment with which you will work. The preparation for an experiment involves the study of the respective material safety data sheets for **all** chemicals used in that experiment. Refer to the chemicals' Material Safety Data Sheet (MSDS) before usage.
- Do not make skin contact with any substances. Use gloves where necessary, always remembering that they are semi-permeable. Gloves typically only provide a short time protection; when you notice the glove to get wet, remove it asap and replace with a new one. This particularly applies for the common single-use protective gloves.
- Experiments must be conducted on clean working surfaces; any spillage should be cleaned immediately. A high standard of tidiness should be maintained at all times. Contaminated surfaces and equipment must be cleaned as soon as it is practicable after use. The equipment should then be put away. Do not clutter bench space with unused equipment and bottles of chemicals.
- Waste should be disposed off in the appropriate containers. Organic chemicals should be disposed in designated waste bottles. Chemical wastes are segregated into three (3) groups and stored separately; halogenated wastes (examples are chloroform, dichloromethane), non-halogenated wastes (examples are acetone, alcohol, toluene, xylene) and other waste, such as mercury (broken thermometer).
- Bags and other personal items should be placed in the lockers provided outside the laboratory and not left along corridors or on benches.
- All accidents and dangerous occurrence must be reported immediately to the lecturer in charge or the demonstrator or the laboratory assistant. The first aid box is located inside the preparation room of the laboratory. The accident book is also kept in the preparation room; the laboratory assistant must file out a report for all incidents.

- It is important to ensure that hands are washed, and all protective clothing removed before leaving the laboratory.
- Do not wear laboratory coats, gloves or other personal protective clothing out of the laboratory and in non-laboratory areas. These clothing may have become contaminated.

Additional Guidelines

Remember that in a laboratory you have fellow students around you. They do not know what you are doing, but they hope and expect that what you are doing is sensible and safe. Always think carefully about what you are about to do.

- Know the lecturer in charge, the demonstrator and the laboratory assistants of the laboratory.
- Undergraduates are not allowed to work or even be in any of the teaching laboratories at any time outside of the specified laboratory hours, unless they have explicit permission from the lecturer in charge. This includes times before and after class, and the lunch break.
- Students should come to the laboratory on time and be prepared by studying the experiment. Therefore, plan your activities before you come to the laboratory.
- Write everything you do, and observations in your notebook so that you can trace your action and make corrections if necessary. Please designate one notebook for this purpose and use it for the whole session / cycle.
- Do not use cracked or broken glassware. Check glassware before using it.
- Never use open flames, unless instructed by the lecturer in charge. If flames are permitted, plan your experiments so that you never leave your flame unattended. There are other sources of heat such as steam baths and hot plates.
- Handle all chemicals with care and read labels before attempting to get them.
- Use a spatula to get solid chemicals. Never using your fingers.
- Be careful not to contaminate reagents with your spatulas or droppers. Do not take more than needed. If you take too much of a chemical or reagent, give it to a fellow student – but **do not return it to the bottle**.
- Do not wander off with the only bottle of reagent that everyone needs; keep it in its assigned location.
- Do not pipette by mouth. Use only mechanical pipetting devices.

- Never look directly into the mouth of a flask containing a reaction mixture.
- Never point a test tube or reaction flask towards yourself or your neighbor.
- When using a separating funnel, vent frequently and remove the stopper immediately upon setting it upright for separation.
- Never use a thermometer as a stirrer! If a mercury thermometer breaks, immediately contact the lecturer in charge, the demonstrator or laboratory assistant.
- Turn off water, burners or electrical equipment when not in use.
- Wash your glassware at the end of the laboratory session. You will have clean and dry glassware ready to be used for the next laboratory class.
- Make sure glassware or equipment is put away in the correct locker – your personal locker or the common locker.
- Clean your work area and equipment used before leaving the laboratory.

Experiments' Planning

The laboratory component is an essential part of SIC1003 course. Attendance at all laboratory classes is compulsory. Students are also expected to be prepared. Students may be prohibited from doing an experiment, if we believe that they are unprepared.

The laboratory component of the course is composed of six (6) experiments. Below is the planning of the experiments sequence to be filled in after discussion with the lecturer in charge.

Laboratory Class	Date	Experiment	Remarks
1			
2			
3			
4			
5			
6			

The Laboratory Notebook

A lab notebook is used to record all the work carried out in the laboratory and the experimental data. In industry or in academic research, it is an important legal document that can be used to provide evidence regarding the discoverer and date of discovery of new chemicals or processes.

In the undergraduate laboratory course, it is important to develop the skill of recording a good lab notebook. The records will be needed to generate lab reports at some point in the course, and the keeping of the lab notebook will be assessed regularly by your lecturer.

Marks will be awarded for continued good use and practices of the notebook throughout the laboratory classes.

All relevant aspects of an experiment should be recorded, together with the order in which steps were carried out. All observations should be noted, in principle even those that at first sight appear unimportant.

General Guidelines

1. Use ballpoint pen and press hard if you are using duplicate pages.
2. Write on one side only.
3. Do not erase or use whiteout. If you make a mistake, draw a single line through the error (strikethrough) and write the correct entry on the top or side of it.
4. Do not remove an original page. If the entire page is incorrect, draw a single diagonal line through the page and state the reason for this line.
5. Record all data and results (with units) directly into your notebook.
   DO NOT record data on scrap paper, your hand etc. to be transferred later. A laboratory notebook does not need to look nice, but must be logically ordered and reasonable readable.
6. Start a new page for each new experiment.
7. Write the title of the experiment, date and your name at the top of each page.
8. NEVER skip a space for later additions.
9. Be neat and thorough! Someone should be able to pick up your notebook twenty years from now and be able to repeat your experiments.

At the beginning of each experiment, record:

- The date
- Structural formula (abbreviated, if necessary) and all reagents in order of addition
- Molecular formula and molecular weights, preferably under the relevant structural formula
- Literature references for the procedure (or for analogous preparations)
- Mass (and number of moles) of each compound used
- List of apparatus (with sketches in unusual cases)
- The purity of all compounds and solvents
- Simplified procedures from your reading of lab manual, it can be a flow chart or schematic diagram, to your preference, which transforms the lengthy and wordy procedures into simple yet informative procedures at a glance.

Components: (this is to be discussed with the lecturer in charge)

A. Pre-Lab – a detailed plan of the work that you will be doing
   1. Brief statement of purpose.
   2. A paragraph discussion of the safety and environmental issues (eg: waste generation, impact on earth, etc.)
   3. Step-by-step procedure in your own words. Be **concise** and **complete**, but DO NOT copy the lab manual. Use diagrams and sketches when necessary. Reference all sources of information. Do NOT mix your preparation instructions with the records that you record during the operation of the experiment.

B. Factual Record – what to record
   1. Keep a running account of all procedures carried out and observations made during experimental work.
   2. Record observations such as physical appearance, color, (odor), and physical properties.
   3. Sketch apparatuses and label parts.
   4. Use a table to record all information about reactants.
   5. Record all data and results, including the crude yield of products and mixtures. Use

tables when possible.

6. For calculations, show the formula and a sample calculation. Examples are yields and percentage yield. If the calculation is repeated, use a table to report your results.
7. Attach all spectra to your notebook, label the axes, and reference the spectra in the procedure section.
8. Do NOT place TLCs into your lab notebook. The chemicals can contaminate your lab notes and even damage your lab notes over time. If you want to keep record of TLC, sketch it instead.

C. Data Analysis/Conclusions:

1. Examine and discuss your experimental results.
2. Summarize the key results and provide a conclusion. Describe any difficulties you came across. Discuss which results are poor and provide explanations. Provide suggestions for improvement.
3. Include literature references, preferably, a variety and not limited to online resources.

A Good Lab Notebook Organization.

The first page of the lab notebook should be used as a cover page and should include name, course and email address (in case of loss). The second page should be left blank to be used as a content's page. This page should be completed as the lab course progresses. Begin to write experimental data into the lab notebook from the third page onwards. A ball point pen is better than a fountain pen as it is less likely to smudge if water is splashed on it.

Lab notebooks need to be looked after carefully. Do not soil them with chemicals as they may transfer hazardous substances out of the laboratory.

What to Include.

The lab notebook is not a copy of the contents of your lab manual. It should expand upon the instructions given in the lab manual. It is important to include the name(s) of any lab partners or group members and the date so that work can be monitored.

The aim of the experiment should concisely explain the task for that lab session. Eg: "To

synthesize xxxx." If it is a synthesis experiment, a correct chemical equation for the reaction should be provided.

The experimental plan explains precisely what is to be done in that session. In cases that detailed experimental plans are provided in the lab manual and the lab notebook can state that these were followed directly. If the lab manual provides only an outline method, a more detailed method should be prepared in the lab notebook before entry to the lab session so that work can begin immediately. For experiments that require the development of a method before the lab session begins, editing may be needed during the session if changes are made. These changes should be clearly noted. When writing a method, use clear language and simple direct statements in a numbered list so that instructions can be followed easily in the laboratory. Do not use personal pronouns (such as "I" or "we"). The experimental plan section should also be used to note any special safety instruction, or to write a risk assessment for the chemical used. A diagram should be used to illustrate novel or unfamiliar apparatus and should show the cross-section of the equipment. Keep it simple. Label where appropriate. Do not use diagrams for common apparatus or procedures.

Observations, measurements and data should be recorded immediately in full (with units, where relevant). Take the lab notebook to the balances to record masses. Do not use scraps of paper and then transfer the data to the lab notebook later. Record all observations, measurements and data honestly. The lab notebook is a record of exactly was observed and measured, not what is predicted to happen or be observed. Do not copy data from someone else after the experiment. If data are to be shared with a partner or group, clearly flag the observations and data as belonging to someone else. Data should be recorded in a table, where possible, and the table should be written in vertical columns using headers and units at the top of each column. Individual cells in the table should only contain a number; units only appear in headers.

The discussion session needs to include clear presentation of any observation or calculations during the experiment. Comments should be made about how the results relate to any hypotheses or how they answer a question posed in the experimental aims.

The conclusion should state the experimental findings and should include any error analysis and any notes about unusual findings or improvements that could be made if the experiment were to be performed again.

Lab Notebook Checklist

The list is not intended to be complete, but it is a very good place to start.

- Experiment title and number
- The date
- The name(s) of any laboratory partner(s)
- Aim of the experiment
- Chemical equations, where required
- Experimental plan and explanation of any experimental decisions
- Diagram or equipment (if required)
- Observations and comments on the chemistry
- Tables of raw and processed data (where required)
- Conclusion

WRITING A REPORT

A good clear report is easy to produce if one has a comprehensive description of the work including all relevant data on the starting materials and products as well as all the experimental details in one's laboratory notebook.

The experimental procedure should be described concisely with neat formula and relevant references.

A report on a preparative experiment should have suitable title. This should include the name of the product, the names of the experiments, and, where relevant, the date. Examples are: "Isolation of cyclopenten-3-one from ....." and "Synthesis of cyclopenten-3-one from ....."

The report may be arranged in the following sections:

(a) Method: Here the overall transformation carried out in each step of a multi-stage synthesis is described.

e.g., "Pinacol is prepared by the reductive dimerization of acetone"

"Endo-bicyclo[2,2,1]hept-2-ene-5-carboxylic acid is formed by the cycloaddition (Diels-Alder Reaction) of cyclopentadiene and acrylic acid".

(b) Reaction scheme: This shows the transformation of starting materials to products by means of formulae (configurational or conformation if necessary). Reaction conditions (reagents, solvents, catalysts, temperature, etc.) are indicated in abbreviated form above and below the arrows in the usual way. The molecular formulae and molecular weights can be appended to the relevant structures. All structures should be numbered. In general, diagrams showing mechanisms are presented separately.

(c) Experimental section: The description of the experiments (past tense, third person, passive voice) should be sufficiently detailed to permit the repetition of the reaction without further consultation of the literature. The report should be sufficiently complete for it to be used in preparing a paper for publication. The weights of all compounds (and the number of moles), the purity of starting materials and solvents (these data on substances used repeatedly in a series of experiments can be collected and placed at the beginning of the experimental

section, if desired), and all relevant reaction conditions (temperature, time, pressure, etc.) should be quoted, as well as the work-up and purification procedures. One should also provide information about the apparatus used, any peculiarities observed, and simple procedures for the following the course of the reaction.

In the text, names of all chemicals should be written out in full: formulae are used only in reaction schemes. On the other hand, abbreviated or trivial names (with the structure numbers used in the reaction schemes) make it easier to follow descriptions when long and complex names are involved.

The yield is quoted (not the average yield over several preparations) with an indication of purity ("crude", "after recrystallisation", etc.), as well as the literature yield with reference (where relevant).

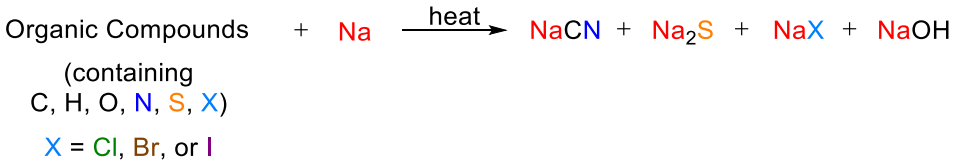
Finally, the physical data used to characterize the compound should be reported (again with literature references): mp, bp, nD (with temperature superscript), Rf (with details of TLC system, IR, UV, NMR, MS, etc.

Some typical expressions and abbreviations

- bright yellow crystals (11 mg, 78%)
- tetramethylsuccinic anhydride (33.8 g, 0.217 mol)
- nitrile (1.15 g, 8.5 mmol)
- a solid residue (68.9 g) remained, and was recrystallized from ... (ca. 250 mL) with charcoal decolorization
- absolute ethanol (2 cm^3)
- poured onto ice (1.5 kg)
- in sodium hydroxide solution (1 N)
- with methyllithium in ether (1.49 M, 16 cm^3)

EXPERIMENT 1
QUALITATIVE ELEMENTAL ANALYSIS

The analysis and identification of the structures of unknown substances constitutes a very important part of experimental organic chemistry. Often, a common first step in the identification of an unknown substance is to determine the elements present in the sample. Organic chemists often use spectroscopic techniques to establish the structure of a compound. However, it is often useful to supplement the spectral data with other information such as the existence of elements other than carbon, hydrogen and oxygen. Elements such as nitrogen, sulfur, iodine, chlorine and bromine in organic compounds can easily be detected by means of straightforward chemical tests. A French chemist, Jean Louis Lassaigne has developed a method used for the qualitative determination of elemental nitrogen, sulfur and the halogens in an organic compound known as the Lassaigne's test or more commonly as the sodium fusion test. In this method, the organic substance is heated with sodium metal under condition that ensure the conversion of nitrogen, sulfur and halides into ionizable inorganic substances as shown below:



PRE-LAB READING/DISCUSSION

- Elemental Analysis
- Lassaigne's test
- Test for different elements

APPARATUS

Pyrex test tube (4.5 x 45 mm)
Test tube
Evaporating dish

CHEMICALS

Sodium metal
Unknown compound (X, Y or Z)
Reagents
Distilled water

PROCEDURE

1. LASSAIGNE'S TEST

Place about 10 mg or one (1) (small) droplet of the unknown (A, B or C) and about 50 mg of freshly cut sodium metal into a glass tube (Note 1). Heat the tube as strongly as possible until the bottom of the tube is glowing red, holding the tube at this heat for about 5 min. For liquid unknown, start with moderate heating to avoid fast evaporation. Quickly plunge the hot tube into an evaporating dish containing distilled water (~ 10 mL) (Note 2) and cover the dish. Boil the solution on a hot plate for a few minutes while gently crushing the residue with a glass rod. Filter and a colorless filtrate should be obtained. If the volume of filtrate is too little, add distilled water to the filtrate. Use the filtrate for the tests below. A colored filtrate indicates incomplete decomposition and the entire fusion procedure will have to be repeated.

Notes:

1. Precautions must be taken when handling sodium. Contact with sodium metal might cause burns on the human skin. When handling sodium metal, avoid all contact with water.
2. Generally, the glass tube will shatter, and any residual sodium will react with water. Cover the dish immediately with wire gauze once the tube is immersed in water to avoid any splatter.

First aid measures to treat sodium induced injuries:

1. If splashed unto eyes, immediately flush water at the eye wash station for at least 15 minutes. Eye washing requires assistance to force the eye open, while reflexes try to shut the eye; attempts to do without help will almost certainly lead to loss of eye sight. Immediate action is required; the first five minutes will decide about saving or losing eyesight.
2. Upon skin contact, wash the part with lots of water for as long as possible.

In all cases, one must seek medical aid as soon as possible.

All accidents and dangerous occurrences must be reported immediately to the lecturer in charge or the demonstrator or the laboratory assistant.

Apart from medical emergencies, sodium might also cause fire!

2. TESTS FOR NITROGEN

Add about 0.5 mL of the filtrate to a tube containing about 0.1-0.2 g of powdered iron (II) sulphate crystals. Heat the mixture gently while shaking until it boils. Without cooling, add just sufficient dilute sulfuric acid to dissolve the gelatinous hydroxides of iron. A Prussian blue precipitate of iron (III) ferrocyanide, $Fe_4[Fe(CN)_6]_3$ indicates the presence of nitrogen. If a blue precipitate is not immediately apparent, allow the mixture to stand for 15 minutes and then filter through a filter paper and wash the paper with water to remove all other colored solution. Any Prussian blue present (if there is any) should be visible on the paper. If there is still doubt as to whether the Prussian blue precipitate was formed, another sodium fusion should be carried out and the test repeated. In the absence of nitrogen, the solution should be pale yellow due to iron salts.

If sulfide ion is present, black precipitate of iron(II) sulfide appears. Add dilute sulfuric acid and boil the mixture for about 30 seconds. The iron(II) sulfide dissolves and a precipitate of Prussian blue appears if nitrogen is present.

3. TESTS FOR SULFUR

Acidify ~ 0.5 mL of the filtrate with dilute acetic acid. Add a few drops of 1% lead acetate solution. A black precipitate of lead sulfide indicates the presence of sulfur.

4. TESTS FOR HALOGENS

i. IF NITROGEN AND/OR SULFUR PRESENT

If either nitrogen or sulfur is present, the cyanide and sulfide ions must first be removed. Acidify ~ 0.5 mL of the filtrate with dilute nitric acid and concentrate to half of its original volume to expel any hydrogen cyanide or hydrogen sulfide that might be present in the mixture (**CAUTION: carry out the reactions in a fume cupboard**). Dilute the mixture with an equal volume of distilled water.

Add 1-2 drops 5% of aqueous silver nitrate solution to 2-3 mL of the fusion solution. An immediate heavy precipitation indicates the presence of chlorine, bromine, or iodine.

ii. IF NITROGEN AND SULFUR ARE ABSENT

Acidify a portion of the filtrate with dilute nitric acid and add an excess of 5% silver nitrate solution. Precipitation indicates the presence of chloride, bromide or iodide. Silver chloride precipitate is white, silver bromide precipitate is pale yellow and silver iodide precipitate is yellow.

Silver chloride, silver bromide and silver iodide have different solubilities in 5% ammonium hydroxide solution. Decant the solvent and treat the precipitate with dilute aqueous ammonia solution. Add 2 mL 5% ammonium hydroxide to the precipitate. Silver chloride is soluble in ammonium hydroxide, silver bromide is slightly soluble and silver iodide is insoluble in ammonium hydroxide solution.

The presence of iodine and bromine may be further confirmed by the following tests. These tests may also be used if it is suspected that more than one halogen is present in the compound.

4.1. TESTS FOR IODINE

Acidify about 3 mL of the filtrate with 10% sulfuric acid solution and heat to boiling for a few minutes. After cooling, add 1 mL of dichloromethane followed by a drop of 5% sodium hypochlorite (bleach). The production of a purple or violet color in the dichloromethane layer indicates the presence of iodine.

4.2. TESTS FOR BROMINE

Acidify about 3 mL of the filtrate with 10% sulfuric acid solution and heat to boiling for a few minutes. After cooling, add 1 mL of dichloromethane followed by a drop by drop of 5% sodium hypochlorite (bleach), while shaking, until a possible purple color (presence of iodine) disappears. The appearance of a reddish-brown color indicates the presence of bromine.

4.3. OTHER TESTS FOR HALOGENS

To test for chlorine in the presence of iodine and/or bromine, acidify the filtrate with 5% nitric acid and boil the solution for a few minutes. Add sufficient amount of 0.1 M silver nitrate to precipitate out the halogen completely as silver halides. Filter the precipitate and add about

3 mL of 0.1% NaOH solution. Boil the mixture for about 2 minutes and filter the solution. Acidify the filtrate with 5% nitric acid and add a few drops of 0.1 M silver nitrate. A white

precipitate indicates the presence of chlorine.

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3. Mahmood, K.; Rahman, N.A. Kaedah Kimia Dalam Pengenalpastian Sebatian Organik, University of Malaya Publisher., 2000.
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POST-LAB QUESTIONS

1. Write the chemical equation for the formation of a black precipitate when sulfur is present in the sample.
2. Explain why the mixture is boiled in a fume cupboard when nitrogen and sulfur are present in the sample?
3. How are the sodium waste from the experiment destroyed?

EXPERIMENT 2

CHEMICAL PROPERTIES OF HYDROCARBONS, ALCOHOLS, ALDEHYDES, KETONES, CARBOXYLIC ACIDS AND AMINES

Before the advancement of spectroscopic techniques, the determination of chemical properties was very important for the identification, characterization, and determination of the structure of a compound. Many reagents and reaction conditions were found to give characteristic and specific results with compounds containing specific functional groups. These reagents or reaction conditions are used as qualitative tests and serve to indicate the presence or absence of certain functional groups in a substance.

There are hundreds of qualitative tests that can be used to characterize or distinguish the functional groups in the unknown substances. The procedures for some of these tests are described below.

PRE-LAB READING/DISCUSSION

- Functional groups and their properties
- Chemical reactivity

1. HYDROCARBONS

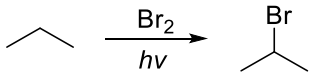
Organic compounds with only hydrogens and carbons are called hydrocarbons. According to the structure, hydrocarbons can be classified into two main groups, which are aliphatic and aromatic hydrocarbons. Generally, aliphatic hydrocarbons are classified as either saturated hydrocarbons such alkanes and cycloalkanes, and unsaturated hydrocarbons, for example alkenes, alkynes and their cyclic analogs.

Alkanes or paraffins are saturated aliphatic hydrocarbons containing only sigma (σ) bond whereas the alkenes and alkynes contain both sigma (σ) and pi (π) bonds.

The non-reactivity of alkanes with most chemical reagents such as acids, bases, oxidizing and reducing agents at room temperature explains why its name is paraffin, which means, inert.

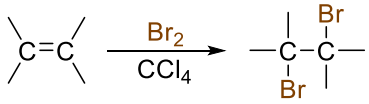
Alkanes react with chlorine and bromine very slowly at room temperature but much faster in the

presence of light. This is a substitution reaction in which one or more halogen atoms will replace one or more hydrogen atoms in the carbon chain. With bromine as the halogen and in the presence of light, the mono-substitution reaction is represented by the following general equation:

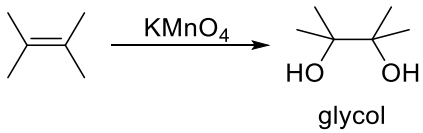


The reaction of hydrocarbons with bromine in carbon tetrachloride is one of the tests used to differentiate between a saturated and an unsaturated aliphatic hydrocarbon. If the substance is an alkane, almost no reaction occurs. However, in the presence of light or sunlight, bromine will decolorize slowly as substitution reaction is taking place and hydrogen bromide is liberated. To test for hydrogen bromide, blow across the mouth of the test tube containing the chemical reactants. If hydrogen bromide is present, it will dissolve in the water vapor and forms streaks of vapor droplets on the inside of the test tube.

Alkenes are reactive at room temperature. The center of reactivity is the double bond that can become saturated by the addition of other molecules. For example, bromine in carbon tetrachloride reacts immediately with alkenes at room temperature to produce dibromide. The discoloration of bromine is evidence that the reaction has taken place, even in the dark, without the liberation of hydrogen bromide. This reaction is used to differentiate between unsaturated and saturated hydrocarbons.



Another good test for unsaturated hydrocarbon is the use of aqueous potassium permanganate solution or known as Baeyer's test. Alkenes react with neutral permanganate solution to form glycol causing the purple permanganate color to disappear and a brown precipitate of manganese(II) dioxide to form.



Hydrocarbons may also be differentiated by their solubility in sulfuric acid. Alkanes are not soluble in concentrated sulfuric acid while both alkenes and alkynes are protonated by the sulfuric acid and become soluble. Aromatic hydrocarbons, on the other hand, do not dissolve easily in

concentrated sulfuric acid but dissolve readily in fuming sulfuric acid.

PROCEDURE

The following alkanes are provided for the tests:
heptane, cyclohexene, and toluene.

1.1. IGNITION TEST

Pour about 0.5 mL heptane into an evaporating dish. With a burning wooden splinter, ignite the alkane. Note the characteristic of the reaction and the color of its flame. Repeat this test for both cyclohexene and toluene.

1.2. SOLUBILITY TEST

Add 1 mL heptane into a tube containing 2 mL of distilled water. Shake the tube and record your observations. Repeat the test for both cyclohexene and toluene. Test the solubility of these hydrocarbons in each other using 1 mL sample in a clean and dry test tube for each test.

1.3. BROMINE TEST

Prepare two test tubes containing about 1 mL heptane. Into each tube, add 4-5 drops of bromine 4% solution in dichloromethane. Place one of the test-tube in a cupboard (dark place) and the second one under sunlight. Observe and record your observations after 15 minutes. Repeat the test for cyclohexene and for toluene.

1.4. POTASSIUM PERMANGANATE TEST

Add 1 mL of the 0.01 M potassium permanganate solution into test tube containing 0.5 mL heptane. Shake the tube and record your observation. Repeat this test for cyclohexene and toluene.

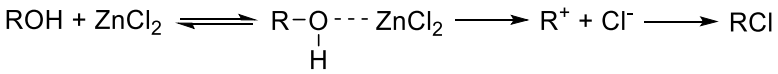
1.5. CONCENTRATED SULFURIC ACID TEST (SULFONATION)

In a dry test tube, pour 1 mL concentrated sulfuric acid carefully. Add 0.5 mL of heptane into the tube and shake. Record your observation. Repeat this test for the other two hydrocarbons.

2. ALCOHOLS AND PHENOLS

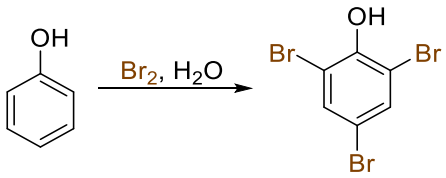
Alcohol is a class of organic compounds containing hydroxyl group, -OH, as the functional group. Alcohol can be classified into three which are primary alcohol (1°), secondary alcohol (2°) and tertiary alcohol (3°).

The three different classes of alcohol can be differentiated through the rate of reaction of the alcohol with hydrogen halide using the Lucas reagent (a mixture of concentrated hydrochloric acid and zinc chloride). Primary alcohols react very slowly while secondary alcohols react within 5 minutes of the addition of the Lucas reagent and form a cloudy mixture due to the formation of alkyl chloride. In the case of tertiary alcohols, two phases will appear almost immediately due to the formation of alkyl chloride upon the addition of the Lucas reagent.



Alcohols can also be oxidized to aldehydes, ketones and carboxylic acids. The product formed depends upon the class of alcohol used. The three classes of alcohols differ in their oxidation behavior. Primary alcohols yield aldehydes and secondary alcohols yield ketones upon oxidation, while tertiary alcohols yield no carbonyl product under the normal oxidizing conditions. The common reagent used for oxidation of alcohols is potassium dichromate.

Phenols are compounds in which the hydroxyl group is attached directly onto a benzene ring. Phenols are usually acidic and usually dissolve in 5% aqueous sodium hydroxide solution. Most phenols react with ferric chloride solution to give red, blue, purple or green complexes. Phenols also react readily with bromine water to give a substituted product in the form of a white precipitate. For example, the reaction between phenol and bromine water gave the 2,4,6-tribromphenol as shown below.



PROCEDURE

The following alcohols are provided for the tests below:

Aliphatic alcohols: ethanol, 2-butanol, and 2-methyl-2-propanol (*t*-butanol)

Aromatic alcohols: phenol, *m*-cresol, and catechol

2.1. IGNITION TEST

Pour about 0.5 mL ethanol into an evaporating dish. With a burning wooden splinter, ignite the ethanol. Observe the characteristics of the flame. Repeat the test for 2-butanol, 2-metyl-2- propanol (*t*-butanol) and phenol.

2.2. SOLUBILITY TEST

Add 0.5 mL ethanol to a test tube containing 1 mL distilled water. Shake the test tube and record your observation. Repeat the solubility test for 2-butanol, 2-metyl-2-propanol (t-butanol) and phenol. Repeat the test for the solubility of ethanol, 2-butanol, *t*-butanol and phenol in 1 mL ether and in 1 mL toluene. Record your observations.

2.3. REACTION WITH SODIUM

Pour about 1 mL absolute ethanol into a dry test tube. Add a small piece of sodium (about half the size of a pea) to the absolute ethanol. Observe and record the reaction. Add some water after the reaction is completed and test the solution with a litmus paper. Repeat the same procedure with both 2-butanol and t-butanol.

2.4. OXIDATION REACTION

Push one end of a 20 cm length copper wire into a cork and coil the other end by making two or three turns about a thin glass rod. Heat the coil in Bunsen flame until it ceases to impart any color to the flame. While still warm, dip the coil into a test tube containing ethanol (1 mL). Repeat this process several times. Cool the test tube in water bath and add one drop of the alcohol into a test tube containing 1 mL of Schiff's reagent. Shake the tube slowly and note the formation of a pink or purple coloration. If the compound does not dissolve in the Schiff‟s reagent, cover the test tube with a cork and shake it vigorously until an emulsion forms. Record

your observation. Repeat the experiment with 2-butanol and t-butanol.

(Important: Before reusing the wire for another compound, ensure that the material from the previous test has been destroyed by heating it until the flame is not colored.)

2.5. LUCAS TEST

The Lucas reagent can be prepared by dissolving 6.4 g of zinc chloride in 4 mL of concentrated hydrochloric acid.

Add 3 mL of Lucas reagent to 0.5 mL ethanol in a dry test tube quickly. Cover the tube with a cork, shake it and let the mixture stand for a while. Observe carefully for any changes taking place. Record the time required for the reaction to occur. Repeat the test using 2-butanol and *t*-butanol.

2.6. ESTERIFICATION TEST

Add 1 mL glacial acetic acid and 5 drops of concentrated sulfuric acid to 2 mL absolute ethanol. Ensure that the mixture is homogeneous and warm it in water bath. Cool and pour the mixture into an evaporating dish containing 5 mL of 10% sodium carbonate. Note the smell of the vapor released. Repeat the test using 2-butanol, t-butanol and phenol.

2.7. IRON(III) CHLORIDE TEST

Dissolve about 0.05 g phenol in 2.5 ml of water. (If the compound does not dissolve, prepare a hot saturated aqueous phenol solution, filter, and use 1 mL of the cold filtrate). Place the solution in a test tube and add 1 drop of neutral 1% iron (III) chloride solution. Observe the change in color of the solution. Add another drop after 2-3 seconds. A positive test is indicated by a transient or permanent coloration (usually purple, blue, or green) of the solution. Repeat the test using *m*-cresol and catechol.

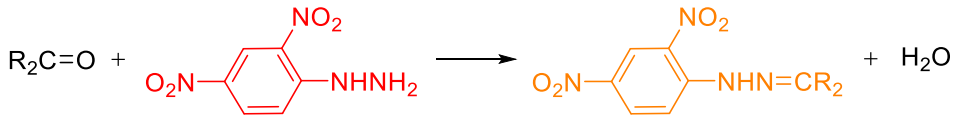
2.8. BROMINE WATER

Dissolve 0.05 g phenol in 2.5 mL of water and add bromine water dropwise until the bromine

color is no longer discharged. The discharge of the bromine color is a positive test for the presence of a phenol. In some cases, a white precipitate of the bromophenol may also form. Repeat the test using *m*-cresol and catechol.

3. CARBONYL COMPOUNDS: ALDEHYDES AND KETONES

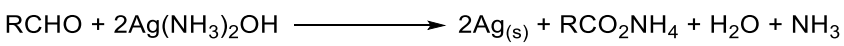
Aldehydes and ketones are organic compounds containing the carbonyl functional group, C=O. Aldehyde has the general formula, RCHO while ketone has the general formula RR'CO where R and R' are alkyl or aryl groups. An aldehyde or ketone will undergo a general reaction with Brady reagent, 2,4-dinitrophenylhydrazine (2, 4-DNPH), to produce 2,4-dinitrophenylhydrazone which will appear as orange or yellow precipitate. This reaction is commonly used to ascertain the presence of a carbonyl group in a compound.



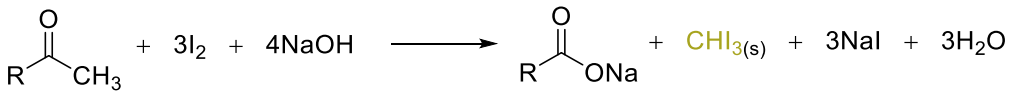
(R = H, alkyl or aryl)

Aldehydes can be distinguished from ketones through several tests. One test involves the use of a Schiff's reagent which will produce a violet-pink solution with aldehydes but not ketones. Some aromatic aldehydes such as vanillin also give a negative result with Schiff's test.

Another test that can distinguish aldehydes from ketones is through weak oxidizing agents such as the Tollen's reagent (ammonium nitrate complex in ammonia solution). A positive reaction is indicated by the formation of a silvery mirror on the side of the tube.



Iodoform test is a useful test for the identification of methyl ketones and secondary methyl carbinols. This test involves a reaction in which the methyl group of the ketone is removed from the molecule and produces iodoform (CHI_3) (see equation below). A positive test is indicated by the formation of yellow precipitates or suspension of iodoform.



Secondary alcohols with a methyl group adjacent to the carbon bearing the hydroxyl group such as ethanol can be oxidized to methyl ketones by "iodine bleach" or hypoiodite. Hence, alcohols such as ethanol will also produce yellow iodoform precipitates as methyl ketones in an iodoform test.

PROCEDURE

The following carbonyl compounds are provided for the tests below:

Aldehydes: propanal and benzaldehyde

Ketones: propanone and acetophenone

3.1. BRADY'S TEST

The 2,4-dinitrophenylhydrazine reagent (Brady's reagent) can be prepared by dissolving 3 g of 2,4-dinitrophenylhydrazine in 15 mL concentrated sulfuric acid. This solution is added, with stirring, to 20 mL water and 70 mL 95% ethanol and filtered.

Note: You can use the Brady's reagent that has been prepared by the lab assistants.

Dissolve about 0.5 mL or 50 mg of the compound to be tested in 2 mL 95% ethanol. Add 2 to 3 drops of this mixture into the test tube containing 3 mL 2, 4-dinitrophenylhydrazine reagent. Shake the tube and observe the formation of any precipitate. If no precipitate forms immediately allow the mixture to stand for 5-10 minutes. Record your observations.

3.2. SODIUM BISULPHITE SOLUTION TEST

The alcoholic sodium bisulfite reagent can be prepared by adding 1 mL ethanol to 4 mL 40% aqueous solution of sodium bisulfite. The reagent must be filtered before use.

Add aldehyde or ketone (about 0.2 mL or 2 mg) into a test tube containing 1 mL alcoholic sodium bisulfite solution.* Plug the test tube with a cork and shake thoroughly. Record any observations.

3.3. TOLLENS' TEST

Tollens' reagent can be prepared by adding one drop of NaOH 10% solution to a 2 mL 5% silver nitrate solution in a test tube. Add ammonia 5% solution drop by drop until all the precipitate (silver oxide) dissolves. Avoid using excess ammonia in order to obtain a sensitive reagent (Note 1).

Add 2-3 drops or 0.1 g of the compound that is to be tested to the Tollens' reagent. Shake the tube slowly and note the formation of silver mirror/precipitate for the presence of an aldehyde group. If there is no precipitation after 10 minutes, warm the mixture in a water bath at 30°C for 5-10 minutes. Record your observation.

Note: The reagent must be prepared fresh before use and should not be stored.

3.4. FEHLING'S TEST

Fehling's solution can be prepared as follows:

Prepare solutions #1 and #2.

Solution #1: Dissolve 17.32 g hydrated copper sulphate crystal in 200 mL water and dilute the solution to 250 mL.

Solution #2: Dissolve 86.5 g sodium potassium tartrate and 35 g sodium hydroxide in 100 mL water and dilute the solution to 250 mL.

Mix 2.5 mL *Solution #1* and 2.5 mL *Solution #2* immediately before use.

Note: You can use the Solutions 1 and 2 that have been prepared by the lab assistants.

Dissolve 0.2 g or 1 mL of the compound to be tested in 5 mL water and add 5 mL of the Fehling's reagent to the solution. Slowly shake the tube and heat the mixture to boiling. Cool the mixture to room temperature and note the occurrence of any precipitation. Record your observations.

3.5. SCHIFF'S TEST

Schiff's reagent is prepared by dissolving 0.005 g 4-rosaline hydrochloride (fuchsin in 50 mL distilled water followed by addition of 2 mL saturated sodium bisulfite solution. After 1 hour, add 1 mL concentrated hydrochloric acid and then leave the solution to stand for 24 hours. This reagent

is colorless and very sensitive.

Add 1-2 drops of the compound to be tested to 1 mL Schiff's reagent in a test tube. Shake it slowly and observe the color develop in 4-5 minutes. If the compound does not dissolve in the Schiff's reagent, cap the test tube with a cork and shake it vigorously until an emulsion forms. Record your observations.

3.6. BENZALDEHYDE OXIDATION

Place benzaldehyde (2-3 drops) in a watch glass and leave for 1 hour at room temperature. Record your observations.

3.7. THE IODOFORM TEST

I_2/KI solution is prepared by adding 20.0 g potassium iodide and 10.0 g iodine in 80 mL distilled water. The mixture is stirred until it forms a deep brown solution.

Place about 5 drops of propanone in a test tube and add 2 mL of distilled water (Note 1). Shake the test tube until all the samples have dissolved. Add 1 mL 10% sodium hydroxide solution and then slowly add the iodine-potassium iodide solution (I_2/KI), with shaking, until the dark color of iodine persists. Continue adding the I_2/KI solution until the iodine color is not discharged for 2 minutes at 60 ^oC.

Remove the excess iodine by adding a few drops of 10% sodium hydroxide solution, while shaking. Add equal amount of water and allow the mixture to stand at room temperature for 15 minutes. A positive test is indicated by the appearance iodoform as of yellow precipitate. Filter, dry the precipitate, and take the melting point of the iodoform (literature m.p.: 119-121 ^oC). Repeat the above test with ethanol and acetophenone.

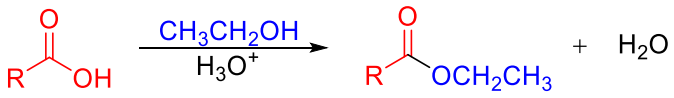
Note 1: Use dioxane if compound is not soluble in water.

4. CARBOXYLIC ACIDS, AMIDES, AND ESTERS

Carboxylic acid is an organic acid with the general structure of RCO_2H and the carboxyl group ($–CO_2H$) as the functional group. They are primarily identified by spectroscopic and solubility

test. Hence, carboxylic acids can be detected by their solubility in 5% NaOH solution as well as in the weakly basic 5% $NaHCO_3$ solution. However, it is also worth noticing that sulphonic acid and several derivative phenols like 2,4-dinitrophenol and 2,4,6-trinitrophenol are also soluble in 5% $NaHCO_3$ solution.

There are also a few chemical tests that can be used to confirm the presence of a carboxyl group. Carboxylic acids react with sodium bicarbonate solution to produce the carboxylate anion and carbon dioxide gas. Another test for carboxylic acid involves esterification reaction of carboxylic acids which give a sweet-smelling ester as the product shown below.



Esters are carboxylic acid derivatives which characteristically have a sweet, fruity smell. The presence of an ester group can be tested by reacting it with hydroxlamine to give an alcohol and hydroxamic acid, which when treated with ferric chloride gives characteristic a burgundy or magenta ferric hydroxamate complex.

Esters can also be cleaved by hydroiodic acid to produce alkyl iodide and carboxylic acid. The alkyl iodide produced can be treated with mercuric nitrate to yield an orange-colored mercuric iodide.

Another carboxylic acid derivative is amide. Like esters, amides react with hydroxylamine hydrochloride to form hydroxamic acid which react with ferric chloride to form the magenta colored ferric hydroxamate.

Amides can also be hydrolyzed to produce the carboxylate salt and ammonia or amine. The presence of ammonia or low molecular weight amine can be detected using litmus paper.

PROCEDURE

The following carboxylic acids and carboxylic acid derivatives are provided for the tests below:
Carboxylic acid: ethanoic acid (acetic acid) and benzoic acid

Amides: ethanamide and benzamide.

Esters: ethyl acetate and methyl benzoate

4.1. REACTION OF CARBOXYLIC ACID WITH SODIUM BICARBONATE SOLUTION

Place 1 mL 5% $NaHCO_3$ in a watch glass. Add 1-2 drops carboxylic acid (or 0.1 g, if solid). Record your observations.

4.2. ESTERIFICATION OF CARBOXYLIC ACID

Add 1 mL glacial acetic acid and 5 drops of concentrated sulfuric acid to 2 mL ethanol in a test tube. Warm the mixture for 2 minutes. Cool, and pour cautiously into aqueous sodium carbonate solution in an evaporating dish and smell immediately. An acid would yield a sweet, fruity smell of an ester. (However, acids of high molecular weight often give almost odorless esters).

4.3. SODIUM HYDROXIDE HYDROLYSIS OF AMIDES

Add 0.2 g ethanamide to 5 mL 10% NaOH solution in a test tube. Shake the mixture and record your observations. Then, heat the solution to boiling and note the smell of the vapor released. Test the vapor with a moist red litmus paper and record your observations.

Cool the test tube and acidify it with aqueous HCl solution and note all your observations. Repeat the test with benzamide.

4.4. ACID HYDROLYSIS OF AMIDES

Heat the solution of 0.2 g ethanamide with 10% sulfuric acid to boiling. Cool the test tube and note the smell of the vapor released. Test the vapor with a moist red litmus paper.

Repeat the test using benzamide.

4.5. TEST FOR ESTER

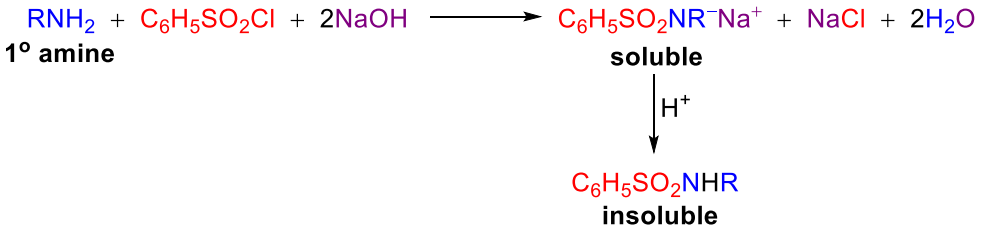
In a test tube, add 1-2 drops ethyl acetate to a saturated alcoholic solution of hydroxylamine hydrochloride (3 drops) and a methanolic solution of 20% potassium hydroxide (3 drops). Heat the mixture to boiling. Cool the mixture and acidify with 0.5 M HCl solution. Add iron(III) chloride solution drop by drop to the mixture and record all observations. Repeat the test with methyl benzoate.

5. AMINES

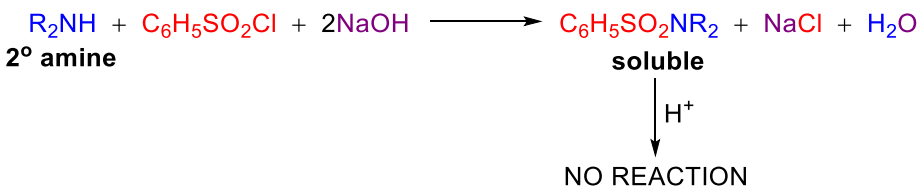
Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. They have the general formula R-NH_2 (primary, 1^o), R_2NH (secondary; 2^o) or R_3N (tertiary, 3^o), in which R is an alkyl or aryl group. The hydrogens on the primary and secondary amines are active and undergo reaction with sodium metal to form a salt and liberate hydrogen gas.

Primary and secondary amines react with acetyl chloride to produce amides which often precipitate out from the solution. Heat is also usually evolved in this reaction. Tertiary amines, however, do not react with acetyl chloride since they lack hydrogen on the nitrogen atom.

The **Hinsberg test** can also be used to distinguish between 1^o, 2^o, and 3^o amines. This test involves the reaction between the amines and the benzenesulfonyl chloride reagent under basic conditions. Primary amines react with benzenesulfonyl chloride under basic conditions to form the sodium salt of sulfonamide which is soluble in the reaction mixture. Precipitation of the sulfonamide will occur when the mixture is acidified.

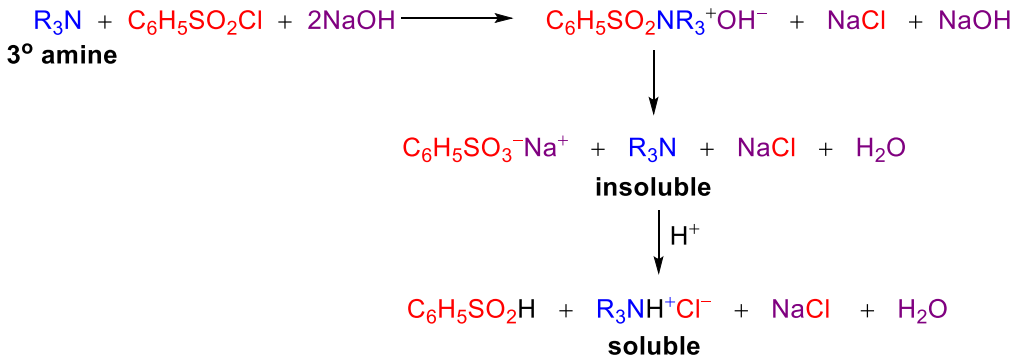


Similarly, secondary amide will react with benzenesulphonyl chloride under basic condition to form the sodium salt of sulfonamide which is insoluble in the reaction mixture and remains insoluble upon acidification.

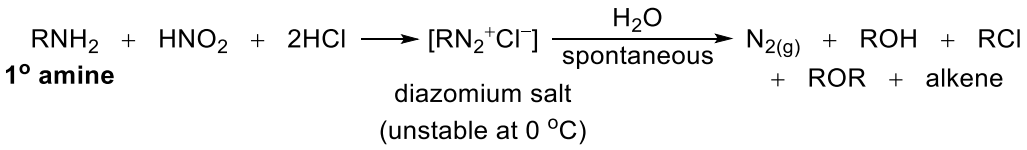


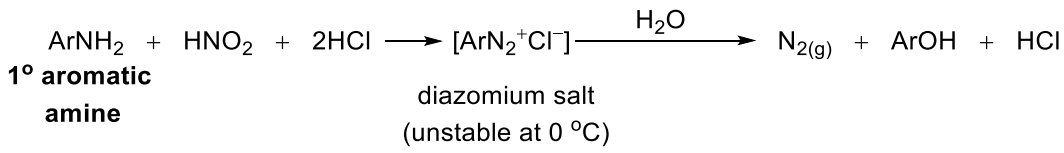
Tertiary amines undergo reactions with benzenesulfonyl chloride under basic condition to

form the quaternary ammonium sulphonate salts which gives sodium sulfonate and insoluble tertiary amines in basic solution. Acidification of the reaction mixture gives sulfonic acids and soluble amine salts.

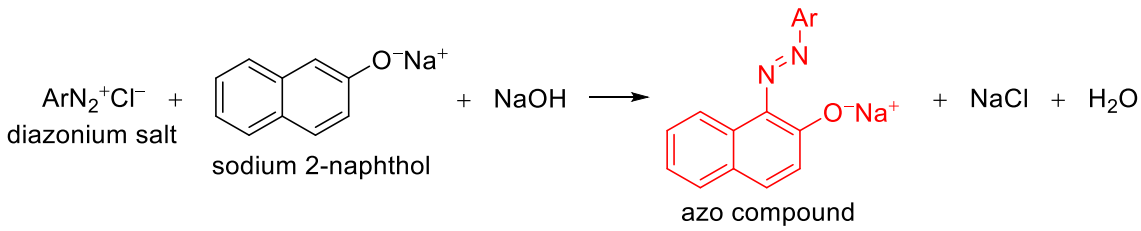


Amines also react with nitrous acid and this reaction is used to distinguish not only 1°, 2°, or 3° amines, but also between aliphatic and aromatic amines. Primary aliphatic amines and aromatic amines react with nitrous acid to form an intermediate diazonium salt with the evolution of nitrogen gas. A primary aliphatic diazonium salt is unstable even at 0 °C and decomposes spontaneously with a rapid loss of nitrogen gas while primary aromatic amine diazonium salt is more stable at 0 °C and decomposes to liberate nitrogen gas only upon heating.

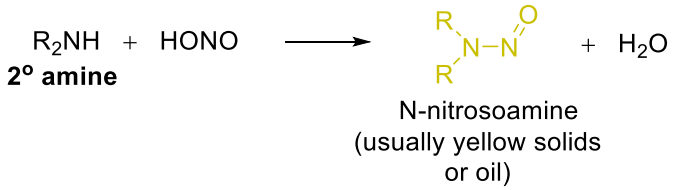




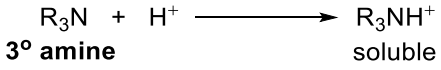
The diazonium salt of the primary aromatic amine reacts with phenolic compounds such as 2-naphthol to form an orange-red azo compound.



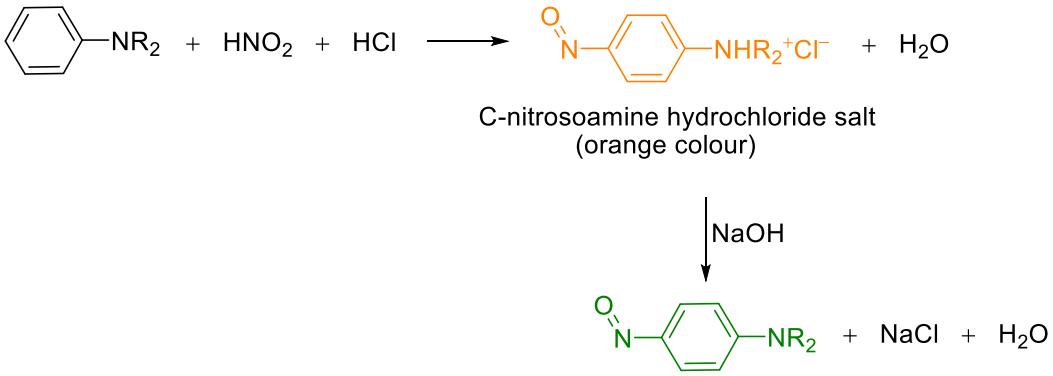
Secondary amines undergo a reaction with nitrous acid to form N-nitrosoamines which are usually yellow low melting solids.



Tertiary aliphatic amines do not react with nitrous acid but form soluble salts as shown below.



However, the orange-colored hydrochloride salt of the C-nitrosoamine is formed when a tertiary aromatic amine is reacted with nitrous acid. Treatment of the C-nitrosoamine salt with base will liberate the C-nitrosoamine as bright green or blue solid.



PROCEDURE

The following amines are provided for the tests below:

Propylamine, diethylamine, triethylamine, aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline

5.1. HINSBERG TEST

To 0.3 mL propylamine (or 300 mg, if solid) in a test tube, add 5 mL 10% NaOH solution and 0.4

mL benzenesulfonyl chloride. Stopper the test tube and shake the mixture vigorously. Test the solution to make sure that it is still alkaline. After all of the benzenesulfonyl chloride has reacted, cool the solution and separate the residue from the solution, if any. Treat the solution with 10% HCl solution and record your observations. Positive tests are indicated as follows:

1° amines: dissolve in base and precipitate in acid.
2° amines: precipitate in base but no change in acid.
3° amines: precipitate in base and dissolve in acid.

Repeat test using propylamine, diethylamine, triethylamine, aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline.

5.2. NITROUS ACID TEST

Add 0.5 mL or 0.5 g of the amine to 1.5 mL concentrated HCl diluted with 2.5 mL water and cool the solution to 0 ^{o}C. Dissolve 0.5 g of sodium nitrite in 2.5 mL water and add this solution dropwise, with shaking, to the cold solution of the amine hydrochloride. Continue the addition until the mixture gives a positive test for nitrous acid. The test is carried out by placing a drop of the solution on starch-iodide paper; a blue color indicates the presence of nitrous acid. If the test is positive, transfer 2 mL of the solution to a clean test tube, warm gently, and examine for evolution of gas.

The presence of a primary aliphatic amine is indicated by a rapid bubbling or frothing as the aqueous sodium nitrate is added at 0 ^{o}C. Primary aromatic amines from diazonium salt with the evolution of gas only upon warming.

The solution from the primary aromatic amine should be subjected further to the coupling reaction as follows:

Add 2 mL of the cold diazonium solution to a solution of 0.1 g 2-naphthol in 2 mL 10% sodium hydroxide solution and 5 mL water. The formation of an orange-red dye with the evolution of gas upon warming indicates the presence of a primary aromatic amine.

A secondary amine will give a pale-yellow oil or low-melting solid without any evolution of gas. An immediate positive test for nitrous acid (as indicated by the blue color on a starch-iodide paper)

with no evolution of gas indicates a tertiary aliphatic amine.

Tertiary aromatic amines will react with nitrous acid to produce a dark-orange solution of the C-nitrosoamine hydrochloric salt. Treating 2 mL of this solution with 10% sodium hydroxide or sodium carbonate solution will give a bright-green or blue nitrosoamine base which can be purified and characterized.

Perform the above test with propylamine, diethylamine, aniline, *N*-methylaniline and *N*,*N*-dimethylaniline.

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EXPERIMENT 3

RECRYSTALLIZATION AND MELTING POINT DETERMINATION

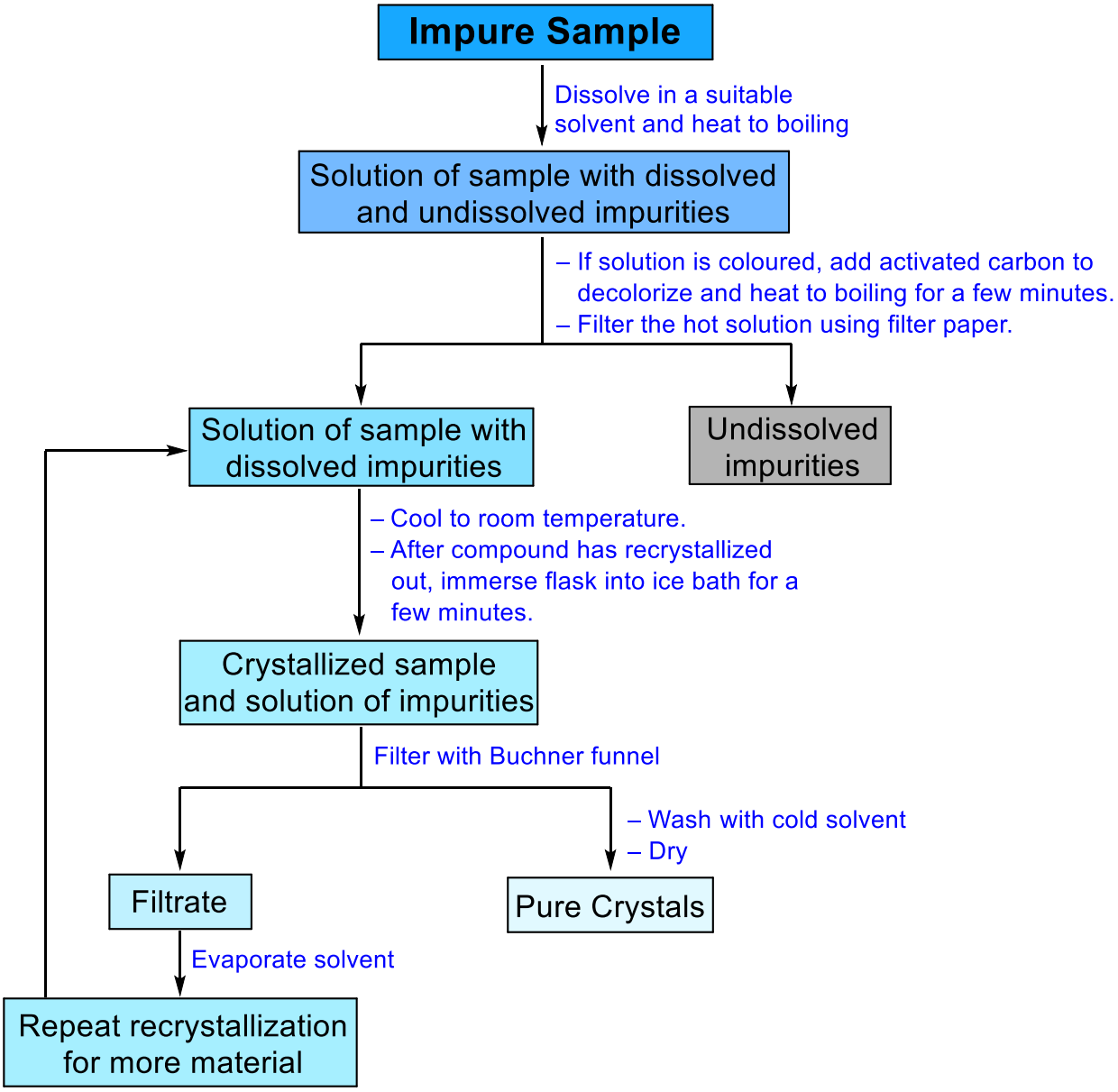
Organic compounds that are solids at room temperature can be purified by recrystallization. The general technique involves dissolving the material to be recrystallized in a hot solvent (or solvent mixture) and cooling the solution slowly. The solid that crystallizes out from the solution is the pure material.

During the recrystallization process, solid impurities (such as dust, filter paper, etc.) that do not dissolve in hot solution are normally eliminated through filtration. The dissolved impurities remain in the cold solution while the pure compound recrystallizes out of the solution.

PRE-LAB READING/DISCUSSION

- Melting point of crystals
- Crystallization process

The general procedure for recrystallization is as shown in the flow chart below:


Impure Sample
Dissolve in a suitable solvent and heat to boiling
Solution of sample with dissolved and undissolved impurities
– If solution is coloured, add activated carbon to decolorize and heat to boiling for a few minutes.
– Filter the hot solution using filter paper.
Solution of sample with dissolved impurities
Undissolved impurities
– Cool to room temperature.
– After compound has recrystallized out, immerse flask into ice bath for a few minutes.
Crystallized sample and solution of impurities
Filter with Buchner funnel
– Wash with cold solvent
– Dry
Filtrate
Pure Crystals
Evaporate solvent
Repeat recrystallization for more material

RECYSTALLIZATION OF BENZOIC ACID

APPARATUS

Conical flasks
Filter funnel
Buchner flask
Hirsch/Buchner funnel
Watch glass

CHEMICAL

Benzoic acid
Distilled water

PROCEDURE

Weigh about 1.0 g benzoic acid into a 100 mL conical flask. Add 15 mL water and anti-bumping granules (3-5 pieces). Heat the mixture on a hot plate until the solvent boils. Add successive small volumes of water (2-3 mL) and continue boiling until all benzoic acid has dissolved (apart from insoluble impurities).

If the solution is colored, remove the solution from the hot plate. Cool the solution to room temperature and add decolorizing charcoal (0.2-0.3 g). Mix thoroughly and boil the mixture for several minutes.

While waiting for the solution to boil, prepare the fluted filter paper and put it in the funnel. Put the funnel fitted with fluted filter paper in a conical flask. Add a little water and anti bumping granules into the conical flask and heat on a hot plate.

Filter the hot mixture of benzoic acid through a fluted filter paper into the heated conical flask. If the filtration is done in batches, keep the remaining solution hot throughout the filtration process. If crystallization occurs on the filter paper, add a minimum volume of boiling water to re-dissolve the crystals, and allow the solution to pass through the funnel. Add hot solvent in small volumes until all crystals are dissolved. After filtration, boil the filtrate to produce a more concentrated solution.

Cover the conical flask with a watch glass and allow the solution to cool to room temperature, then in an ice-bath after the crystallization has occurred. If no recrystallisation occurs at this stage, it may be due to the fact that too much water was used. Concentrate the solution by heating on the hot plate and cool. When all the benzoic acid crystals have crystallized out, filter the crystals through a Hirsch/Buchner funnel at the suction/water pump. Transfer all the crystals in the flask into the

funnel by rinsing the flask with some of the filtrate. Wash the crystals with a little cold water and air dry. Place the crystals in a watch glass to air dry or dry the crystals rubbing between two filter papers. Let the crystals dry completely before taking the melting point.

Weigh the pure benzoic acid recovered, calculate the percentage yield.

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POST-LAB QUESTIONS

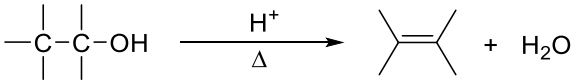
1. Explain why anti bumping granules are added before any solution is heated?
2. What is the purpose of the recrystallisation process?
3. Why is suction filtration favored over gravitational filtration when separating pure crystals from its supernatant liquid after the recrystallisation?
4. Explain how the washing of crystals is carried out.
5. Why it is necessary to remove all the solvent before the melting point of the pure compound can be determined?
6. In general, water is not a good solvent for the recrystallisation. Explain this statement.

EXPERIMENT 4

PREPARATION OF CYCLOHEXENE FROM CYCLOHEXANOL

Alkenes can be prepared from alcohols by heating the alcohol in the presence of an acid. Two of the common methods used are heating the mixture of alcohol with sulfuric acid or phosphoric acid or passing the alcohol vapor over activated alumina at high temperature. The latter is an industrial method.

In both reactions, water is eliminated and hence the reaction is known as dehydration.



In this experiment, the students will perform the dehydration of cyclohexanol, by heating the cyclohexanol in the presence of sulfuric acid. The acid catalyzes the reaction by protonating the hydroxyl group, making it a good leaving group. Elimination of water from the protonated alcohol produces an alkene.

According to Le Chatelier's principle, elimination of one species from a product mixture will shift the equilibrium to the side that favors the formation of the product. Therefore, in this reaction, the cyclohexene and water formed are distilled out once they are formed. The elimination of these products shifts the equilibrium to the right and increases the yield of cyclohexene produced.

After washing and drying of the crude product, distillation gives pure cyclohexene. The technique used in the washing of a liquid is essentially an extraction process.

PRE-LAB READING/DISCUSSION

- Le Chatelier's Principle
- Dehydration of alkane

APPARATUS

Flat round bottomed flask
Fractional distillation column
Still head
Thermometer
Receiving adapter
Separating funnel
Conical flask
Condenser
Pear shaped flask

CHEMICAL

Cyclohexanol
Concentrated H_2SO_4
10% sodium carbonate solution
Anhydrous calcium chloride

PROCEDURE

Place cyclohexanol (20.0 g, 21 mL) and concentrated sulfuric acid (2 mL) into a 100 mL round flat bottomed flask, with constant shaking. Add in a few pieces of anti-bumping granules. Fit in the fractional distillation column complete with Still head, thermometer, condenser, receiving adapter and a receiving flask to collect the product.

Heat the reaction mixture slowly using a hot plate so that cyclohexene and water formed will distill out through the fractional column. Continue distilling until only a small volume of residue is left in the flask (not to dryness). Ensure that the temperature at the top of the column does not exceed 100°C during the distillation process.

Pour the distillate (crude product) into a separating funnel and wash with a solution of 10% sodium carbonate (1-2 mL). Transfer the hydrocarbon layer into a conical flask (clean and dry) and add anhydrous calcium chloride. Leave for 15-20 minutes to dry.

While waiting for the crude product to dry, set up the distillation apparatus. Filter the crude product into the distillation flask and distill using a water bath. Record the boiling point and the mass of the cyclohexene.

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POST-LAB QUESTIONS

1. Give two advantages of using phosphoric acid over sulfuric acid in the dehydration reaction of an alcohol.
2. The by-product formed in the dehydration of cyclohexanol is dicyclohexyl ether. Write the mechanism for the formation of this by-product.
3. If 2-methylcyclohexanol undergoes dehydration process, what is/are the alkene/s formed?
4. Why do you need to wash the distillate with a solution of sodium carbonate?
5. Why the temperature at the top of the condenser in the fractional distillation cannot exceed 100 °C?

EXPERIMENT 5

SEPARATION OF COMPOUNDS USING CHROMATOGRAPHIC TECHNIQUES

"Chromatography" literally means color graphing and this technique was first used by a Russian botanist in the early 1900"s to describe the separation of colored plant pigments by passing a plant extract down a column of calcium carbonate and washing it with petroleum ether. Today, chromatography is a procedure which is commonly used to separate components in mixtures.

In general, chromatographic method involves putting a mixture to be separated on a stationary phase and a mobile phase is then passed through the stationary phase. The stationary phase can be of porous solids or a layer of liquid covering the surface of a suitable solid support while the mobile phase can be either a liquid or a gas. The adsorbents that are normally used as stationary phase are sucrose, cellulose, starch and inorganic carbonates but most separations are carried out using silica gel or alumina. The solvent used as the mobile phase usually has low boiling point and low viscosity, such as petroleum ether, ligroin, diethyl ether, dichloromethane, ethyl acetate, acetone, ethanol and methanol.

The principle of chromatographic separation relies on that fact that the different components in the starting mixture are adsorbed by the stationary phase and desorbed back into the mobile phase to different degrees, as they are moved with the mobile phase. The difference in the adsorption-desorption properties result in each compound passing through a given amount of stationary phase (often a column) at a different time (retention time). Thus, the components of the mixture are separated.

There are a variety of chromatographic techniques which may be used depending upon what types of compounds are present in a mixture.

Thin layer chromatography (TLC) is carried out on a very thin layer of chromatographically active material dispersed on the surface of an inert support such as plastic or glass. A small volume of a solution of the mixture to be separated is 'spotted' onto the stationary phase, near the bottom of the paper or plate (the location is marked for later reference). The solvent from the solution is evaporated and TLC plate is then placed in a 'tank' containing the mobile phase. The level of the

mobile phase should be below the location of the spot. The mobile phase then moves up the TLC plate and the separation is stopped when the mobile phase has nearly reached the top of the stationary phase. The mobile phase boundary is then marked and the mobile phase is allowed to evaporate. The locations of the different components in the mixture are then identified either visually (for colored compounds), by UV light, or by a chemical development (iodine vapor, ceric nitrate spray, sulfuric acid spray, etc.). The R_f of each component (distance travelled by component divided by distance travelled by the mobile phase) is then calculated. The R_f is a constant for a given compound under a fixed set of conditions (mobile and stationary phase). By comparing with R_f values for known compounds (standards), the components in the sample mixture can be identified.

In a column chromatography, the stationary phase (typically alumina or silica) is held in a column (usually glass) and the mobile phase is passed down this column by aid of gravity. A column used is typically 5-50 cm long and 5-50 mm wide and usually has a stopcock (tap) on the bottom to halt the flow of the mobile phase. The stationary phase is usually held in place with an inert material at bottom (sintered glass, cotton or glass wool etc.) and is often protected at the top with fine sands or some inert powder. The column is usually established by pouring the slurry absorbent into the column. The solvent is then allowed to pass through the column until the level is just above the top of the stationary phase. The mixture to be separated is then added to the top of the column (in a solvent) and solvent is allowed to flow until the stationary phase is just covered with solvent. The mobile phase is then added to the top of the column and is allowed to pass through the column in order to separate the mixture components. Fractions are collected from the bottom of the column and analyzed so as to locate and identify the individual components.

In this experiment column chromatography is used to separate various components in a mixture and thin layer chromatography (TLC) is used to test the purity of the compounds separated.

PRE-LAB READING/DISCUSSION

- Hydrophobicity and hydrophilicity

APPARATUS

Column
Chromatographic plate (2.5 cm x 10 cm)
Test tube, capillary tube
Chromatographic tank
Glass wool
Beaker
Conical flask (50 mL)/test tube

CHEMICAL

Mixture of *m*-nitroaniline and pyrene
Silica gel
Hexane
Ethyl acetate
Anhydrous sodium sulphate

PROCEDURE

1. COLUMN CHROMATOGRAPHY

Packing the Column: The Slurry Method

Stir hexane with silica gel (4-4.5 g, depending on the length of the column) into a thin, homogeneous slurry mixture in a conical flask.

Pack the column by filling the column half full with the eluent solvent mixture of hexane:ethyl acetate (2:1). Place a loose plug of glass or cotton wool at the bottom of the column using a long glass rod. Ensure all entrapped air has been forced out. Pour a small amount of anhydrous sodium sulphate (or fine sand) into the column so that a small clean layer is formed on top of the glass wool. Tap the column to level the surface of the sodium sulphate. Wash down any sodium sulphate that adheres to the side of the column with a minimum volume of solvent. The sodium sulphate layer forms a base that supports the column adsorbent and prevents it from washing through the stopcock.

To pack the column with the slurry of adsorbent prepared earlier, open the stopcock of the column and allow the solvent to drain slowly into a beaker. Pour the slurry in portions into the column. While pouring, tap the column constantly and gently at the side with a pencil fitted with

a rubber stopper or with a rubber tube. Continue tapping until all the material has settled. Drain the solvent until it is just level with the top of the absorbent. Do not let the column run dry. Add anhydrous sodium sulphate to the surface of the adsorbent to protect the surface of the adsorbent from been disturbed.

Applying the sample to the column

Apply the mixture of *m*-nitroaniline and pyrene carefully around the circumference of the adsorbent using a capillary pipette so that a layer of the mixture is formed evenly on to top of the sodium sulphate covering the absorbent. Care should be taken not to disturb the surface.

Drain out the solvent until to bring the liquid level to the top of the absorbent again. Pipette a little eluent around the inside of the column to rinse down any inherent sample and once again, drain out the solvent until the liquid level to the top of the absorbent again. Carefully add the eluent and begin collecting the eluate. Continue adding the eluent to ensure that the liquid level is nearly constant throughout the elution. Collect the eluate in a clean, dry flask. When the first component in the mixture has been completely eluted, change to another flask and begin collecting the second component in the mixture. Continue elution until the yellow band is completely drained from the column. Concentrate both the colorless and yellow eluates by heating on the water bath. The purity of both the compounds separated is then tested by TLC.

2. THIN LAYER CHROMATOGRAPHY

Spotting the plate

Dissolve both the *m*-nitroaniline and pyrene that has been separated above in dichloromethane. Using a pencil, draw a straight line on the thin layer chromatography plate and mark two spots on the plate as shown in Diagram 1. These spots must be high enough (a point about 1 cm from the bottom) to ensure that the compounds placed on it will not dissolve in the developing solvent. Fill a capillary tube with the solution to be examined by dipping one end of the tube into the solution. Capillary action fills the tube. Empty the tube by touching it lightly to the thin layer plate on the spot marked. When the tube touches the plate, the solution is transferred to the plate as a small spot. It is important to touch the plate very lightly so that the adsorbent layer on surface of the plate is not scratched or broken.

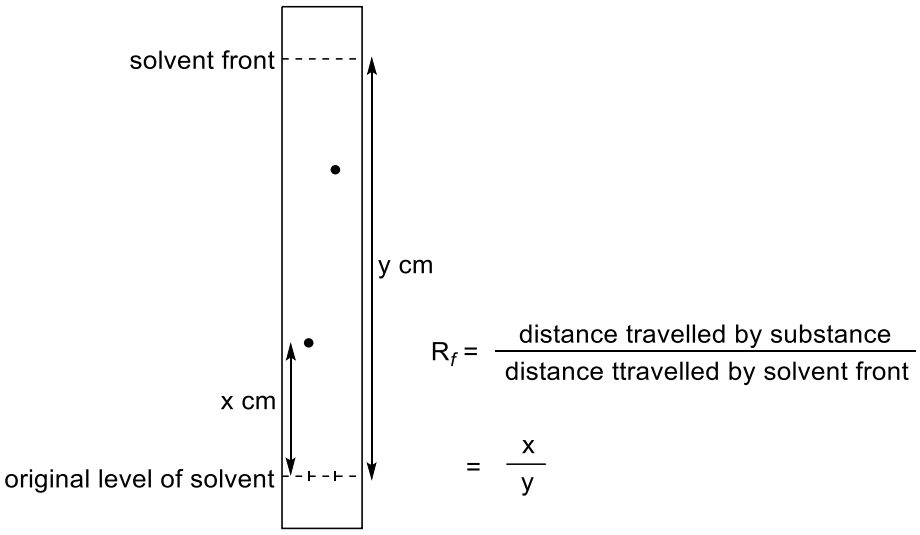

Diagram 1. Preparing the TLC plate

Line the inside of the developing tank/ jar with a piece of filter paper. Pour the eluent solvent (hexane-ethyl acetate (2:1)) into the developing tank/jar to a depth of a few millimeters and cap the developing tank/jar. Before the development, make sure the filter paper inside the tank thoroughly moistened with the eluent solvent. Once the filter paper liner is saturated, adjust the level of developing solvent in the bottom of the tank to a depth of about 5 mm. Cover the tank until it ready for use.

Developing the TLC plate

Place the spotted plate vertically (the end where the spots are, is at the bottom) into the developing tank and replace the cap. The eluent level must be below the spots. The solvent will rise slowly in the absorbent by capillary action. As the solvent rises, the plate becomes visibly moist. Do not move or open the chamber during the developing process. When the solvent has reached within 5 mm of the end of the coated surface, remove the plate and immediately draw a line across the plate to mark position of the solvent front with a pencil. Allow the solvent to evaporate from the plate.

Visualization

If the substance in the sample is colored, they may be observed directly. If not, they can be visualized by shining an ultraviolet (*uv*) light on the plate. Mark the visible spots with a pencil and calculate the R_f values for both compounds. The colorless spots on the TLC plate may also be

exposed to iodine vapour for visualization.

REFERENCES

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2. Skoog, D.A.; West, D.M.; Holler, F.J.; Crouch, S.R. Fundamentals of Analytical Chemistry, Eight Edition. Brooks/Cole Cengage Learning, US, 2004.
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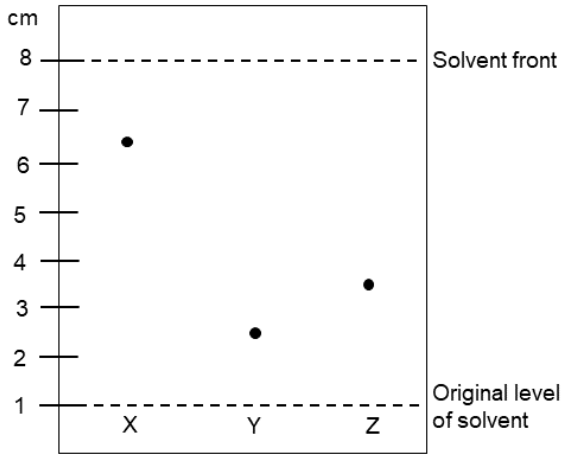
POST-LAB QUESTIONS

1. Explain the following terms in relation to chromatography.
   - Mobile phase
   - Stationary phase
   - R_f value
2. Calculate the R_f value for compounds X, Y and Z in TLC plate given below.



3. Suggest one suitable chromatographic technique which can be used to separate a mixture of amino acid.
4. What are the advantaged of column chromatography over TLC?
5. Arrange the following compounds in the order of increasing polarity.
   ortho-nitroaniline, *para*-nitroaniline, *meta*-nitroaniline

EXPERIMENT 6
STEREOCHEMISTRY

6.1. GEOMETRY AND CONFORMATIONS

Molecular building kits are in limited supply in the laboratory. If required, students are advised to share.

1. Construct a model of methane, the simplest organic compound. Note that all the hydrogens are as far apart as possible. What is the angle between any two hydrogen atoms, as measured through the carbon atom?

2. Construct a model with 2 saturated carbon atoms and the appropriate number of hydrogens. How many hydrogens are needed to complete all the covalence in the C_2 model?

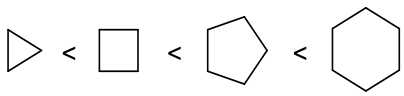
3. (a) Construct a model of pentane. Observe that the chain is not straight and note the tetrahedral geometry of each carbon.

   (b) Make molecular models of the other two constitutional isomers for the five-carbon alkane: isopentane (or 2-methylbutane) and neopentane (or 2,2-dimethylpropane). Identify all the primary, secondary and tertiary hydrogens in all three C_5 isomers.

4. Make a model of bicyclo[3.2.1]octane. Draw its structure.

5. Using Newman projections draw all conformations that result when 2-methylbutane is rotated around the C2–C3 bond. Draw a graph of energy versus dihedral angle for the different conformational isomers.

6. The relative stabilities of cycloalkanes are as follows. Why?



   (a) Construct models of cyclopropane, cyclobutene, and cyclopentane.
      (i) Would you expect the molecules to be planar?
      (ii) Are there angle strains in the above molecules?

(b) Construct a model of cyclohexane.

(i) Do the carbons in the ring all lie in one plane?

(ii) By rotating some of the bonds you should be able to make your model look like the figure below. The model should sit firmly on the desktop with three hydrogens serving as legs. This model is the chair conformation of cyclohexane.

(iii) Look straight down each of the carbon-carbon bonds in the molecule. Are the bonds staggered or eclipsed?

(iv) Does the chair conformation of cyclohexane possess any torsional strain?

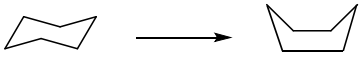
(v) Do any of the bonds in the chair conformation appear to be strained or bent?

(vi) What are the bond angles in the chair conformation?

Note that in the chair conformation, three of the hydrogens point straight up and three point straight down. These hydrogens are said to be in axial positions. The other six hydrogens radiate outward along the perimeter of the ring. These hydrogens are in equatorial positions.

(v) Draw the chair conformation of cyclohexane and label all of the hydrogens as equatorial or axial.

Grasp one of the carbons with an axial hydrogen pointing down and force it to point upwards (bond rotations are required). You should be able to get your model to look like a boat (See figure below). This unstable conformation is known as the boat conformation.

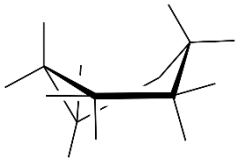


(vi) Are the C-C bonds all staggered in the boat conformation? If not, draw the boat and indicate which bonds are eclipsed.

(vii) Does the boat conformation of cyclohexane possess any torsional strain?

Other conformations of cyclohexane include the ***half chair*** and the ***twist*** conformations (see below).

half chair

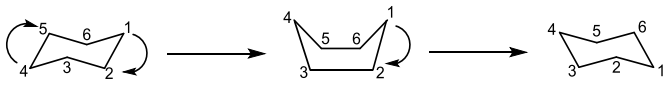


twist

(c) Consider chair conformations of the cyclohexane ring only.

Remove an equatorial hydrogen from the cyclohexane model and add a CH_3 group in its place to form **methylcyclohexane**. Draw the structure represented by the model.

Now grasp and invert C-1 (the carbon with the methyl group) to form a boat conformation. Then take C-4 and invert it to remake a chair conformation. This process inverts the chair conformation and is called ***chair flipping***.



(i) After the chair flip, what is orientation of the methyl group?

(ii) Draw the structure represented by the model.

(iii) Which chair conformation of methylcyclohexane is more stable? Why?

7. Conformations of Disubstituted Cyclohexanes

(a) Replace the equatorial hydrogens on C-1 and C-2 of cyclohexane with methyl groups to make a model of **1,2-dimethylcyclohexane**. Are the methyl groups in this model *cis* or *trans*?

Flip the ring to its other chair conformation.

(i) What are the orientations of the two methyl groups now?

(ii) Are the methyl groups in this model *cis* or *trans*?

(iii) Which of the two chair conformations is more stable? Explain.

(b) Now make a model of 1,2-dimethylcyclohexane with one of the methyl groups in an equatorial position and the other in an axial position. Are the methyl groups in this model *cis* or *trans*?

Flip the ring to its other chair conformation.

(i) What is the orientation of the bonds that connect the methyl groups to the ring?

(ii) Are the methyl groups in this model *cis* or *trans*?

(iii) Which of the two chair conformations is more stable? Explain.

Now make models of *cis* and *trans* 1,3-dimethylcyclohexane. Find the most stable chair

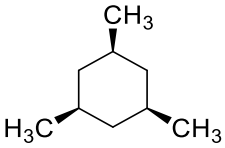
conformation of each.

(a) Draw the most stable conformation of the *cis* isomer.
(b) Draw the most stable conformation of the *trans* isomer.
(c) Which isomer is more stable, *cis* or *trans*? Why?

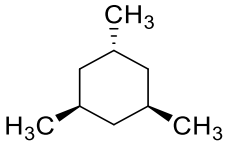
Now make models of *cis* and *trans* 1,4-dimethylcyclohexane. Find the most stable chair conformation of each.

(a) Draw the most stable conformation of the *cis* isomer.
(b) Draw the most stable conformation of the *trans* isomer.
(c) Which isomer do you think is more stable, *cis* or *trans*?

8. There are two stereoisomers of 1,3,5-trimethylcyclohexane, all-*cis* and *cis-trans-trans*. Make models of these molecules.



all-*cis*



cis-trans-trans

(a) Determine the more stable isomer.
(b) Draw the molecule in its most stable (chair) conformation.

6.2. STEREOISOMERS

1. Construct a model of compound with four different groups attached to a central carbon (the stereogenic centre). Make its mirror image. Manipulate the two models to convince yourselves that they are not superimposable. Make a similar model that contains only three different groups. Show that these are superimposable.

2. Construct a model of 2-chloropropane and its mirror image.
   (a) Does the molecule have a stereogenic centre?
   (b) Are the two models identical?
   (c) Are they enantiomers?

3. Construct a model of 2-butanol and identify its stereogenic centre. Make its mirror image.

(a) Are the two models superimposable?

(b) What is the relationship between the two models?

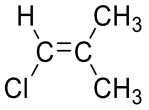
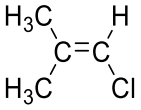
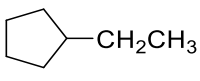
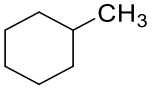
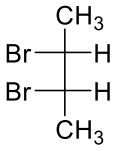
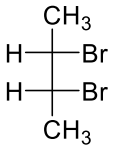
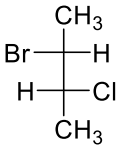
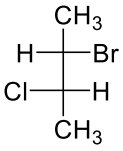
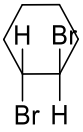
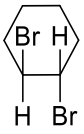
(c) Draw the two models and name them using the (*R*), (*S*) convention.

4. Construct a model of 3-bromo-2-butanol.

(a) How many stereogenic centres are present in the molecule?

(b) How many stereoisomers are possible for this molecule? Determine the stereochemical relationship between each pair of molecules.

5. Consider the following pairs of structures. Identify their relationship as representing molecules of the same compound, constitutional isomers, diastereomers, enantiomers, or *meso* compounds.

(a)	 and 	(b)	 and 
(c)	 and 	(d)	 and 
(e)	 and 	(f)	 and 

6. Construct models and draw Fischer projection formulas for the following.

(a) (*R*)-1-bromo-1-chlorobutane

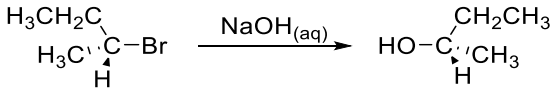
(b) (2*R*, 3*R*)-2,3-dibromopentane

(c) A compound with a molecular formula of $C_2H_2(NH_2)_2Cl_2$ whose structures are

(i) optically active

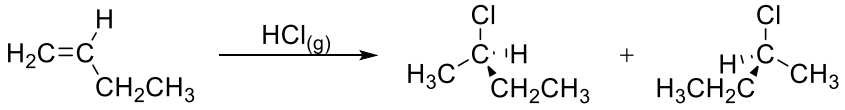
(ii) optically inactive due to a plane of symmetry

7. The following reaction shows that an inversion of configuration has occurred.



Construct models of the two molecules and show that both have different configurations.

8. The following reaction gives a racemic product. Explain this observation.



What is the stereochemical relationship between the two products?