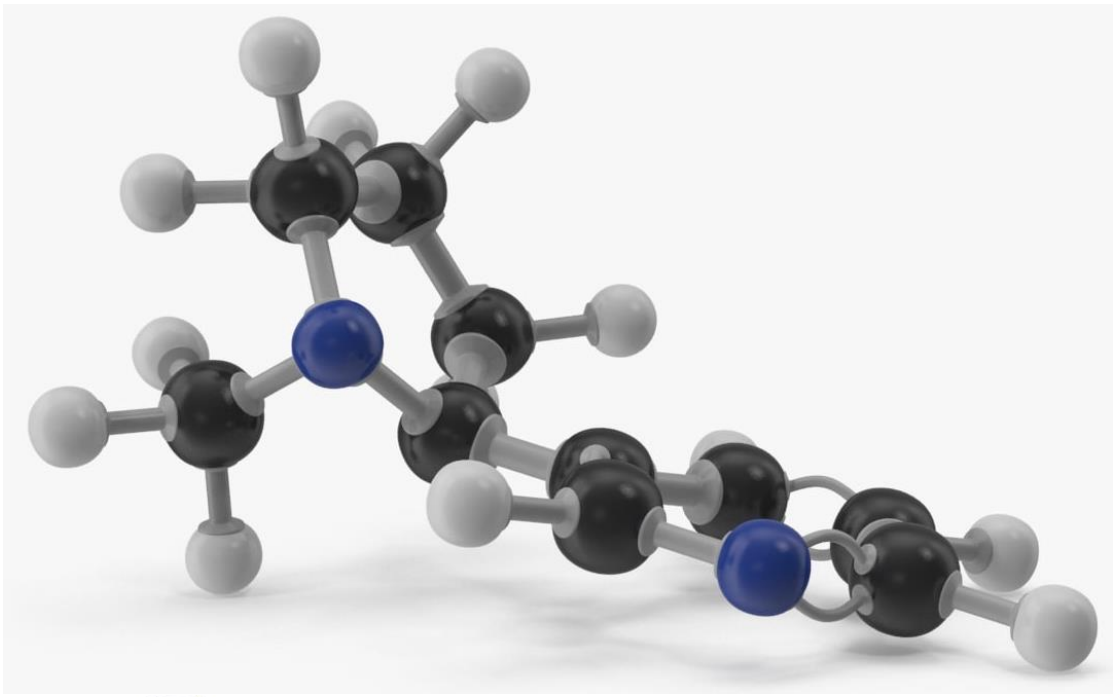

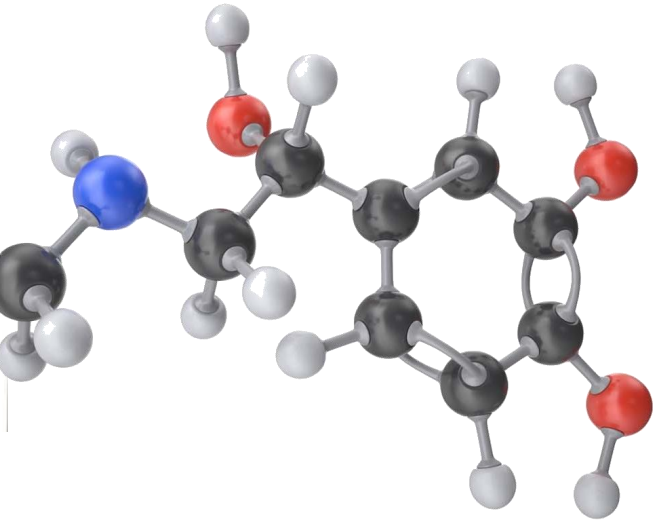

ORGANIC CHEMISTRY III

.: SIC3023 :: SIC3002 :: SID3002 :.

Laboratory Manual

Department of Chemistry

Universiti Malaya

Name :

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 authorised 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 jeopardised.

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 organised. 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 authorised 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 unauthorised 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 must not be worn in the lab as chemicals can get between the eye and the lens.
14. Lab experiments have been designed to minimise 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.
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

Department's copy

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Safety in the Third 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 IN LABOROTARY

1. **WEAR GOGGLES OVER YOUR EYES WHENEVER ANY STUDENT IN THE ROOM IS DOING LABORATORY WORK. YOU NEED GOGGLES EVEN IF YOU WEAR GLASSES**.
2. Observe all instructions and all precautions stated in your lab book or lab sheet.
3. **DO NOT** handle apparatus or chemicals until you receive instructions.
4. Unauthorised experiments are strictly forbidden.
5. Be sure to follow directions given to you for lighting a Bunsen burner. Should the burner strike back, turn the gas off at the valve. **DO NOT** touch the burner.
6. **DO NOT** stand too close to any apparatus in which material is heated or in which reactions are carried out.
7. When heating a liquid in a test tube, incline the test tube and point its mouth away from yourself and your neighbour. It is safest to do it under the hood.
8. Keep flammable liquids such as alcohol, benzene, and gasoline away from flames. **NEVER** pour such liquids in to the sink. Use the covered receptacle on the instructor's desk.
9. Be careful to read the labels on the reagent bottles to make sure that you are using the correct chemicals. **NEVER** return excess reagent to the original stock bottle.
10. Be careful when pouring acid or basic solutions. Pour these only over a sink. Stoppers should not be allowed to rest on tabletops. Add acid to water dropwise with constant stirring.
11. If any acid or base is exposed to your skin or clothes, flood it with water immediately. Report to your instructor immediately thereafter.
12. **DO NOT** inhale poisonous gases such as bromine, hydrogen sulphide, etc. Work with these gases as far back as possible in the hood. When it is necessary to smell the gas, the instructor will demonstrate a safe method.
13. **NEVER** push glass tubing, or a thistle tube, thermometer, etc. through a hole in a rubber stopper or cork. Be sure to use water or glycerol and then hold the glass close to the stopper and TWIST it on.
14. Report all accidents immediately.
15. Report to the instructor or lab assistant in case of thermometer break.
16. Work quietly. Accidents are less likely to happen in orderly labs.
17. Handle water faucets only when needed for procedure or cleanup.
18. Lab coats or aprons are required.
19. Throw all solids, paper, matches, etc. into the waste bin — **NOT INTO THE SINK**!
20. Mop up immediately, all materials spilled on the floor.
21. **NO EATING OR DRINKING IN THE LABORATORY AT ANY TIME**!
22. Use tongs or oven mitts to handle hot pieces of equipment.

LABORATORY NOTEBOOK

The lab notebook is used as a legal document detailing everything that occurred in the lab. You need to use it in lab to keep track of what you have done and what you have to do. It is therefore very important to prepare your notebook well and take meticulous notes. All writing in the notebook should be in non-erasing black ballpoint pen.

General Usage Directions

Preparing your notebook

Title your lab and fill out the top of the notebook page. Include any objectives.

If you are doing a reaction, write the balanced reaction and underneath the reaction write down any pertinent information (such as bp, fw, expected moles, expected grams, density, volume). Leave space for actual moles and actual grams. In fact, write down pertinent information for all chemicals for every lab

Write down a concise but complete outline of the procedure to be followed. Remember to leave room to add information or make changes. As you are preparing your notebook, remember to leave room to record amounts that you actually use.

Make a drawing of the apparatus you will use.

Using your notebook in lab

Your notebook will contain all of your calculations, observations and measurements. Record every measurement, observation, mistake and reasoning. Example: “We started over because we dropped the reaction flask.” Label each entry in a meaningful manner that indicates the part of the experiment that corresponds to the entry.

Because a lab notebook is a working document, it will most likely contain errors. Errors should have a single line drawn through them. There should be no erasures or white out used in the lab notebook.

At the end of the lab period, sign and date each page and then let your instructor verify & initial your notebook.

COURSE CONTENT

The Course is designed so that on completion you should know of the following:

(a) How to separate and identify organic compounds by classical and spectroscopic techniques and chromatographic techniques.

(b) How to do routine operations such as crystallisation, distillation, and extractions.

(c) How to syntheses compounds and study reaction mechanisms.

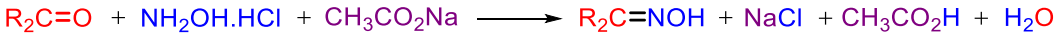
The following is an approximate guide as to how you should spend your time in the lab:

1. Two organic synthesis experiments.
2. Spectral and qualitative analysis of a binary mixture.

EXPERIMENT 1

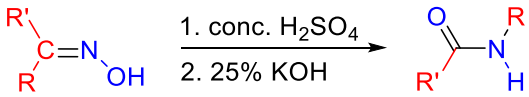
PREPARATION OF CAPROLACTAM *VIA* BECKMANN REARRANGEMENT REACTION

Condensation of a ketone with hydroxylamine hydrochloride in the presence of excess sodium acetate solution forms an oxime (Scheme 1a).



Scheme 1a

Reaction of an oxime with concentrated sulphuric acid produces an amide that is formed through a rearrangement reaction (Scheme 1b).



Scheme 1b

Conversion of any oximes to a substituted amides in the same reaction condition as mentioned above is known as Beckmann rearrangement. The reaction involves the formation of an electron-deficient nitrogen atom, followed by a migration/shift, normally involves a migration of an alkyl group to the electron deficient centre. This is an example of a reaction that involves a 1,2- shift/migration.

Apparatus

100 mL conical flask with ground joint
250 mL round-bottomed flask
500 mL beaker
separating funnel

Chemicals

7.5 g hydroxylamine hydrochloride
7.5 g cyclohexanone
Potassium hydroxide solution (25%)
12 g sodium acetate crystals
10 mL concentrated sulphuric acid
Petroleum ether (60–80 °C)

Procedure:

(a) Preparation of Cyclohexanone oxime

Dissolve 7.5 g of hydroxylamine hydrochloride [Note 1] and 12 g of sodium acetate crystals in 30 mL of water in a 100 mL conical flask with ground joint. Heat the mixture to 40 °C and add 7.5 g of cyclohexanone. Stopper the flask and shake vigorously for 10 minutes. Oxime will separate as crystalline solids. Cool the flask in an ice bath, filter the solid using a Büchner funnel, and wash with cold water. Recrystallize the oxime from petroleum-ether (60-80 °C) and air-dry the crystal using a filter paper. Record the melting point and percentage of the product obtained. Interpret the infrared spectrum of your product.
(Lit.; mp. of cyclohexanone oxime 89-90 °C).

(b) Preparation of Caprolactam

Add 10 mL of concentrated sulphuric acid in a 500 mL beaker. While stirring, slowly add 5 g of cyclohexanone oxime (a) [Note 2] to the mixture. Carry out this process in a fume cupboard because the reaction is exothermic and liberates heat. If heat is not liberated, heat the mixture on a steam bath for 5 minutes. Let the reaction subsides, and then cool the beaker in an ice-bath.

Pour the reaction mixture into a beaker containing 150 g of ice. Cool the beaker in an ice-bath, and slowly add potassium hydroxide solution (25%) until the mixture becomes alkaline. Make sure that the temperature of the reaction does not exceed 10 °C. If precipitate of potassium sulphate is formed, add water or filter the precipitate, wash with dichloromethane and combine the dichloromethane wash with dichloromethane extracts.

Extract the alkaline solution with dichloromethane (3 x 75 mL), wash the dichloromethane layer with water and dried over anhydrous magnesium sulphate. Remove the solvent using rotary evaporator and extract crude oily product with boiling petroleum ether (60–80 °C). Cool the petroleum-ether extracts and caprolactam will crystallise out as colourless crystals. Record the melting point and percentage of product obtained. Interpret the infrared spectrum of your product.

Notes:

1. Hydroxylamine is very toxic and be careful when handling it.

2. It is essential that the oxime has been sufficiently dried, else the hygroscopic effect of sulphuric acid is insufficient to initiate the rearrangement. In view of hydrogen bonding, therefore, it is not recommended to convert the oxime at the preparation day.

Questions:

1. What is the role of sodium acetate in the formation of oxime?

2. Write a mechanism for the formation of cyclohexanone oxime.

3. What is the function of adding potassium hydroxide (25%) to the acidified reaction products of cyclohexanone oxime?

References

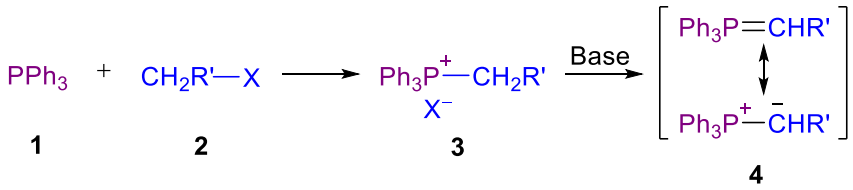
1. Experimental Organic Chemistry: A small scale approach, Charles F. Wilcox, Jr and Mary F. Wilcox, Prentice Hall, 1995.

EXPERIMENT 2

SYNTHESIS OF 3-PHENYLPROPENOIC ACID

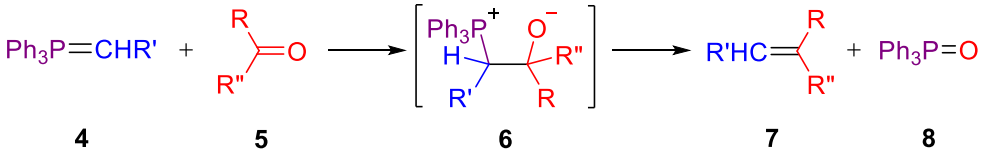
Background

The Wittig reaction is used to convert the carbonyl group of aldehydes and ketones into an alkene group. This reaction is named after Georg Wittig, who won the Nobel Prize for the reaction in 1979. In a typical Wittig reaction, triphenylphosphine (**1**) reacts with an alkyl halide (**2**) to form phosphonium halide (**3**). Subsequently, addition of a strong base eliminates the hydrogen halide to form an ylide, alkylidenephosphorane (**4**) (Scheme 2a).



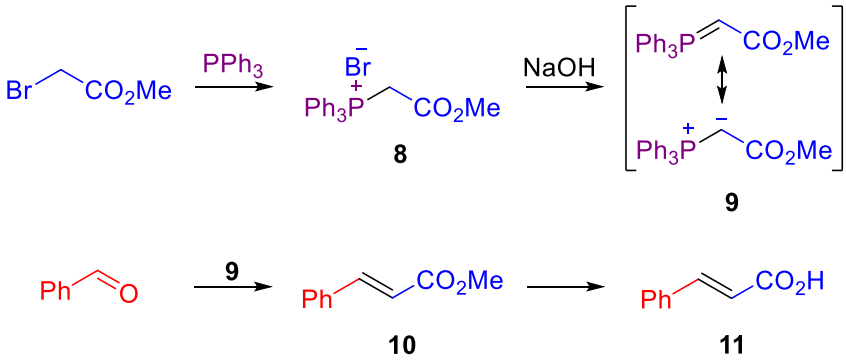
Scheme 2a

The carbon of the ylide acts as a nucleophile and adds to the carbonyl group (**5**) to form a betaine intermediate (**6**) which undergo an *in situ* 1,2-elimination to give an alkene (**7**) and triphenylphosphine oxide (**8**) as the product (Scheme 2b).



Scheme 2b

This experiment illustrates the general procedure with the preparation of (*E*)-3-phenylprop-2-enoate (**10**) from the reaction of the ylide, methyltriphenyl-phosphoranylethanoate (**9**) and benzaldehyde. The ester formed (**10**) is then hydrolyzed with a base to give 3-phenylpropenoic acid (**11**), which is isolated as crystalline solids (Scheme 2c).



Scheme 2c

Procedure

(I) Preparation of triphenylphosphoranyl ethanoate (9) from methoxycarbonyl - methylenyltriphenylphosphonium bromide.

Dissolve triphenylphosphine (5 g, 20 mmol) in dry toluene (50 mL) in a clean and dry 250 mL conical flask. Add methyl bromoacetate (1.9 mL, 20 mmol) [Note 1] into the mixture and warm it to 60 ˚C. Shake the mixture occasionally and keep the temperature constant at 60 ˚C for 10 minutes. Cool the reaction mixture to room temperature and leave for 1 hour at this temperature. Collect the phosphonium salt (**8**) (~4 g) using a Büchner funnel and wash with cold toluene [Note 2]. Weigh the product and record its melting point.

Dissolve the phosphonium salt (**8**) (4.2 g, 10 mmol) in toluene (100 mL) [Note 3] in a 250 or 500 mL conical flask and add an aqueous solution of 0.38 M NaOH (100 mL) into the mixture. Stir the mixture vigorously for 1 hour (or until the liquid phase becomes clear). Separate and dry the toluene layer by adding anhydrous Na_2SO_4.

Remove the solvent by using rotary evaporator to obtain the crude product (**9**). Record the weight and melting point of the product. If necessary, the crude product could be recrystallised using ethyl acetate/petroleum ether (40–60 ˚C) mixture as the solvent.

(II) Preparation of (*E*)-3-phenylpropenoic acid

Dissolve the crude product (**9**) (3 g, 8.9 mmol) in dichloromethane (20 mL) and add a solution of benzaldehyde (0.95 mL, 9.4 mmol) in dichloromethane (10 mL). Reflux the mixture in a water bath for 1 hour. Remove the solvent *in vacuo* to obtain a yellowish white solid containing methyl 3-phenylpropenoate (**10**). Add saturated sodium carbonate solution (20 mL) and water (100 mL) to the solid and stir the mixture vigorously for 30 min to hydrolyse the ester to an acid salt. At this stage, it is suitable to leave the mixture overnight before proceeding to the next step.

Reflux the mixture and distil off the excess benzaldehyde [Note 4]. Cool the mixture and add water to replace the amount that was distilled off. Filter the mixture to remove the crude triphenylphosphine oxide. Acidify the filtrate with concentrated HCl to precipitate out the 3-phenylpropenoic acid (**11**). Recrystallise the 3-phenylpropenoic acid from a mixture of water-ethanol solution (3:1, v/v). Weigh and take the melting point of the acid. Record its IR spectra.

Notes:

1. Methyl bromoethanoate is a lachrymator. Please use the fume-cupboard for operating the chemical.
2. More precipitate could be obtained if the filtrate is kept overnight.
3. The phosphonium salt is insoluble in toluene. A solution is only obtained upon treatment with NaOH and this reflects the phosphoylide.
4. Distilling around 50 mL emulsion (or until the appearance of the distillate is not turbid) is sufficient to remove any volatile compound from the reaction mixture.

Questions:

1. What is the structure of the triphenylphosphoranyl ethanoate (**4**)?
2. Write the mechanism for the formation of (*E*)-3-phenylpropenoic acid.
3. What is the limiting reagent in the above reaction?

EXPERIMENT 3

ANALYSIS OF A BINARY MIXTURE

Students are provided with a mixture comprising about an equal amount of two components. The objective of the experiment is to separate and identify the two compounds using a combination of classical qualitative analysis and spectroscopy. Subsequent derivatives preparation of the isolated component will be carried out.

Guide to Qualitative Analysis of Mixtures

It is necessary to separate a mixture before the individual components can be identified. Observe the physical state of unknown mixture. Do simple tests on very small amounts, e.g., solubility in polar and non-polar solvents, acidic or basic aqueous solutions. Observe carefully if the mixture is partially soluble and if any reaction occurs. These properties could form a basis for separation as well as an idea of the nature of the compound.

The following are brief descriptions of possible methods of separation:

(a) Solubility Differences

This involves extraction and is probably the easiest way, but it is unlikely that one encounters such a simple mixture. One component can be extracted into a solvent, the other component being insoluble. This component can then be isolated by distillation or evaporation of solvent. Normally, solvent with wide differences in polarity are tried first, e.g. water and petroleum ether. Some examples where this method will work are sucrose/ naphthalene, acetamide/ diphenyl and glycine hydrochloride/ benzophenone, where contrasting differences in polarity of the components exist.

(b) Chemical Differences

(see the flow chart at page 20)

A derivative is synthesised and separated from the other components by precipitation or extraction.* The usual type of derivative is formation of a salt, e.g., if given an acidic/neutral mixture insoluble in water, the acidic component can be extracted into aqueous basic solution. Similarly, a phenol/neutral mixture can be treated in the same way as most phenols are sufficiently acidic to be extracted into aqueous sodium hydroxide. For a basic/ neutral mixture, extraction into aqueous acid will affect a separation. For example, a mixture of benzoic acid benzophenone can be separated by aqueous NaOH/ ether; a mixture of aniline and chlorobenzene can be separated by aqueous HCl/ether. The separated components are then recovered and purified.

***Caution:** It is wise to try out on a small scale first. Water soluble organic compounds may be troublesome, so it is best to avoid too much of aqueous reagents. A mixture of a phenol and a ketone with α-hydrogens would both dissolve in NaOH. Solution of the phenol may be affected with very dilute NaOH and done rapidly to avoid decomposition of the carbonyl compound. Some amines form salts which may not dissolve readily in H_2O, a different acid may be used.

(c) Boiling Points Differences

Two liquids which do not form a constant boiling point mixture and have widely separated boiling points can be separated by fractional distillation using a simple fractionating column. The boiling points must be at least 25 °C apart. For high boiling mixtures this can be done under reduced pressure, preferably under nitrogen if the compound decomposes.

(d) Recrystallization

Often one component can easily be obtained from a mixture by a suitable choice of solvents for recrystallization.

(e) Chromatography Methods

Generally, TLC, LC and other chromatographic methods are extremely effective separation methods, but they can be long and tedious. Furthermore, it is limited to small scale work involving less than 1 g unless appropriate facilities are available.

The above methods should only serve as a guide. Usually, methods (b) and (c) would be suitable. Also note that many problems could arise in the process of recovering the separated components (refer text). In principle, all the given amounts should be recoverable unless they are accidently thrown away or are extremely volatile. It may be wise to try a small-scale separation to assess on your separation method before scaling up.

Compounds that are separated and purified should have good physical constants, e.g., m.p., b.p., etc., before it is sent for spectra analysis. Proceed to determine the elements present, run both NMR and IR spectra and do some wet tests to determine the functional type. Make at least one good derivative. If no derivative is possible, do a chemical transformation to give a product that can be easily characterised by NMR. Comparison of R_f values or retention times with standards under different conditions is also acceptable.

References:

1. Shriner, Hermann, Morrill, Curtin, and Fuson, The Systematic Identification of Organic Compounds (Wiley).
2. Furniss, Hannaford, Smith, and Tatchell, Vogel's Textbook of Practical Organic Chemistry (Longman).
3. Williams and Fleming, Spectroscopic Methods in Organic Chemistry (McGraw-Hill).
4. Silverstein and Webster, Spectrometric Identification of Organic Compounds (Wiley).

Qualitative Analysis

Course Code: _____

Name: _____ Date: _____

Unknown No: _____ Unknown Name:_____

Structure of the Unknown:

1) Physical Properties:

a) Physical appearance: _____ d) Ignition test: _____

b) Odour: _____ e) Observed mp/bp: _____

c) Colour: _____ f) Literature value (mp/bp): _____

2) Lassaigne's Test:

Cl	Br	I	N	S

3) Solubility Test:

(see page 19 for group assignment)

H_2O	Ether	5% NaOH	5% $NaHCO_3$	5% HCl	Conc. H_2SO_4

Solubility Group: _____

4) Functional Group Test:

Reagent/ Test	Results	Conclusion

Functional groups present based on the tests above:

5) **Spectroscopic Analysis** (Indicate major bands and their characteristics):

a) Infrared Spectrum (IR)

Wavelength, λ/ cm^{-1}	Possible functional group

b) Nuclear Magnetic Resonance Spectrum (NMR)

i. ^{1}H NMR Spectrum:

Chemical shift/ ppm	Integration	No of proton	Partial structure

ii. ^{13}C NMR Spectrum:

Chemical shift/ ppm	No of carbon	Partial structure

Draw the possible functional group present based on spectroscopic analyses:

6) Possible compounds:

(All possible compounds should be recorded in the table below)

Name of possible compounds	m.p./ b.p. ºC	Suggestion for further test

Draw the structures of possible compounds:

7) Confirmation test:

Test/ Reagent	Results	Conclusion

8) Possible derivatives:

Name of possible compounds	Possible derivatives and their melting points	
	Derivative 1	Derivative 2

9) Preparative of derivatives:

Name of Derivatives	Observed m.p. ºC	m.p. ºC reported/ Literature

Two derivatives are required for each unknown. Please submit your derivatives in a labelled plastic sample together with your report.

Write all relevant chemical equations:

10) Specific comments:

11) Literature and references

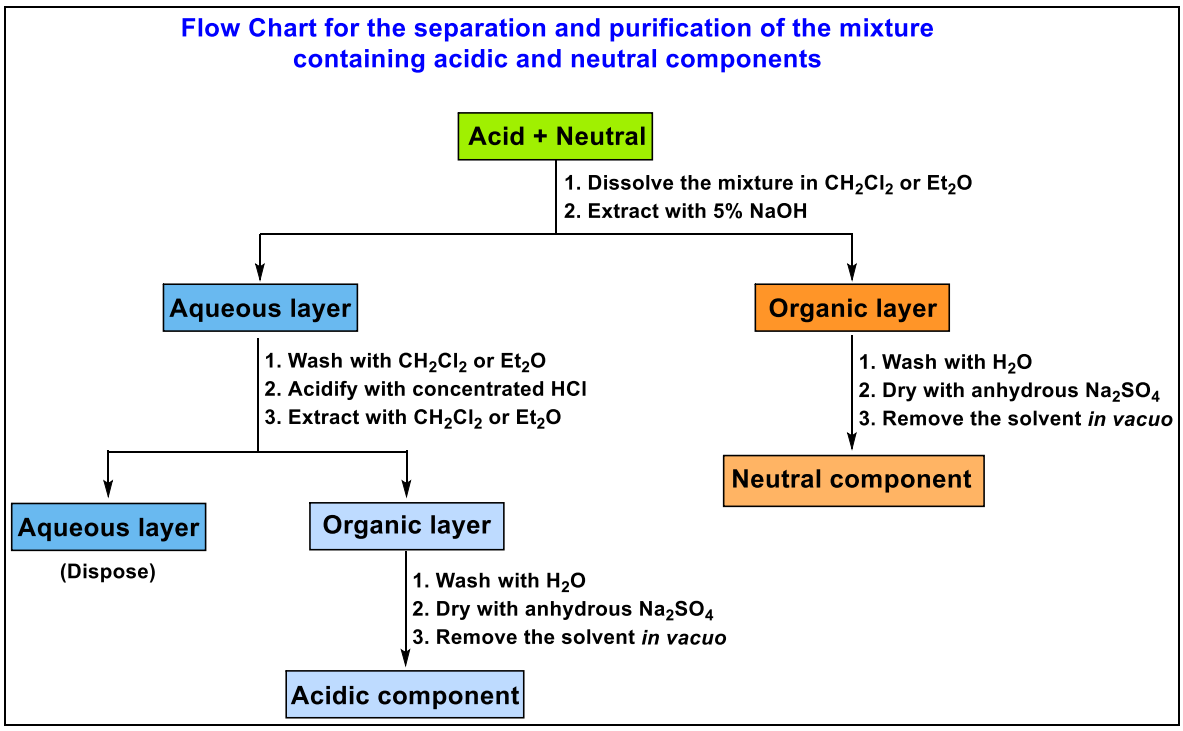
Classification of compounds according to their solubility*

Group	Condition	Compounds
I	**Dissolve in H_2O and diethyl ether**	• Members with low homologous series: • Alcohol, • Carbonyl compounds, • Acid, ester, • Phenol, • Anhydride, • Amines, • Nitrile, • Polyhydroxy-phenol
II	**Dissolve in H_2O but not in diethyl ether**	• Polybase acids and hydroxy acids, • Glycols, polyhydroxy alcohol, • Aldehydes and polyhydroxy ketones, • Some amides, amino acids, alcohol amines, • Sulfinic acid, • Sulfonic acid, • Salt
III	**Dissolve in 5% NaOH**	• Carboxylic acids, • Phenol, • Imides, • Some primary and secondary nitro compounds, oximes, • Thiols, thiophenols, • Amino acids, sulfinic acids, sulfonic acids and sulfonamides acids, • Some diketones and keto ester
IV	**Dissolve in 5% HCl**	• Primary amines, • Secondary aliphatic amines, • Arylalkyl amines, • Aliphatic and some tertiary aryl-alkyl amines, • Hydrazines
V	**Do not contain N or S. Dissolve only in conc. H_2SO_4**	• Unsaturated hydrocarbons, • Some aromatic hydrocarbons, • Polyalkyls, • Alcohols, • Carbonyl compounds, • Esters, anhydrides, • Ether, acetals, • Lactones, • Acyl halides
VI	**Do not contain N or S. Do not dissolve in conc. H_2SO_4**	• Saturated aliphatic hydrocarbons, • Cycloalkanes, • Aromatic hydrocarbons, halogenated hydrocarbons, • Diaryl ether
VII	**Contain N or S, and could not fit into group I – IV**	• Tertiary nitro, • Amides, • Carbonyl derivatives, • Nitriles, • Nitroso, azo, hydraso, • Sulfones, • Secondary amide sulphonamides, • Sulfides, sulfates, sulfur compounds

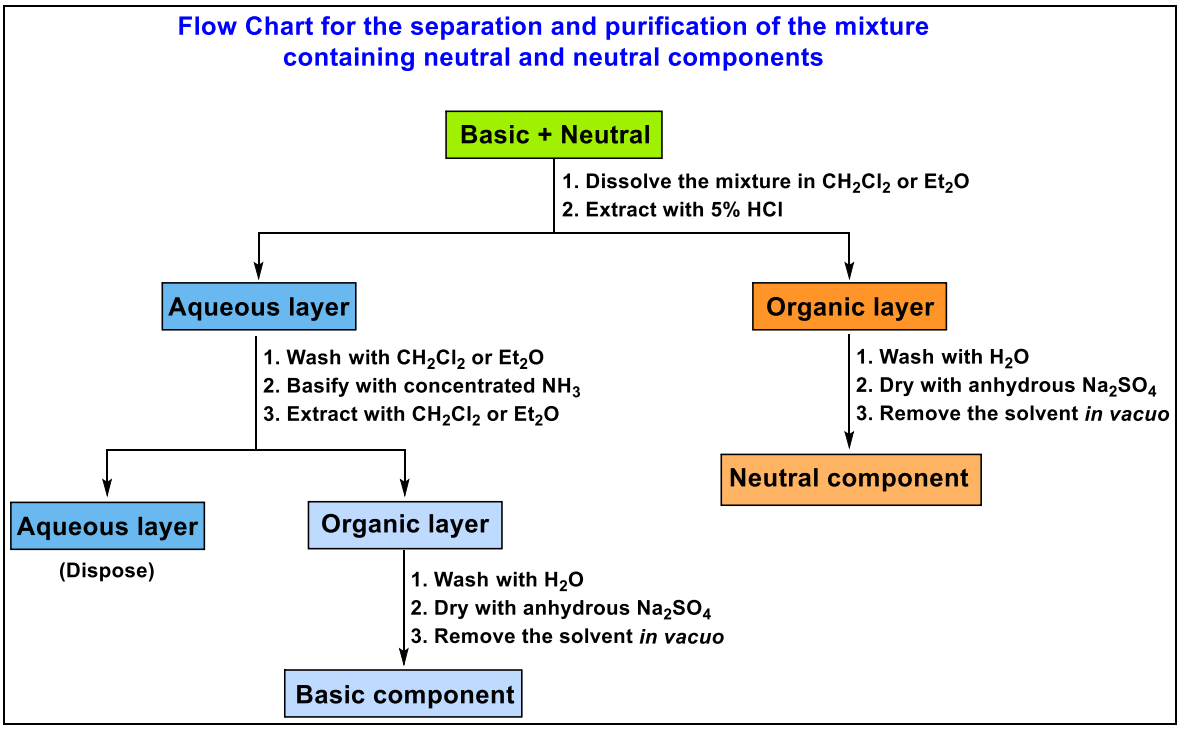
* Kamaliah Mahmood and Noorsaadah Abd Rahman (2005). Kaedah Kimia dalam Pengenalpastian Sebatian Organik (Penerbit Universiti Malaya).

Flow Chart: Separation of a Binary Mixture*

A) Binary Mixture of Acidic and Neutral Organic Compound



B) Binary Mixture of Basic and Neutral Organic Compound



* Kamaliah Mahmood and Noorsaadah Abd Rahman (2005). Kaedah Kimia dalam Pengenalpastian Sebatian Organik (Penerbit Universiti Malaya).