EXPERIMENT I

RECRYSTALLIZATION AND DETERMINATION OF MELTING POINT

A. Competency

- Student able to determine solvents that are most commonly used for recrystallization
- Students able to purifying solid organic compounds by recrystallization and determine the melting point.

B. The problem / task before practicum

1. Explain some methods of purification of organic compounds!
2. Mention the terms of solvent that can be used for recrystallization!
3. Find the solubility of acetanilide, naphthalene, salicylic acid in water and ethanol solvent at room temperature and at boiling point! From the data determine which compound was recrystallized with a solvent of water and which can be recrystallized with ethanol?
4. How do you know that the crystals obtained from recrystallization has a high purity?
5. Explain what is meant: Buchner funnel, heat funnel. Describe and explain the principle tool works!

C. Literary review

The most common method of purifying solid organic compounds is by recrystallization. In this technique, an impure solid compound is dissolved in a solvent and then allowed to slowly crystallize out as the solution cools. As the compound crystallizes from the solution, the molecules of the other compounds dissolved in solution are excluded from the growing crystal lattice, giving a pure solid.

Crystallization of a solid is not the same as precipitation of a solid. In crystallization, there is a slow, selective formation of the crystal framework resulting in a pure compound. In precipitation, there is a rapid formation of a

solid from a solution that usually produces an amorphous solid containing many trapped impurities within the solid's crystal framework. For this reason, experimental procedures that produce a solid product by precipitation always include a final recrystallization step to give the pure compound.

The process of recrystallization relies on the property that for most compounds, as the temperature of a solvent increases, the solubility of the compound in that solvent also increases. For example, much more table sugar can be dissolved in very hot water (just below the boiling point) than in water at room temperature. What will happen if a concentrated solution of hot water and sugar is allowed to cool to room temperature? As the temperature of the solution decreases, the solubility of the sugar in the water also decreases, and the sugar molecules will begin to crystallize out of the solution. (This is how rock candy is made.) This is the basic process that goes on in the recrystallization of a solid.

The steps in the recrystallization of a compound are:

a. Find a suitable solvent for the recrystallization;
b. Dissolve the impure solid in a minimum volume of hot solvent;
c. Remove any insoluble impurities by filtration;
d. Slowly cool the hot solution to crystallize the desired compound from the solution;
e. Filter the solution to isolate the purified solid compound.

D. Equipment and chemicals

Equipment:

1. Test tube
2. Analitycal balance
3. Thermometer
4. Spatula
5. Beaker glass
6. Erlenmeyer
7. Graduated cylinder
8. Melting point apparatus
9. Water bath
10. Drying oven
11. Filter Flask
12. Buchner Funnel
13. Hot water jackets for funnel
14. Capillary tube

Chemicals:

1. Impure solid (acetanilide, naftalene, salicylic acid, etc.)
2. Solvent (water, ethanol, methanol, ethyl acetate, diethyl ether, hexane, toluene, etc.)
3. Activated carbon
4. Filter paper

E. Procedures

1. Choosing a solvent

Finding a solvent with the desired properties is a search done by trial and error. First, test the solubility of tiny samples of the compound in test tubes with a variety of different solvents (water, ethanol, methanol, ethyl acetate, diethyl ether, hexane, toluene, etc.) at room temperature. If the compound dissolves in the solvent at room temperature, then that solvent is unsuitable for recrystallization. If the compound is insoluble in the solvent at room temperature, then the mixture is heated to the solvent's boiling point to determine if the solid will dissolve at high temperature, and then cooled to see whether it crystallizes from the solution at room temperature.

a. Provides several test tubes (in accordance with a given solid sample)
b. Add to each test tube with 5 mL water
c. Than add to each test tube with already contains water with a spatula tip of solid samples provided
d. Heating each tube into a water bath until all solids dissolved, than cool at room temperature.Observe the change that accur.
e. Repeat the experiment by replacing the water solvent with another solvent.
f. From this experiment the students can determine the appropriate solvent for recrystallization, and comparing with data obtained from literature about the solubility of organic compounds in certain solvent.

2. Recrystallization and determination of melting point

a. Measure 2 g of impure solid and put in the beaker glass 250 mL

b. Adding the appropriate solvent for recristallization (based on the results of the experiment 1). The volume of data used are based on crystal solubility in solvents used.

c. Heat up slowly, stirring until all solids dissolved.

d. If there is a solution of colored, add activated carbon and simmer a few minutes to remove the color.

e. Filter the boiling solution with heat filter.

f. Hot filtrate was cooled quikly with ice bath.

g. Filter the crystal with a Buchner funnel.

h. Wash the crystals with a volume of cold solvent, press the solids in the funnel with a spatula.

i. Dry the crystals by placing on watch glass, enter into a drying oven at a given temperature below the melting point of crystal.

j. Weigh the recrystallized crystals, and determine its melting point using the melting point apparatus.

F. Post-Lab Quentions

1. What is the definition of the melting point?
2. How is the relationship of a compound with a melting point of its purity?
3. Explain the function of the addition of activated carbon in the experiment?
4. Explain what to do for the results obtained by recrystallization of pure enough and not much is wasted?
5. How to find out that the crystal is completely dry?

*****CBM*****

EXPERIMENT II

SYNTHESIS OF CHLOROFORM

A. Competency

1. Students can conduct synthesis of chloroform in laboratory-scale
2. After doing this experiment students are expected to have skills:
    a. stringing ordinary distillation apparatus,
    b. mentioning the name of the distillation apparatus and explain the function of each part of the appliance,
    c. to use funnel to separate mixtures that are not intermingled with each other,
    d. calculate how the amount of materials needed when you want a certain amount of chloroform,
    e. calculate the yield of chloroform produced.

B. The problem / task before practicum

1. Find the equation for synthesis of chloroform!
2. Draw a series of ordinary distillation apparatus, mention the name of each tool and its purpose!
3. If desired gained as much as 10 g of chloroform, acetone and calculate how much chlorine is used (acetone discharged react / oxygen barrier)

C. Literary review

When chlorine is passed into boiling alcohol, both chlorination of the methyl group and oxidation of the primary alcohol group to an aldehyde occur, giving trichloro-acetaldehyde or chloral: When chloral is treated with caustic alkali, fission of the C-C linkage occurs, giving chloroform and a formate. Acetaldehyde and also many ketones, such as acetone, containing the CH_3CO- group behave similarly when treated with calcium or sodium hypochlorite, chlorination of the CH_3CO- group being immediately followed by

fission of the molecule by the alkali present in the hypochlorite solution. The acetone method clearly gives a much cheaper product than the alcohol method.

D. Equipment and chemicals

Equipment:

1. Simple distillation apparatus
2. Separator funnel
3. Beaker glass
4. mortar

Chemicals:

1. Bleaching powder
2. Acetone
3. $CaCl_2$ anhydrous
4. NaOH 2%
5. Aquadest

E. Procedures

1. Place amount of calcium hypochlorite (based on the result of calculated) in a mortar and add water in small quantities at a time: between each addition grind the mixture of bleaching powder and water well together.
2. Decant the cream-like suspension through a funnel into a flat-bottomed flask. Finally, when all the water has thus been used, only a gritty residue remains in the mortar.
3. Fit the flask with an efficient reflux water-condenser, pour amount of acetone in small quantities, at a time, down the condenser and mix by thorough shaking after each addition. The reaction usually starts spontaneously after a few minutes, and a bath of cold water should be available into which the flask may be dipped if necessary to moderate the reaction. Should the reaction show no signs of starting within 5 minutes of the addition of the acetone.
4. Warm the flask cautiously on a boiling water-bath until the reaction starts, and then remove it immediately. When the vigorous boiling has subsided, heat the flask on a boiling water-bath for a further 5-10 minutes (not more) to complete the reaction.

5. Cool the flask in cold water (to prevent loss of chloroform vapour whilst the apparatus is being rearranged) and then fit the flask with a fairly wide delivery-tube and reverse the water-condenser for distillation.
6. Heat the flask on a water-bath until distillation of the chloroform is complete.
7. The chloroform thus obtained is usually acidic. Therefore shake it thoroughly with dilute sodium hydroxide solution in a separating-funnel. (If the chloroform tends to float on the alkaline solution, it still contains appreciable quantities of acetone: in this case the soda should be run out of the funnel and the chloroform shaken with water to extract the acetone. The extraction with the soda can then be performed after the water has been removed.)
8. Carefully run off the heavy lower layer of chloroform into a small conical flask
9. Dry it over calcium chloride for 15-20 minutes, and then filter it directly into a 75 ml. distilling-flask fitted with a clean dry water-condenser.
10. Distill the chloroform, collecting the fraction of bp. 60-63^{o}C.

F. Post-Lab Quentions

1. Write the reaction mechanism of synthesis of chloroform in this experiment?
2. Calculate the yield of chloroform obtained in this experiment!
3. Explain the properties of chloroform?
4. Mention the use of chloroform?
5. Explain what the purpose of adding water to the distillate container, and in acetone?

*****CBM*****

EXPERIMENT III

SYNTHESIS OF AMYL ACETATE

A. Competency

1. Students can perform the synthesis of compounds amyl acetate which is a derivative of alcohol by esterification reaction.
2. After doing this experiment students are expected to have skills:
   a. stringing tools reflux,
   b. mentioning the name of the tool reflux and explain the function of each part of the appliance,
   c. stringing ordinary distillation apparatus,
   d. mentioning the name of the distillation apparatus and explain the function of each part of the appliance,
   e. use funnel to separate mixtures that are not intermingled with one another,
   f. calculate how the amount of materials needed when you want a certain amount of amyl acetate,
   g. calculate randemen amyl acetate produced.

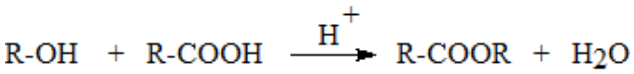
B. The problem / task before practicum

1. Write equation and reaction mechanism of synthesis of amyl acetate from the reaction of amyl alcohol with acetic acid in the presence of sulfuric acid catalyst!
2. Name two other reactions which can result in amyl acetate! Write the reaction equation.
3. Draw a series of tools reflux, mention the name of each piece of equipment and specify its purpose!
4. Draw a series of ordinary distillation apparatus, mention the name of each piece of equipment and specify its purpose!
5. If desired 8 g of amyl acetate, calculate how much acetic acid and amyl alcohol to be treated? (Alcohol as a delimiter)

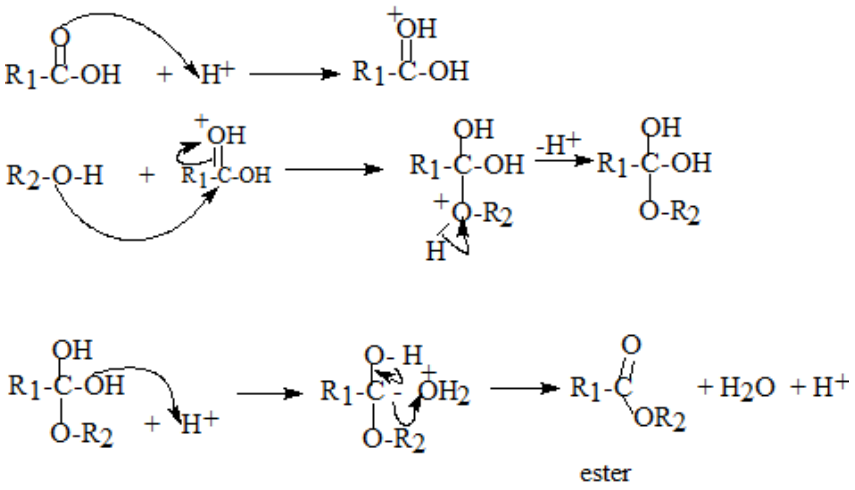
C. Literary review

Esters are produced when carboxylic acids are heated with alcohols in the presence of an acid catalyst. The catalyst is usually concentrated sulphuric acid. Dry hydrogen chloride gas is used in some cases, but these tend to involve aromatic esters (ones where the carboxylic acid contains a benzene ring). The reaction of an alcohol and a carboxylic acid to form ester and water is known as the Fischer Esterification.

The esterification reaction is both slow and reversible. The equation for the reaction between an acid RCOOH and an alcohol ROH is:



The Mechanism for the esterification is:



D. Equipment and chemicals

Equipment:

1. Reflux apparatus
2. Simple distillation apparatus
3. Separator funnel
4. Beaker glass
5. Erlenmeyer
6. Graduated cylinder

Chemicals

1. Amyl alcohol
2. Glacial acetic acid
3. Concentrated sulfuric acid

E. Procedures

1. Entering amyl alcohol, glacial acetic acid (according to the results of the calculation) and concentrated sulfuric acid reflux into the gourd
2. Refluxing the mixture for 4-6 hours. Tool equipped with a reflux condenser with a heating magnetic stirrer (magnetic stirrer with hot plate),
3. Cool the mixture.
4. Distillation cold mixture, distillate consists of two layers.
5. Separating the distillate with a separating funnel.

F. Post-Lab Quentions

1. What was the purpose of adding the sulphuric acid concentrated in this experiment?
2. Mention the use of ester compounds!
3. In step distillation distillate is obtained consisting of two layers, explain why?
4. Which is a layer of amyl acetate?
5. In addition to glacial acetic acid, mention two substances that can be reacted with amyl alcohol amyl acetate that will result?
6. Calculate the yield of amyl acetate?

CBM

EXPERIMENT IV
SYNTHESIS OF PHENYL BENZOATE

A. Competency

1. Students can perform the synthesis of phenyl benzoate compounds.
2. After doing this experiment students are expected to have skills:
    a. understanding of substitution reactions at the carbonyl group,
    b. understanding of nucleophile and leaving group,
    c. calculate how the amount of materials needed when you want a certain of phenyl benzoate,
    d. calculate the yield of phenyl benzoate.

B. The problem / task before the lab:

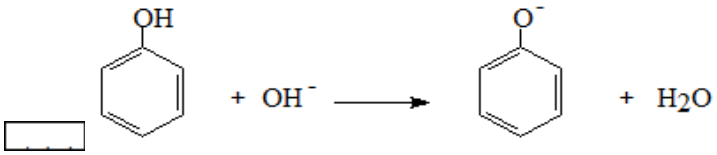
1. Explain what is meant by:
a. leaving group
b. nucleophile
2. Write the equation for synthesis of phenyl benzoate!
3. Can the reactants in this experiment benzoyl chloride was replaced by benzoic acid or benzoic anhydride? Explain your answer!
4. Calculate how many grams of reactants are needed if the phenyl benzoate will be synthesized as much as 8 g (phenol as a delimiter)!

C. Literary review

If you add an acyl chloride to an alcohol, you get a vigorous (even violent) reaction at room temperature producing an ester and clouds of steamy acidic fumes of hydrogen chloride.

Benzoyl chloride has the formula C_6H_5COCl. The -COCl group is attached directly to a benzene ring. It is much less reactive than simple acyl chlorides like

ethanoyl chloride.The phenol is first converted into the ionic compound sodium phenoxide (sodium phenate) by dissolving it in sodium hydroxide solution.



phenol phenoxide ion

The phenoxide ion reacts more rapidly with benzoyl chloride than the original phenol does, but even so you have to shake it with benzoyl chloride for about 15 minutes. Solid phenyl benzoate is formed.

D. Equipment and chemicals

Equipment:

1. a wide-mouthed reagent bottle
2. Buchner funnel
3. Heat funnel
4. Funnel glass
5. Watch glass
6. Erlenmeyer
7. Beaker glass
8. Drying oven
9. Melting point apparatus

E. Procedures

1. Dissolve amount (based on calculated)of phenol in 10 percent sodium hydroxide solution contained in a wide-mouthed reagent bottle or conical flask of about 200 ml capacity.
2. Add amount of redistilled benzoyl chloride, cork the vessel securely and shake the mixture vigorously for 15-20 minutes. At the end of this period the reaction is usually practically complete and a solid product is obtained.
3. Filter off the solid ester with suction, break up any lumps on the filter, wash thoroughly with water and drain well.
4. Recrystallise the crude ester from rectified spirit, use a quantity of hot solvent approximately twice the minimum volume required for complete solution in

order to ensure that the ester does not separate until the temperature of the solution has fallen below the melting point of phenyl benzoate.

5. Filter the hot solution, if necessary, through a hot water funnel or through a Buchner funnel preheated by the filtration of some boiling solvent. Colourless crystal of phenyl benzoate, m.p. 69^{O}C, are thus obtained

F. Post-Lab Quentions

1. Write the mechanism of synthesis phenylbenzoate!!
2. Explain the function of NaOH in the experiment!
3. Explain why the concentration is dilute NaOH used? What is happen if used with the concentration of NaOH solution more concentrated?
4. List some solvents that can be used to purify of phenylbenzoate?
5. Explain why benzoilchloride more reactive to nucleophiles attack when compared with aliphatic acid chlorides?

*****CBM*****

EXPERIMENT V
SYNTHESIS OF ACETONE-2,4-DINITRO-PHENYLHYDRAZONES

A. Competency

1. Students can perform the synthesis of acetone-2 ,4-dinitrofenilhidrazon
2. After doing this experiment students are expected to have skills:
   a.clear understanding of addition reactions of carbonyl compounds-elimination both aldehydes and ketones with hydrazine compounds or their derivatives,
   b. write-elimination mechanism of addition reactions of carbonyl compounds both aldehydes and ketones with hydrazine compounds or their derivatives,
   c.stringing tools reflux,
   d. mentioning the name of the tool reflux and explain the function of each part of the appliance,
   e. make crystal recrystallization acetone-2 ,4-dinitrofenilhidrazon with ethanol-water solvent.
   f. calculate how much material is needed if the desired compound of acetone-2,4-dinitrofenilhidrazon certain amount,
   g. calculate the yield of acetone-2 ,4-dinitrofenilhidrazon.

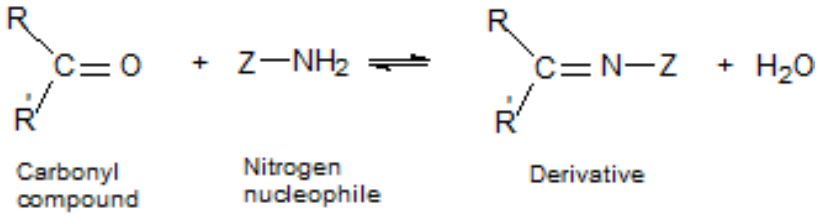
B. The problem / task before the lab:

1. Write the equation for synthesis of acetone-2,4-dinitrofenilhidrazon from the reaction of acetone with 2,4-dinitrophenylhydrazine!
2. Draw the apparatus for reflux in these experiments, mention the name of each piece of equipment and specify used!

3. Calculate the amount of each reactant to be used if will be synthesized as much as 12 g (acetone as the compound delimiter)!
4. Explain how to recrystallization acetone-2,4-dinitrofenilhidrazon with ethanol-water?

B. Literary review

Derivatives of carbonyl compounds are conveniently prepared by substitution reactions with nitrogen nucleophiles. The most common derivatives of this type are the 2,4-dinitrophenylhydrazones [Z= 2,4-$(NO_2)_2C_6H_3NH$-], phenylhydrazones [Z= C_6H_5NH-], semicarbazones [Z= H_2NCONH-], and oximes [Z= HO-].



2,4-Dinitrophenylhydrazones and phenylhydrazones are prepared by the same general method. However, the 2,4-dinitrophenylhydrazones derivatives are generally easier to prepare and purify than the phenylhydrazones derivatives. Therefore, they are usually the derivative of choice, especially for lower molecular weight carbonyl compounds. A 2,4-dinitrophenylhydrazone derivative can often be isolated by filtration from the chemical characterization test employing this reaction. If the crystalline derivative is carefully washed with cold 50% aqueous ethanol to remove excess 2,4-dinitrophenylhydrazine, it is usually not necessary to recrystallize the product.

C. Equipment and chemicals

Equipment:

1.Reflux apparatus 6. Buchner funnel

2. Water bath
3. Heat funnel
4. Funnel glass
5. Watch glass
7. Beaker glass
8. Drying oven
9. Melting point apparatus
10. magnetic stirrer with hot plate

Chemicals:

1. 2,4-dinitrophenylhidrazine
2. acetone
3. ethanol
4. aquadest

D. Procedures

a. Enter of 2,4-dinitrophenylhydrazine reagen to Erlenmeyer flask.

b. Add dropwise of the acetone and mix thoroughly.

c. Warm the mixture on a steam bath and then allow the mixture to stand at room temperature for 5 minutes.

d. If no precipitate is apparent, add water dropwise until the solution is cloudy.

e. Cool the mixture and isolate the crystals by filtration

f. Wash the crystal carefully with two 5 mL portion of cold 50% aqueous ethanol.

g. The derivative may be purified by recrystallization from ethanol-water.

F. Post-Lab Questions

1. Explain what is meant by nucleophilic substitution reaction?
2. Write the mechanism of nucleophilic substitution reactions in general!
3. Write the reaction mechanism of synthesis of compounds of acetone-2, 4 - dinitrophenylhydrazone!
4. In the synthesis of compounds of acetone-2, 4 - dinitrophenylhydrazone which acts as a nucleophile?
5. Calculate the yield of acetone-2 ,4- dinitrophenylhydrazone!

*****CBM*****

EXPERIMENT VI
SYNTHESIS OF BENZYLANILINE

A. Competency

1. Students can perform the synthesis of benzylaniline (secondary amines) from aniline (primary amine).
2. After doing this experiment students are expected to have skills:
   a. explain the classification of amine compounds,
   b. write the equation and reaction mechanism of synthesis of benzyl aniline
   c. stringing tools reflux,
   d. mentioning the name of the tool reflux and explain the function of each part of the appliance,
   e. identify the types of amines with reagents Hinsberg
   f. calculate how much material is needed if the desired compound benzylaniline certain amount,
   g. calculate the yield of benzylaniline

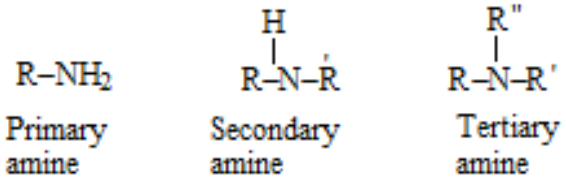
B. The problem / task before practicum

1. Explain the classification of amine compounds!
2. Write the equation of benzylaniline synthesis from the reaction of aniline with benzyl chloride!

3. Calculate how many grams of reactants required to synthesize 15 g benzilanilina (aniline as limiting reagent)
4. Draw the apparatus for reflux in this experiment!

B. Literary review

Amines are divided into three subclasses on the basis of their chemical structure: Primary (1^O) amines have one hydrocarbon substituent and two hydrogens attached to the nitrogen atom. Secondary (2^O) amines have two hydrocarbon substituents and one hydrogen attached to nitrogen. In tertiary (3^O) amines the nitrogen atom is bonded to three hydrocarbon substituents.



Amines can also be classified as aliphatic amines, compounds in which nitrogen is bonded directly to only saturated carbon atoms or hydrogen atoms, and aromatic amines, compounds in which nitrogen is bonded to one or more aromatic ring. Amines react as bases due to the nonbonded pair of electrons on nitrogen. Aliphatic amines are relatively strong bases. Because aryl groups are electron withdrawing, aromatic amines are much weaker bases than are aliphatic amines or ammonia.

D. Equipment and chemicals

Equipment:

1. Three-neck flask
2. Buchner funnel
3. Condenser
4. Magnetic stirrers with hot plate
5. Heat filter

6. Watch glass
7. Water bath
8. Melting point apparatus
9. Drying oven
10 Test tube

Chemicals:

1. Benzylchloride
2. toluene
3. Distilled aniline
4. Concentrated HCl
5. Reagent Hinsberg

E. Procedures

1. Enter aniline into three-neck flask, while stirring add dropwise benzylchloride by separating funnel (stirring using a magnetic stirrer).
2. Heat the mixture with a water bath for 1 hour, stirring frequently. The temperature is maintained approximately 95^{o}C
3. Adding distilled water and concentrated HCl on heating the mixture is continued until all precipitate dissolves.
4. Separating impurities in hot conditions with heat filter.
5. Cool the clear filtrate thus obtained a white crystal.
6. Filtering crystal with Buchner funnel
7. Washing the crystals with toluene, washing done three times.
8. Dry the crystals by placing on watch glass, enter into a drying oven at a given temperature below the melting point of crystal.
9. Determining the melting point
10. Identification of amines with the reagent Hinsberg.

F. Post-lab Question

1. Explain what is meant by primary amine, secondary, and tertiary?
2. Write the synthesis reaction mechanism of benzylaniline!

3. Why basicity aromatic amines are weaker than the aliphatic amine?
4. Write the reaction of amines with the reagent Hinsberg!

CBM

EXPERIMENT VII

PRACTICUM FREE CHOICE

A. Competency:

Students can design and perform the synthesis of derivative compounds alcohols, phenols, aldehydes, ketones, carboxylic acids, amines which are different from the experiment that has been done previously.

B. Problems / Tasks Before Practicum

1. Pick one compound synthesis reaction of alcohol derivatives, phenols, aldehydes, ketones, carboxylic acids, and amines which are different from the experiments have been done before (every group is different).
2. Make the experimental design which would you do, include:
   a. Title of experiment
   b. Competency

c. Basic theory

d. Equipment and chemicals

e. Procedures

3. Consulted the experimental design to lecturer.

C. Learning Experience

1. Experimenting in accordance with the experimental design that has you stacking.
2. Writing temporary observation data in the report.
3. Making a formal report based on the data from the temporary report and should be collected to the assistanton

*****CBM*****

REFERENCE

1. Doyle Mungal. 1980. *Exsperimental Organic Chemistry*. New York: John Wiley and Sons.

2. Furniss, B.S, P.W.G. Smith, A.R. Tatchel.1978. *Vogel's Textbook of Practical Organic Chemistry.* Fourth edition. London: Longman Group Limited.

3. Raymound, B. S. 1971. *Exsperimental Organic Chemistry.* New York: Barnes and Nobel Publisher

4. Rajak Bansal. 1980. *Laboratory Manual in Organic Chemistry.* New Delhi: Wiley Eastern Limited.