KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS
DEPARTMENT OF CHEMISTRY
B. Sc CHEMISTRY

Semester-II

17CHU 213 OXYGEN CONTAINING FUNCTIONAL 2H 1C

GROUPS - PRACTICAL

Instruction Hours/week:L: 0 T:0 P:2 Marks: Internal: 40 External: 60 Total:100

Scope

The laboratory course deals with the qualitative analysis of the organic containing functional groups and the preparations of organic compounds b acylation and benzyolation reactions.

Objective

It enables the students to

1. To test the organic functional groups like alcohols, phenols carbonyl and carboxylic acid groups
2. To carry out the preparations of organic comounds by acylation reactions
3. To carry out the preparations of organic compounds by benzyloation reactions.

Methodology

Laboratory experiments, acylation, benzyolation

1. Functional group tests for alcohols, phenols, carbonyl and carboxylic acid group.
2. Organic preparations:

i. Acetylation of one of the following compounds: amines (aniline, o-, m-, p- toluidines and o-, m-, p-anisidine) and phenols (β -naphthol, vanillin, salicylic acid) by any one method:
   a. Using conventional method.
   b. Using green approach

ii. Benzolyation of one of the following amines (aniline, o-, m-, p- toluidines and o-, m-, p-anisidine) and one of the following phenols (β -naphthol, resorcinol, p- cresol) by Schotten-Baumann reaction.

iii. Oxidation of ethanol/ isopropanol (Iodoform reaction).

iv. Selective reduction of meta dinitrobenzene to m-nitroaniline.
v. Hydrolysis of amides and esters.
vi. Semicarbazone of any one of the following compounds: acetone, ethyl methyl ketone, cyclohexanone, benzaldehyde.
vii. S-Benzylisothiouronium salt of one each of water soluble and water insoluble acids (benzoic acid, oxalic acid, phenyl acetic acid and phthalic acid).
viii. Aldol condensation using either conventional or green method.

The above derivatives should be prepared using 0.5-1g of the organic compound. The solid samples must be collected and may be used for recrystallization and melting point.

Suggested Readings

Text Books:

1. Mann, F.G. & Saunders, B.C. (2009). *Practical Organic Chemistry*. Pearson Education.
2. Furniss, B.S., Hannaford, A.J., Smith, P.W.G. & Tatchell, A.R. (2012). *Practical Organic Chemistry*. 5th Ed., Pearson.

Reference Books:

1. Ahluwalia, V.K. & Aggarwal, R. (2000). *Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis*. University Press.
2. Ahluwalia, V.K. & Dhingra, S. (2000). *Comprehensive Practical Organic Chemistry: Qualitative Analysis*. University Press.

PREPARATIONS

1. ACETYLATION OF ANILINE TO ACETANILIDE

PRINCIPLE:

Aniline can be acetylated easily by reflecting a mixture of acidic anhydride and sodium acetate

$CH_6H_5NH_2$ + $(CH_3CH_2)_2$ O + CH_3COONa → C_6 H_5 NH $COCH_3$ + CH_3 COOH

REQUREMENTS:

Chemicals:

$C_6H_5NH_2$ (freshly prepared)	–3ml
Acetic anhydride	-- 4ml
Glacial acetic acid	--4ml

APPARATUS REQUIRED:

Reflex conteser, glass beaker (250ml), wire gase, test tube (10ml) and round bottle flask

PROCEDURE:

Galacial acetic acid is mixed with acidic anhydroxide in dry and tested an shaken well and aniline is taken in round bottom flask and the above mixture is added slow to aniline with contantshaking . A bit of broken borceline is added into the flask to prevent pumping . The flask is fitted with a reflex condenser and heated gently for above 30min over a wire gasze the hot liquid is poured into ice cold water taken in formed product is filtered , dryed and the yield is noted .

RECYSTILLATION:

About 1g of the crud acetanilide sample is dissolve in minimum amount of hot water , 1g of animal char coal is added and then heated the hot liquid is rapidly filtered

(through hot water , fume is available). The filtered allowed to cool , the acetanilide crystallize in a rhompic plates .

RESULT:

1. MELTING POINT: …………………
2. EXPECTED YIELD: …………………..

2. PREPARATION OF BENZAMIDE FROM ANILINE

AIM

To prepare a few sample of crystals of Benzamide from aniline.

PRINCIPAL

Aromatic amines react with benzyl chloride in aqueous medium to yield the respective benzanilides. In the Scotten Burman method of benzoylation's amino compound is treated with a site excess of NaOH solution and benzyl chloride, on vigorous shaking. Benzylation taken place radically and the product separates as a solid.

$C_6H_5NH_2 + C_6H_5COCl + NaOH$ -------------- $C_6H_5NHCOC_6H_5 + NaCl + H_2O$

CHEMICAL REQUIRED

Aniline	- 2.5 ML
Benzyl chloride	- 3.5 ML
NaOH	- 10% 25ML

PROCEDURE

2.5ML of aniline and 25ml of 10% NaOH are placed in a 100ml conical flask and stopped well. 3.5ml of benzyl chloride are introduced into to the flask vigorously shaken well for 10-15 mints. The progress of reaction is known by the exothermal process. The completion of reaction is tested by smelling the presence of benzyl chloride in the flask. If the smell precisive add little more NaOH and shake for a while. The white crystals of benzyl chloride are filtered at the pumb washed well with H2O and dried.

RECRYSTALLISATION

A little amount of the sample is recrystalized from hot methylated split it. It is filtered to hot water funnel. The colourless crystals are separated and dried in air.

RESULT

The yield of benzylanilide -

3. Preparation of benzoic acid from ethyl benzoate

Principle:

Ethyl benzoate is hydrolysed to sodium salt of benzoic acid by a solution of sodium hydroxide. Benzoic acid is obtained from sodium benzoate by acidification.

Step:1

$C_6H_5COOC_2H_5 + NaOH \rightarrow C_6H_5COONa$

Step:2

$C_6H_5COONa + HCl \rightarrow C_6H_5COOH$

Requirements:

1. Ethyl benzoate-2.5g
2. Sodium hydroxide-2g

Procedure:

2g of sodium hydroxide are dissolved in about 20 ml of water taken in a R.B flask. 2.5 g of ethyl benzoate are added to the R.B flask. A few porous pieces are added to ensure smooth boiling. The flask is then fitted with a Liebig's condenser and heated over a wire gauze for about 45 mins. The hydrolysis is complete when no more oily drops are seen in the flask. The contents are now cooled and transferred completely to a beaker. Concentrated HCl is added with constant stirring till the solution is distinctly acetic. The precipitated benzoic acid is filtered, washed and dried. The yield is noted. About 1g is recrystallized from hot water and melting point is determined.

Result:

1. The yield of benzoic acid =……….. g
2. The melting point of benzoic acid =…………….˚C

4. Oxidation of Iodoform

Principle:

Iodoform is prepared by the joint action of iodine and alkali upon ethanol.

$$CH_3CH_2OH + 3I_2 \rightarrow CI_3\text{-}CH_2OH + 3HI$$

$$CI_3\text{-}CH_2OH + NaOH \rightarrow CHI_3 + CH_3COONa$$

Requirements:

Ethanol- 3.5ml

Potassium carbonate- 5g

Powdered iodine- 5g

Procedure:

The Potassium carbonate is dissolved in 20ml of water contained in a 100ml conical flask. Ethanol is added to the solution. The powdered iodine is then added in small quantities at a time with stirring.

The mixture is gradually warmed on a water bath to 70 – 80˚ C for about 15 mins. On cooling, the iodoform seperates as yellow crystals and is collected by filteration. The product is washed with water, recrystallized from alcohol and dried. The yield and melting point is determined.

Result:

1. The yield of iodoform =……….. g
2. The melting point of iodoform =…………….˚C

5. Preparation of m-Dinitrobenzene

Principle:

m-Dinitrobenzene is prepared by the nitration of nitrobenzene. The nitration is effected by fuming nitric acid in presence of conc.H2SO4.

Requirements:

nitrobenzene- 1ml

Fuming nitric acid- 5ml

Conc. H_2SO_4-10ml

Procedure:

7ml of fuming nitric acid is taken in an R.B flask and 10ml of Conc. H_2SO_4 is added, a little at a time, cooling the flask during the addition. 1ml of nitrobenzene is then added in small quantities at a time to the nitrating mixture, shaking well after each addition. Finally it is heated for about 45mins by immersion in a boiling water-bath, till a small quantity of the reaction mixture when added to small quantity of water in a test-tube gives a solid immediately. The contents of the flask are then poured in fine stream while still hot into 100ml of water contained in a beaker. The mixture is shaken very vigorously during the addition. M-Dinitrobenzene separates as a solid which is filtered at the pump, washed several times with water, dried and the yield noted. A small portion is recrystallized from alcohol and the melting point is determined.

Result:

1. The yield of m-dinitrobenzene =……….. g
2. The melting point of m-dinitrobenzene =…………….˚C

ORGANIC QUALITATIVE ANALYSIS

TESTS FOR FUNCTIONAL GROUPS

I. Compounds in which carbon, Hydrogen and Oxygen are present

I.1. Carboxylic Acids

(a)	A pinch of the substance is shaken up with about 1 ml of water. One drop of phenolphthalein is added and then very dilute sodium hydroxide solution is added drop by drop with shaking.	A pink colour is produced only after adding a number of drops of sodium hydroxide. A pink colour is got even with the first drop of sodium hydroxide.	Presence of carboxylic acids. Acids absent
(b)	*Ester formation:* About 0.2 gm of the substance is mixed with about 2 ml of rectified spirit in a dry test tube; 2 to 3 drops of conc. H_2SO_4 are added, shaken well and gently heated for a minute. The mixture is then poured into about 30 ml of a dilute solution of sodium carbonate, stirred well and the smell is noted.	A pleasant ester smell is obtained.	Carboxylic acid is present.
(c)	*Fluorescein reaction:* A small amount of the substance is mixed with a few crystals of resorcinol in a dry test tube. 2 drops of conc. H_2SO_4 are added, shaken well, heated gently and then poured into about 100 ml of water, stirred well and then an excess of sodium hydroxide solution is added.	The mixture turns deep-red on heating; forms a red solution with water; on adding sodium hydroxide, an intense greenish yellow fluorescein is obtained.	Dicarboxylic acids present.

I.2. Phenolic Group

(a)	*Libermann's Reaction:* A small amount of the substance is heated with a crystal of sodium nitrite in a dry test tube, cooled, two drops of conc. H_2SO_4 are added, shaken well and the mixture is poured into about 100 ml of water, stirred well and then an excess of sodium hydroxide is added.	A red solution is got which turns blue or green on adding sodium hydroxide.	Phenolic group present. **Note:** all phenols do not give this test.
(b)	*Phthalien fusion Test :* A small amount of the substance is mixed with about 0.5 gm of phthalic anhydride in a dry tube; 2 drops of conc.H_2SO_4 are added, heated gently for a minute. The mixture is poured into about 100 ml of water and the sodium hydroxide is added in slight excess.	A pink or red colour is obtained. A yellowish green fluorescence is obtained.	Phenols like phenol, o-cresol, m-cresol, salicylic acid. Resorcinol **Note:** The colour depends on the nature of the phenol.
(c)	*Azo-Dye Formation :* About 5 drops of aniline are treated with 3 to 5 ml of dil. HCl, 10 to 15 drops of strong solution of sodium nitrite are added drop by drop with constant shaking and cooling, and the diazotised solution obtained is added to a solution of the substance in 2 to 3 ml of 10% NaOH solution in small quantities.	A scarlet red or brownish red or orange red precipitate of a dye is obtained.	Phenols like β-naphthol, α-naphthol, resorcinol etc.
(d)	About 1 ml of Fehling's solution 'A' is mixed with 1 ml of Fehling's solution 'B'. The mixture is treated with a small amount of the substace and boiled well.	A red brown precipitate of cuprous oxide is obtained.	Polyhydric Phenol.

I.3. Aldehydes and Ketones

(a)	About 3 drops of the substance are added to a saturated solution of sodium bisulphite solution and shaken well.	A white crystalline precipitate is obtained.	Aldehydes and certain ketones present. [ketones with the keto group directly attached to benzene ring does not answer this test]
(b)	A small amount of the substance is added to about 3 ml of Borsche's reagent, a drop of conc.HCl added, gently heated for about 2 minutes and cooled well.	A yellow or red-brown crystalline precipitate is obtained.	Aldehydes and ketones present.
(c)	A mixture of 5 drops of Phenylhydrazine and 5 drops of glacial acetic acid are taken in dry test tube. A small amount of the substance is added, gently heated for a minute. Excess of cold water is added and shaken well.	(a) A yellow or yellowish-white precipitate is obtained. (b) A bright yellow crystalline precipitate.	Presence of Aldehydes and certain Ketones. Reducing sugars present.
(d)	About 0.3 gm of semicarbazide hydrochloride id dissolved in H_2O. About 0.5 gm of sodiumacetate crystals are added,shaken well to dissolve the solid and to this 2 ml of an alcoholic solution of the substance is added, heated in a water bath for 15 minutes and cooled.	A white crystalline precipitate of the semicarbazone is got.	Aldehydes and Ketones present.
(e)	A small amount of the substance is added to about 3ml of Schiff's reagent and shaken well.	A violet colour is produced quickly.	Aldehydes confirmed.
(f)	A small amount of the substance is added to 2 ml of Fehling's solution A and B and gently heated.	A reddish brown precipitate is got.	Presence of Aliphatic aldehydes (reducing sugars, and polyhydric phenols also answer).

1.4. Carbohydrates

(a)	Molisch test: A small amount of the substance is dissolved in 2 ml of water, a few drops of a strong solution of (10%) of α-naphthol in pure alcohol is added, shaken well, and 2 ml of conc.H_2SO_4 are carefully added along the side of the tube so that the acid forms a separate layer at the bottom.	A violet, purple or red ring is formed at the junction of the two layers and the colour slowly spreads throughout the liquid.	Carbohydrates confirmed.
(b)	A small amount of the substance is shaken up with one ml of water. The solution is added to about 2 ml of Fehling’s A and B and heated on a water bath for 15 minutes.	A red brown precipitate is obtained.	Reducing sugar present.
(c)	About 0.3 gm of the substance is dissolved in about 5 ml of water, a mixture of 2 ml of phenylhydrazine and 2 ml of glacial acetic acid is added, the contents heated in a boiling water bath for about 15 minutes with occasional shaking and then cooled.	A bright yellow crystalline precipitate is obtained.	Reducing sugars like glucose, fructose, and lactose present.

1.5. Esters:

(a)	**Hydroxamic acid Test:** About 3 drops of the liquid and a pinch of hydroxylamine hydrochloride are added to about 5 ml of 10% NaOH solution. The contents are gently boiled for 3 minutes cooled, acidified with conc.HCl, added drop by drop	A violet or deep red brown colour obtained.	Esters present.

(b)	and then about 5 drops of $FeCl_3$ solution are added and shaken well. The liquid is refluxed with 10% NaOH solution. The residue is acidified with con.HCl and cooled.	A white precipitate is obtained.	Ester of an aromatic acid is present.