ORGANIC CHEMISTRY
Practical-II
M.Sc. Chemistry
First Year, SEMESTER-II,
206CH24

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
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ACHARYA NAGARJUNA UNIVERSITY
CENTRE FOR DISTANCE EDUCATION
M.Sc. CHEMISTRY :: SEMESTER–II
ORGANIC CHEMISTRY
Practical -II 206CH24

(Minimum Five Experiments must be carried out)

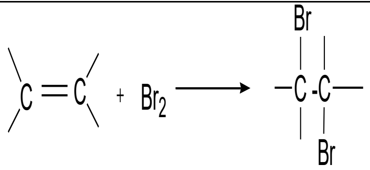
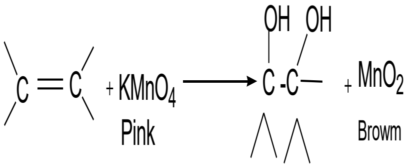
1) Identification of Functional Groups in Organic Compounds: Phenol, bases, organic acid, ketone, aldehyde, amide and carbohydrate with preparation of two solid derivatives.
   (i) Identification of given two compounds with preparation of two solid derivatives and
   (ii) Reporting of the melting points for derivatives.

2) Purification of Derivatives: The student must do recrystallization to final derivatives(s) and submit the sample. If the sample is an impure liquid, the distillation process must be carried out.

Preliminary investigation

S. No	Test	Observation	Inference
A.	**Primary tests:** a. ***Physical state***: note whether the compound is a solid or liquid. If solid whether it is crystalline or amorphous, if it is liquid whether it is mobile or viscous.		
	b. ***Colour:***	Yellow	Nitro compound
		Orange	Ortho nitro Aniline.
	c. ***Odour***:	Fruity odour of esters or ethers, pungent	
	d. ***Litmus test***: Keep the moistened litmus paper in contact with a little of the substance in water	Blue to red Red to blue Neutral	Presence or acids or phenols Presence of base Ketones, ester, carbohydrates etc.,
	e. Melting or boiling points		
B.	**Ignition test**	Smoky	Aromatic compound
		Non luminous	Aliphatic compounds containing low percentage of carbon
		Charring	Compounds such as carbohydrates and its salts get charred on ignition.
C.	**Solubility**: To one drop of the liquid or small quantity of the solid is dissolved in the following.		
	(a) Ether	Insoluble	May be carbohydrate/amide/imide/anilide
	(b) Water	Soluble, Solution is neutral to litmus	May be carbohydrate
		Solution turns blue to red	May be acidic compound

	(c) Saturated $NaHCO_3$ solution	Soluble with effervescence and regenerated on acidification with dil. HCl	May be carboxylic acid
		Slow effervescence	Poly hydric phenols
		Slow effervescence & solution turns yellow	Nitro phenols
	(d) dilute NaOH solution (changes in the cold are observed & heated if necessary	No characteristic change	Presence of ketones, amines, aromatic nitro compounds
		Dissolves readily in the cold & substances regenerated on adding conc. HCl	Aromatic acids, phenols may be present
		Dissolves & solution turns yellow & colour is removed on adding HCl	Nitro phenols, phenolic aldehydes may be present
		Dissolves readily forming a yellow or brown solution on boiling	Carbohydrates may be present
		Dissolves in cold & solution turns yellow, brown & finally dark on shaking	Polyhydric phenols may be present
		Ammonia gas is evolved on boiling	Amides may be present
		Oil drops are formed with aniline like odour on boiling	Anilides, or toulinides may be present
	(e) Dilute Na_2CO_3	1. Soluble with effervescence	May be carboxylic acid
		2. Soluble without effervescence	May be phenolic group
	(f) Dilute HCl	1. Soluble and regenerates on adding alkali	May be basic compounds like amines
D.	**Action of concentrated sulphuric acid:**		
	To a small quantity of compound in a dry test tube add conc. H_2SO_4 and note the change in the code and then warm gently	Blackening with effervescence With the evolution of CO (or) CO_2 and SO_2	Carbohydrates (or) certain hydroxyl aliphatic acids like tartaric acid.
		Blackening without effervescence	Polyhydric phenols like resorcinol.
		CO and CO_2 evolved, no blacking	Oxalates (or) oxalic acid.
E.	**Test for Unsaturation:**		
	a) Action of Br_2 in CCl_4 : To one mL of Br_2 in CCl_4 add a drop of the liquid or small quantity of the solid	Decolorization of Bromine with evolution of HBr which can be detected with the	Unsaturated compound

		introduction of ammonia rod when white fumes are observed	
		No decolorization	Saturated compound
	b. action of Bromine water: To one mLof bromine in water add a drop of liquid or small quantity of solid	a.Decolorization without evolution of HBr	Unsaturated compound
		b.Decolorization with evolution of HBr	Aromatic compound
		c. No decolorization	Saturated compound
	c. Bayer's Test: action of dil. $KMnO_4$ 	Decolorization of $KMnO_4$ with brown precipitate	Unsaturated compound
		No decolorization	Saturated compound

Detection of extra elements (or) Elemental Analysis

C, H and O are considered as basic elements of organic compounds. Other than the three elements, the elements that are most commonly present in organic compounds are Nitrogen, Sulphur and Halogens. The presence of these elements is detected by Lassaigne's test.

Preparation of Sodium Fusion Extract or Lassaigne's Test:

Heating procedure for liquids:

Gently heat a small piece of freshly cut and dried sodium in an ignition tube in the beginning and then to the red hot. Remove the red-hot ignition tube from the flame and one drop of liquid. Repeat the heating process again until the tube becomes red hot, remove and add another drop of the liquid. Repeat the operation for two or three times.

Heating procedure for solids:

Gently heat a small piece of freshly cut and dried sodium in ignition tube in the beginning and then to red hot. Remove the red-hot ignition tube from the flame and add a few milligrams of solids. Repeat the heating process again until the tube becomes red hot. In the case solids there is no need to add the compound again.

Take 3 to 4 mL of distilled water in a mortar and immerse the red-hot ignition tube in the water. Grind the ignition tube to pieces with the pestle, filter. Divide the filtrate into three parts and perform the following experiments.

Compounds containing C, H, N, O, S, Halogens (X) + Na → $NaCN$ + $NaOH$ +Na_2S + NaX

Experiment	Observation	Inference
LASSAIGNE'S Test :		
(i) Test For Nitrogen: To one portion of sodium fusion extract add 2 drops of freshly prepared $FeSO_4$ solution. Boil, cool and acidify with shaking until the solution is clear. Now add few drops of $FeCl_3$	Bluish/Green Precipitate/ colour Prussian blue colour No colour change	Nitrogen may be present Nitrogen absent
$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$ $3\ Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6] + 6\ Na_2SO_4$ $FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6\ NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$		

$$2\,Na_4[Fe(CN)_6] + 4Fecl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

(Prussian blue Color)

(ii) Test for Sulphur: (a) To the second portion of sodium fusion extract,2-3 drops of freshly prepared Sodium nitroprusside.	Violet or Purple colour No purple colour	Sulphur present Sulphur absent

$$\underset{\text{Sodium Nitroprusside}}{Na_2\,[Fe(CN)_5NO]+Na_2S} \rightarrow \underset{\text{Purple colour}}{Na_4[Fe(CN)_5NOS]}$$

(b) Acidify small portion of the extract with acetic acid and lead acetate solution.	A black precipitate	Sulphur present

$$Na_2S + 2CH_3COOH \rightarrow 2CH_3COONaH_2S$$

$$(CH_3COO)_2Pb+H_2S \longrightarrow PbS\ (\text{Black ppt})+ 2CH_3COOH$$

(iii) Test for both Sulphur & Nitrogen: (a)Acidify the small portion of the extract with dil.HCl and add 2 drops of $FeCl_3$ solution.	Blood red colour	Both Nitrogen and Sulphur are present

$$Na + C + N + S \rightarrow NaCNS$$

$$3NaCNS + FeCl_3 \longrightarrow Fe(CNS)_3 + 3NaCl$$

Ferric Sulphocyanide or Ferric thio-cyanate)

(iv) Test for halogens: a) **Beilstein test:** Heat a copper wire at one end in a non-luminous flame till it ceases to impart green colour. Dip the hot wire in the organic compound and again heat,	Green or bluish green colour No Green colour blue colour	Halogens may be present Halogens absent

NOTE: *Beilstein test fails to detect compounds like pyridine, quinoline, purines, urea, thiourea etc., are free halogen may also give green colour. No green or blue colour confirms the absence of halogen.*

(b) To the small portion of the extract, add dil. Nitric acid and then two to three drops of silver nitrate solution	While precipitate soluble in NH_4OH	Chlorine present
	Yellow precipitate partially soluble in NH_4OH	Bromine Present
	Yellow precipitate insoluble in NH_4OH	Iodine present

$$NaX + HNO_3 + AgNO_3 \rightarrow AgX + NaNO_3 + H_2 \qquad X=Cl, Br, I$$

(v) Detection of halogens in the presence of Nitrogen and Sulphur:

NaCN and Na_2S if present in the extract will interfere with the halogen test. Hence, they are to be removed as gaseous compounds by boiling the acidified extract.

Acidify 2.0 mL of the extract with dil. HNO_3 and boil until the volume is reduced to half Cool and add $AgNO_3$ solution	A heavy precipitate	Presence of halogens

$$NaCN + HNO_3 \rightarrow HCN + NaNO_3$$

$$Na_2S + 2HNO_3 \rightarrow H_2S + 2NaNO_3$$

$$NaX + AgNO_3 \rightarrow AgX + NaNO_3$$

Detection of Organic Functional Groups

A simple organic compound has one functional group but it may contain two or more functional groups. All the commonly found functional groups have been divided into four groups. These groups correspond to various elements in the organic compounds and are given below.

Type	Elements present in the organic compound	Organic compound and its functional group
1.	(a) C & H (b) C, H, O	Hydrocarbons Carboxylic acid, Phenol and Alcohol, Aldehyde, Ketone, Ether, Ester
2.	(a) C, H, N (b) C, H, N, O	Amines Amides, Nitro compounds, Anilide
3.	(a) Halogens C, H, X (b) Halogens and O, C, AX	Halogenated hydrocarbons Acid halides, chloral hydride
4.	Sulphur C, H, S, O	Sulphuric acid

3.1 Compounds containing C, H with (or) without Oxygen:

1. **Tests for Carboxylic groups (-COOH):**

(a) Sodium bicarbonate Test: Add 1 mL of saturated sodium bicarbonate solution to a small amount of compound	CO_2 gas evolved No CO_2 gas	Carboxylic acid Carboxylic acid absent
$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$		
(b) Ester formation Test: Warm a small amount of the acid with 2 parts of the absolute ethanol and 1 part of conc.H_2SO_4 for 2 minutes cool and pour it into aqueous solution of sodium carbonate contain in a beaker and smell immediately.	Sweet, fruity smell of ester	Presence of carboxylic acid group
$RCOOH + C_2H_5OH \rightarrow RCOOC_2H_5$		
*(**Note:** fruity odour is due to the formation of esters which are sweet smelling)*		

(c) Ferric chloride Test: Dissolve 0.5 gm of acid in 3 mL of H_2O to this add a slight excess of ammonia solution and a piece of unglazed porcelain. Boil the solution to remove excess ammonia. Cool and add a few drops of neutral $FeCl_3$ solution.	A reddish brown ppt or deep red colourisation. A buffer brownish colour ppt Violet or blue colour	Aliphatic mono carboxylic acid Aromatic acids Ortho substituted Ar-hydroxy acids.

$$RCOOH + NH_4OH \longrightarrow R\text{-}COONH_4 + H_2O$$
$$3R\text{-}COONH_4 + FeCl_3 \longrightarrow (RCOO)_3Fe + 3NH_4Cl$$

*(**Note**: Phenols and α-Naphthylamine also produce characteristic colour with $FeCl_3$)*

(d) Phenolphthalein Test: Dissolve 0.2 gm of compound in water/alcohol. Add a drop of Phenolphthalein and dil. NaOH solution drop wise.	Pink color	Presence of carboxylic acid

Note: This test is negative with nitrophenols, m-&p- hydroxy benzoic acids.

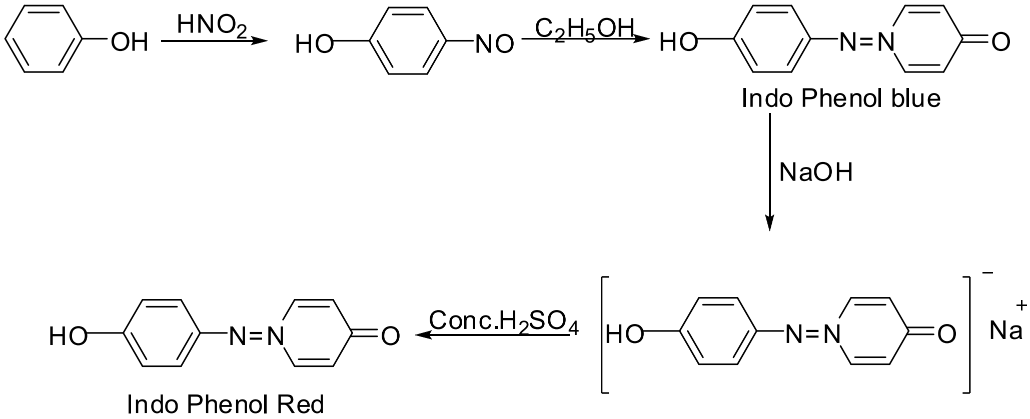
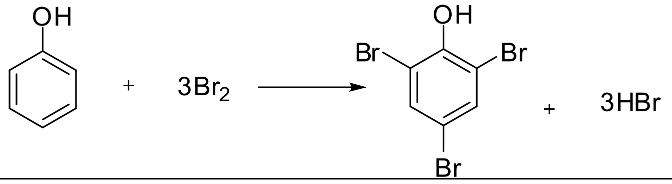
(e) Fluorescein Test: Heat gently 0.2 gm of compound with 0.5 gm of resorcinol and few drops of conc.H_2SO_4 in a test tube for 2 min. Cool and pour the mixture in a beaker containing NaOH and dilute with water.	Intense green or orange colour Fluorescence	Presence of Aromatic 1,2-dicarboxylic acid
(f) Iodate – Iodide Test: This is a very sensitive test for detection of even weak carboxylic acids. To a small quantity of compound add two drops of 5% KI solution. Cork the tube and place it in a boiling water bath for two minutes. Cool the contents and add few drops of freshly prepared starch solution.	Blue colour solution	Carboxylic acid present

$$6RCOOH + 5KI + 3KIO_3 \longrightarrow 6RCOOK + 3H_2O + 3I_2$$

(I_2 gives blue colour with starch)

2. Tests for Phenols:

(a) Ferric Chloride test: Dissolve one drop of liquid or small amount of solid in 1mL of alcohol and add 1drop of neutral $FeCl_3$.	Violet, blue, pink, green colour which disappears on acidification with dil. HCl.	Phenolic group present
$6ArOH + FeCl_3 \longrightarrow [Fe(OAr)_6] + 3HCl + 3H$ (coloured complexion)		
	Violet Blue changing to Red Violet red (only after boiling with water) White ppt changing to violet or red White opalescence Bluish violet Green No colour change	Phenol, O-Cresols, aspirin Hydroquinone, pyrogallol m- and p-nitro phenols α-Naphthol β-Naphthol α-Naphthol Cresols, resorcinol, β-Naphthol Absence of Phenolic group
***[Note:** m-, p-Hydroxy benzoic acids, di- and trinitro phenols, tri-bromo phenol etc. do not produce characteristic colour with $FeCl_3$, α-Naphtylamine gives a blue colour with $FeCl_3$]*		
(b) Liebermann's Nitroso reaction: Dissolve one drop of liquid or small number of solids in 1ml of alcohol, add crystal of $NaNO_2$, heat for 1minute, cool and add 5 drops of conc. H_2SO_4.	A deep green to blue solution formed turns red on pouring water	Phenolic group
*[**Note**: Nitro phenols, hydroquinones, catechol & hydroxyl acids do not give this test]*		

 Indo Phenol blue Indo Phenol Red		
(c) Phthalein Test: To a small amount of compound add phthalic anhydride and a drop of conc.H_2SO_4 and heat the contents for a minute. Cool and make it alkaline with dil. NaOH. Pour the contents into Water.	Red colour Blue Fluorescent green Deep violet Green/Faint Green	Phenol/Cresol m-Cresol/Catechol Resorcinol Hydroquinone α-Naphthol/β-Naphthol
(d) Test with Bromine Water: Small amount of compound dissolved in water or dil. HCl and add bromine water drop wise until decolourisation is slow.	White ppt	Presence of phenols
		

3. Tests for Alcoholic group (-OH):

(a) Reaction with Sodium: Add a piece of anhydrous calcium chloride to about 2ml of compound to absorb water if present. Now add a very small piece of Sodium metal to the above clear liquid.	Brisk effervescences due liberation of Hydrogen gas	Presence of Alcoholic group
$ROH + Na \rightarrow RONa + \frac{1}{2} H_2$		
(b) Ceric ammonium nitrate test: To the aqueous solution add few drops of ceric ammonium nitrate. [CAN]	Red colour	Alcoholic hydroxyl group
$2ROH + (NH_4)_2Ce(NO_3)_6 \rightarrow R(OH)_3 + 2NH_4NO_3 + Ce(NO_3)_4)$		
(c) Xanthate test: To the aqueous solution add pellets of KOH, heat and cool then add 1.0 mL of either followed by the addition of 2-3 drops of CS_2.	Yellow ppt	Presence of Alcoholic group
(d) Distinction between 1^0, 2^0 and 3^0 alcohols: To 2 mL of the compound add about 8 mL Luca's reagent and shake	Separation of insoluble layer at once Appearance of cloudiness after 4 to 5 minutes Solution remains clear	3^0 Alcohol 2^0 Alcohol 3^0 Alcohol

1. Tests for Carbonyl Compounds

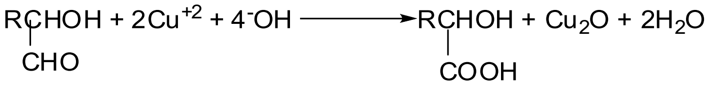
(a) Reaction with 2,4-DNP: To 0.1 gm of the compound add 3 mL of 2,4-dinitrophenyl hydrazine reagent and shake and Stand it for few minutes.	Yellow or Orange colour ppt	Presence of carbonyl group
(b) Schiff's Reagent Test: To small amount of compound add 2 mL of reagent and heat for 2 min.	Pink/magenta colour	Presence of Aldehydes group
(c) Tollens Test: To small amount of compound add 2 mL of reagent and heat the mixture on water bath for few Minutes.	Silver mirror or grey ppt	Aldehyde or reducing sugar present
(d) Fehling's Test: Add 2 mL of reagent (1 mL each of A+B) to small amount of compound and heat the mixture.	Red ppt	Aldehyde or reducing sugar present
(e) Sodium nitroprusside test: To small amount of compound add 2 drops of acetone in 1mL water add 1% solution of sodium nitroprusside and 10 % NaOH (3 drops each). Divide the solution into 2 parts. (i) To 1 part add 3 drops of glacial acetic acid. (ii) observe the colour of second part after 20 min.	Orange colour develops first changes to purple Changes to Yellow	Presence of Carbonyl group Presence of $COCH_3$ group
Note : *Repeat the reaction with acetophenone. The red colour first formed will change to blue on acidification with acetic acid. This colour reaction is helpful in distinguishing acetone from aceto phenol.*		
(f) To a small amount of compound add 2 mL of alcohol, add 8 drops of phenyl hydrazine reagent. Shake the tube well, heat for 10 min. and cool.	PPt or Turbidity	Presence of carbonyl group

2. Tests for Esters:

(a) Hydroxylamine acid Test: To one drop of compound add 5 drops of hydroxylamine hydrochloride and 0.5 mL of alc. KOH, boil for 1 min., cool, just acidify with dil. HCl and add 2 drops of $FeCl_3$ solution.	Deep red or violet colour	Presence of Ester group
$RCOOR + NH_2OH.HCl + KOH \longrightarrow RCOONHONa + R'OH$ $3RCONHOH + FeCl_3 \longrightarrow$ Burgundy or Magenta colour		
(b) Phenolphthalein test: Dissolve 0.5 gm of compound in 5 mL of alcohol and add a drop of Phenolphthalein indicator. A pink colour is produced by Phenolphthalein in alkaline medium. Heat the reaction mixture for 5 min.	Pink colour disappears	Presence of Ester group
$RCOOR + NaOH \longrightarrow$ Phenolphthalein $\longrightarrow RCOONa + ROH +$ Phenolphthalein Pink colour (colourless)		

6.Tests for Carbohydrates:

(a) Molisch's test: To 1 mL of aq. Solution of compound add 2 to 3 drops of 10% alcoholic 2-Naphthol (Molisch reagent). To this add 1 mL of conc.H_2SO_4 dropwise along the sides of the test tube and allow it to stand for few minutes.	Appearance of a violet ring at the junction of two liquid layers	Presence of carbohydrate
(b) Fehling's test: To the aq. Solution of the compound add 2 mL of Fehling's reagent and heat on water bath.	Red PPt	Presence of a reducing sugar
$C_6H_{12}O_6 + 2CuO \longrightarrow Cu_2O + C_6H_{12}O_7$		

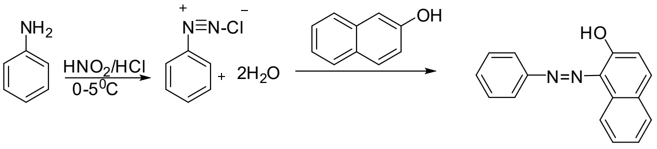
(c) Benedict's solution: To the aq. Solution of the compound add 2 mL of Benedict's reagent and heat on water bath	Red PPt	Presence of a reducing sugar
 $\underset{CHO}{RCHOH} + 2Cu^{+2} + 4^{-}OH \longrightarrow \underset{COOH}{RCHOH} + Cu_2O + 2H_2O$		
(d) Barfoed's test: To the aq. Solution of the compound add 2 mL of freshly prepared Barfoed's test reagent and heat for 2 to 3 min.	Yellow orange red ppt Red ppt after long heating	Glucose/ fructose/ galactose present.

3.2 Compounds containing C, H, N with or without Oxygen:

7. Test for Amines: (The following tests must be supplemented by a positive Lassaigne's test for nitrogen, also determine that the given compound is aromatic or aliphatic and perform the reactions related to that type only). If is absent, it is not necessary to carried out this reaction.

(a) Test for Primary amine:

a) Carbylamine Test: (i) Boil 2 mL each compound with $CHCl_3$ and alc. KOH (aliphatic & aromatic primary amines give this reaction).	Foul smelling of Carbylamine	Presence of Primary amine
$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$		
b) If the compound is aliphatic nitrogen containing (from flame test) dissolve 2 drops of liquid or small amount of solid in slight excess of dil. HCl, cool in ice to 5 °C add 10% aq. $NaNO_2$ dropwise in slight excess.	Colourless nitrogen gas is evolved.	Aliphatic primary amine
$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$		

c) Diazotization and coupling: If it is aromatic nitrogen containing compound, repeat the above procedure and add 10% alkaline 2-naphthol solution.	Bright orange red colour or ppt	Aromatic primary amine
d) Nitrous acid test: Dissolve a pinch of the compound in 5 mL of dilute HCl slowly with constant stirring by means of a dropper and with constant stirring. After the completion of reaction add a cold solution of 0.4 gm of 2-Naphthol in 4 mL of 5% NaOH.	Formation of orange red coloured azo dye.	Aromatic primary amine.
 Orange-red dye		

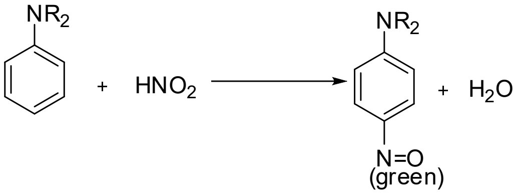
(b) Test for secondary amine:

(a) If the compound is aliphatic, dissolve 2 drops of liquid or small amount of solid in 3 or 4 drops of dil. H_2SO_4, add cooled 4ml solution of $NaNO_2$ and gently warm the mixture, Nitrousamine collects as yellow oil on the surface.	Deep blue solution which turns to red on pouring onto water and turns blue or green on adding alkali.	Aliphatic secondary amine
$(CH_3)_2NH + HNO_2 \longrightarrow (CH_3)_2NNO$(N-nitroso-di methyl amine) + H_2O		

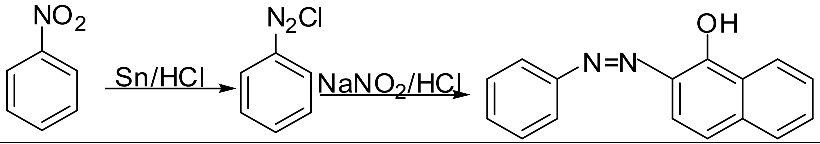
(b) Extract with 5 mL of ether, evaporate ether. Add one drop of phenol, heat gently, cool and add 5 drops of conc. H_2SO_4.	The above reaction is absent	Not a secondary aliphatic amine

(c) If the compound is aromatic repeat the above procedure.	Intense green which turns to pale red on pouring into water and turns deep bluish green on adding alkali.	Secondary aromatic amine present

(d) Dissolve pinch of the compound in 5 mL of dil. HCl and cool it in ice. To this add cold solution of 5 mL $NaNO_2$ solution dropwise and with constant shaking allow the solution to stand for 5 min.	Formation of yellow oil	Presence of aliphatic secondary amine
$R_2NH + HNO_2 \rightarrow R_2N - NO + H_2O$		
(e) Liberman Nitroso Reaction: Add 1 mL of conc. H_2SO_4 to the above prepared nitroso compound.	Formation of red colour, In alkaline solution red colour is changed to blue colour.	Presence of aromatic secondary amine
(f) Hinsberg's Test: **a)** Take 0.1 gm of compound and 0.2 gm *p*- toulene sulphonyl chloride and 5 mL of 10% NaOH in a test tube. Shake the test tube for 5 min. Heat the reaction mixture on a steam bath for 1 min and cool in ice.	Clear solution which gives precipitate on acidification with dil. HCl	Primary amine
b) If precipitate appears add 5 mL of water and shake. If solution is clear acidify with dil. HCl.	Precipitate not affected by addition of dil. HCl	Secondary amine
	Precipitation which dissolves on acidification.	Tertiary amine
(c) Test for tertiary amine: Dissolve a pinch of compound in 5 ml of dil. HCl cool the contents in ice bath and 2 mL of ice cold 10% aq. Solution of nitrite drop wise with constant stirring.	Colourless solution	Tertiary aliphatic amine

Dark orange red solution or on orange crystalline ppt is formed, allow it to stand for 5 min. in ice bath and then add dil. NaOH solution	Bright green colourisation	Tertiary aromatic amine
		

8. Test for Nitro group: Mulliken and Barker's reaction:

(a) A little substance is dissolved in alcohol. A few drops of calcium chloride solution and a pinch of zinc dust are added. Boiled for 5 min. cooled and filtered in to a test tube containing Tollen's reagent.	A bright silver mirror or a black precipitation is obtained	Presence of Nitro group
$RNO_2 + 4H \xrightarrow[\text{Cacl}_2]{\text{Zn and}} RNOH + H_2O$ $RNHOH + 2[Ag(NH_3)_2]OH \longrightarrow RNH + 2Ag + 4NH_3 + 2H_2O$		
(b) Dye Test: Take a pinch of the compound in few drops of conc. HCl and add a piece of metal. Heat the solution for few min allow it to stand for few min and filter the product. To the cold filtrate add ice cold 10% aq. NaNO$_2$ solution slowly by means of a dropper with continuous stirring and then add a cold solution of 0.4 gm of β-Naphthol in 4 mL of 5% NaOH	Formation of orange red colour azo dye	Nitro group is present
		

(9) Test for Amides:

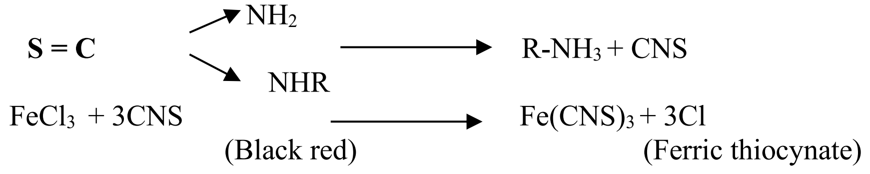
(a) Action of NaOH solution: A little of the substance is heated with Sodium Hydroxide solution.	(a) Ammonia is evolved (b) Separation of oil or formation of emulsion	Presence of Amide Presence of Anilides
$RCONH_2 + NaOH \longrightarrow RCOONa + NH_3$		
(b) Action of Sodalime: little substance is heated with excess of dry soda lime in a dry test tube.	Ammonia is evolved	Presence of amide and anilide
(c) Nitrous acid Test: To 0.2 gm of substance add 2 mL of dil. HCl followed by 2 mL of 2% aq. $NaNO_2$ and shake	Brisk effervescence due to liberation of nitrogen No effervescence	Amide present Amide absent
(d) Hydroxylamine hydrochloride Test: To 0.2 gm of organic compound in alcohol add the reagent boil for 5 min.	Blue red colour	Aliphatic amide present
$RCONH_2 + NH_2OHHCl \longrightarrow RCONHOH + NH_4HCl$		
$H_2NCONH_2 + 4NaOH \longrightarrow 2NH_3 + Na2CO_3 + Na_2S + H_2O$ $Na_2S + Pt(CH_3COO)_2 \quad Pbs + 2\ CH_3COONa$		
$2H_2NCONH_2 \longrightarrow NH_2CONHCONH_2 + NH_3$		

3. 3 Compounds containing C, H, and Sulphur with Oxygen (Perform this test when sulphur is present)

(10) Test for urea

1. Biuret test: A little substance is heated in a dry test tube until it melts and then solidifies. The residue is dissolved in a little water, add a dil. Solution of copper sulphate followed by NaOH sol. drop by drop.	A violet colour is produced	Presence of amide like urea

(11) Test for Thiourea

(a) Test for Thiourea: Boil a small amount of substance with 2 mL of NaOH solution for 1 min. Ammonia Oduor is evolved, cool and add 1 drop of lead acetate solution.		
(b) Thio urea and substituted Thio ureas: HgO Test: To a small amount of organic compound alcoholic add alcoholic Solution of Hgo and warm.	Black ppt	Thiourea or Substituted Thiourea present
(c) Fusion Test: Fuse a small amount of the compound in a test tube cool and dissolve the resultant product in water, add a few drops of ferric chloride solution.	Blood red colour solution	Thiourea or Substituted Thiourea present
(d) To 2 mL of dil. acetic acid add the organic compound and heat until the solution is complete. To the hot solution add 2 mL of aq. $K_4[Fe(CN)_6]$.	Green colour changing to blue	Thiourea present
 $\mathbf{S=C}\begin{matrix}NH_2\\NHR\end{matrix} \longrightarrow R\text{-}NH_3 + CNS$ $FeCl_3 + 3CNS \longrightarrow Fe(CNS)_3 + 3Cl$ (Black red) (Ferric thiocynate)		

(e) To a small quantity of compound add 2 mL of aq. NaOH and heat. After cooling add a drop of aq. Lead acetate.	Black or dark brown colour/ppt	Thiourea present

12. Detection of Hydrocarbons:

a) Nitration test for Aromatic Hydrocarbons: Take 1mL or 0.5 gm of compound in a boiling tube to this add 5 mL of Nitrating mixture drop wise shaking the solution and heat the contents for few minutes, pour the contents in cold water.	Yellow oily liquid or ppt	Presence of Aromatic Hydrocarbons
b) $KMnO_4$ test: Dissolve 0.2 gm or 0.2 mL of the compound in 2 mL of acetone and add 2% solution of $KMnO_4$ solution drop.	solution gets decolorized	Presence of Hydrocarbons
c) Iodine test: Dissolve 2-3 drops of compound in 5ml of benzene to this add 5 mL very dil. solution of Iodine in Benzene and shake well.	Solution remains in Violet color	Presence of Hydrocarbons

PREPARATIONS OF DERIVATIVES

In general, the following derivatives have been recommended for different classes of organic compounds.

S.No	Class of organic compounds	Suitable derivative
1.	Carboxylic acids	Amides, anilides, ammonium salts nitro derivates in aromatic compounds
2.	Alcohols, (aliphatic hydroxyl compounds)	Acetyl or benzoyl derivative
3.	Phenols (aromatic hydroxyl compounds)	Acetyl or benzoyl derivative, 3,5-di nitro benzoyl, picrate
4.	Aldehydes & ketones	2,4 – dinitrophenyl hydrazones
5.	Carbohydrates	Osazones, acetyl derivatives
6.	Esters	Acids, amides, anilides
7.	Hydro carbons (aromatic)	Nitro derivatives, picrates
8.	Amino compounds (amines)	Acetyl, benzoyl, picrates
9.	Nitro compounds(Aromatic)	Poly- nitro, Amino
10.	Amides	Acids, picrates
11.	Aryl halides	Nitro, picrates

1. Derivatives of Carboxylic acids:

Place 0.5 gm of the acid into a flask fitted with reflux condenser add 2.5 to 5 mL of thionyl chloride and reflux gently for 30 min (it is advisable to place a plug of cotton wool in the top of the condenser to exclude moisture) rearrange the condenser and distill off the excess of thionyl chloride. Residue in the flask consists of the acid chloride of the acid chloride. t is used for the preparation of derivatives of acid.

(a) Amide Derivative:

Treat the acid chloride with about 10 mL of conc. ammonia solution and warm for a few min. If no solid separates on cooling evaporate to dryness on a water bath. Recrystallize the crude amide from water or dilute ethanol.

$$R\text{-}COOH + SOCl_2 \longrightarrow \underset{\text{(acid chloride)}}{RCOCl} + SO_2 + HCl$$

$$R\text{-}COCl + NH_4OH \longrightarrow \underset{\text{(amide)}}{RCONH_2} + HCl + H_2O$$

(b) Anilide derivative:

Dilute the acid chloride with 5ml of pure ether or benzene and add a solution of 2 gm of pure aniline in 15-20ml of some solvent until the order of the acid chloride has disappeared. shake with excess of dil. HCl to remove aniline and its salts wash with ether or benzene layer with 3-5 mL of water and evaporate the solvent. Recrystallize the anilide from H_2O.

$$R\text{-}COCl + C_6H_5NH_2 \longrightarrow R\text{-}CONHC_6H_5$$

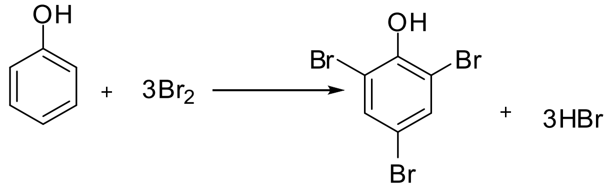
(Anilide)

2. Derivatives of Phenols:

a) Bromo Derivative:

To 0.5 mL of phenol add 10 mL of water and then add a solution of bromine in Glacial acetic acid drop wise with vigorous shaking the reaction is condensed in ice-bath.

Yellow colour solid is obtained. To this add ice pieces filter and recrystallize from alcohol.



(b) Benzoyl Derivative:

1 mL of the compound is taken in a R.B flask and 5 mL of 10% NaOH is mixed and added 2 mL of benzoyl chloride cork the flask and shake it vigorously for about 30 min. When a white solid separate. The completion of the reaction is indicated by the disappearance of the smell of benzoyl chloride add about 50ml of cold water to the flask. Filter the crude phenyl benzoate in a funnel and recrystallize with rectified spirit.

$$C_6H_5COCl + C_6H_5OH \longrightarrow C_6H_5COOC_6H_5 + HCl$$

(c) Acetyl Derivative:

To 1 mL of substance in a dry test tube add 3 mL of acetic anhydride and 1drop of conc.H_2SO_4 shake the contents for 2 min. and then pour it in to 10 mL water in a porcelain dish and stir until the only liquid solidifies. If solidification occurs in the test tube itself, then add water to the test tube and stir.

Filter the solid so formed and wash with water. Dry and crystallize from rectified spirit or acetone. Dry and determine the melting point.

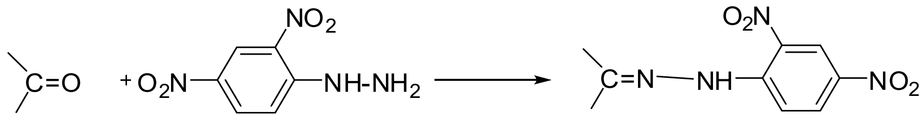
$$\mathrm{Ar.OH + CH_3COCl \longrightarrow ArCOOCH_3 + HCl}$$

(Acetate)

3. Derivatives of Carbonyl compounds:

(a) 2,4-dinitrophenyl hydrazone:

Take a small amount of solid 2,4-DNP in a dry test tube and 1 mL of conc. HCl and 8-10 mL of ethanol and then add small amount of the carbonyl compound and heat just to boiling allow to cool. Filter off 2,4 DNP and recrystallize from ethanol or Glacial acetic acid.



(b) Semi-carbazone:

Dissolve 1 gm of semi carbazide hydrochloride and 1 gm of crystalline solid acetate in 10 mL water and add small amount of the given organic compound and shake it then add alcohol and shake the mixture for 5 minutes allow to stand. The reaction may be accelerated, if necessary, by warming the mixture on a water bath for few minutes and then cool in ice water. Filter off the crystals and recrystallize from water or ethanol.

$$\mathrm{C_6H_5CHO + NH_2NHCONH_2 \longrightarrow C_6H_5CH{=}NHCONH_2}\ \text{(semi carbazone)}$$

4. Derivatives of Alcohols:

(a) Benzoate Derivative:

Take 1 mL of given Alcohol ,10 mL of acetone, 5 mL Benzoyl chloride, and 20 mL of 10% NaOH in a flask cool the contents cork the flask and shake the contents vigorously till the odour of Benzoyl chloride disappears. Filter the solid compound dry and recrystallize from alcohol(R-OH)

$$\mathrm{R{-}OH + C_6H_5COCl \longrightarrow R{-}COOPh + HCl}$$

(Benzoate)

(b) Phenyl Urethane derivative:

In a test tube mix 1mL of alcohol with about 3 gm of phenyl Isocyanate and keep the tube in boiling water for 10 min. cool and allow to stand when crystals of phenyl urethane appear. Filter the crystals and recrystallize from alcohol.

5. Derivatives of Ester:

(a) Hydrolysis

Boil 1 gm ester with 15 mL of 10 % NaOH under reflux for 30 min. Distill of the liquid through the same condenser the solution in the flask is acidified with dil. HCl a crystalline ppt is formed. Filter and recrystallize from alcohol.

6. Derivatives of Carbohydrates:

(a) Osazone formation

1 gm of the Carbohydrate is dissolved in 5 mL of water to this add phenyl hydrazine hydrochloride and crystalline solid acetate in 4 mL of water. Stopper the tube loosely with a cork and immersed in a beaker containing boiling water. shake periodically and note the exact time required for the appearance of precipitate of osazone. Filter the solid product and recrystallize from alcohol.

(b) Acetyl Derivative

To 1 gm of Carbohydrate add 7 gm of solid acetate in a boiling tube fitted with an air condenser add into it 5 mL of acetic anhydride and heat the contents with occasional shaking on a water bath until a clear solution is obtained. Continue heating for 1hr more and then pour the hot solution into ice-water slowly stir the contents vigorously. Filter the solid dry and recrystallize from diisoamyl alcohol or methylated spirit.

7. Derivatives of Amines:

A. For Derivatives of Primary and Secondary Amines

(a) Acetylation

The amine 0.5 gm and acetic anhydride (1 mL) are boiled for 5 min with the addition of a dehydrating agent like fused sodium acetate or zinc chloride (0.5g) or a few drops pyridine. The solution is poured into 10 mL water, filtered and crystallized from dil. ethanol

(b) Benzoylation

Dissolve 0.5 g of amine in 5 mL of water contained in a test tube, add 0.5 cc of benzoyl chloride and then 10 % sodium hydroxide solution, until it is strongly alkaline. cork the test tube and shake vigorously. Cool under the tap, pour the oily product into plenty of water and rub with a glass rod to induce crystallization. Filter, wash with plenty of water containing a little alkaline and finally with water, recrystallize the solid from 50% alcohol.

(c) Azo dye

0.2 gm oh the amine is dissolved in 5 cc. of alcohol and 2cc. of concentrated hydrochloric acid are added. The mixture is cooled in ice and a slight excess of cooled saturated solution of sodium nitrite is added. To this mixture add cooled solution of 0.2 gm of β – naphthol in 2cc. of 10% NaOH. The precipitate gradually separates out. The mixture is diluted with water. The precipitate is filtered, dried and recrystallized from light petroleum. Determine the melting point.

B. For Derivatives of Tertiary Amines

(a) P-Nitroso derivative

Dissolve 1 gm of compound in 10 mL of dil. HCl. Cool to 0-5 °C and slowly add with stirring a solution of 0.7 gm of sodium nitrate in 4 mL of water. After 20-30 min filter the precipitated yellow HCl. Dissolve the ppt in the minimum volume of water. Add a solution of Na_2CO_3 to decompose the HCl and extract the free base with ether. Evaporate the ether and recrystallize the residual green crystals of P-Nitroso dimethylaniline from toluene.

(b) Picrate derivative:

Dissolve 0.5 gm of amine in the 5 mL of rectified spirit and add 5 mL of picric acid solution in ethanol, warm on a water bath for 5 min. and allow to cool. Collect the picrate ppt and recrystallized it from boiling water or ethanol.

8. Derivatives of Amides:

(a) Hydrolysis

The amides are easily hydrolyzed by 15 % aq. NaOH, Ammonia is evolved out. The separation is neutralized with acid. If the acid is insoluble, it is filtered and recrystallized from boiling water. If the acid is soluble, the acid is converted into corresponding anilide or toluide and identified.

In case of aromatic compounds, the hydrolysis is carried out differently. 1 gm of the substance and 10-15 cc of conc. HCl are boiled in a small flask fitted with an air condenser, for half an hour. The separated acid, on cooling is filtered and recrystallized from boiling water. If the acid is soluble, then it is identified by preparing suitable derivative.

(b) Anilides

Amides are easily converted into anilides by heating with aniline, ammonia being evolved.

$$RCONH_2 + ArNH_2 \longrightarrow RCONHAr + NH_3$$

The compounds generally given for analysis and type of derivative that should be prepared.

9. Derivative of Thiourea:

Take 3.5 gm of compound and 0.5 gm of Benzyl chloride and 3 ml of alcohol, reflux it for a considerable period. Cool, filter the ppt and recrystallize from alcohol.

10. Derivatives of Hydrocarbons:

(A) Nitration:

(i) Mono nitro derivative:

0.25 gm of the hydrocarbon is added solely to a mixture of 1 cc con. HNO_3 and 1 cc conc. H_2SO_4 shaking thoroughly after each addition. the mixture is gently warmed for a minute by immersing in a hot water bath maintained at 60-70 °C. After cooling, the reaction mixture is poured into a little ice water. The nitro compound usually separates as oil and can be purified by crystallization from alcohol. Determine the M.P.

(ii) Poly nitro derivative:

Add a mixture of 1cc of fuming nitric acid and 1 cc of 5% fuming H_2SO_4 or ordinary conc.H_2SO_4 to 0.2 of the hydrocarbons. The mixture is warmed on the boiling water bath for 2 to 3 min. After cooling the reaction mixture is poured into a little ice water. The nitro compound usually separates as an oil and can be purified by crystallization from alcohol. Determine the M.P

(B) Picrates:

Make a saturated solution of hydrocarbon in 1 cc of benzene or alcohol and add a similar solution of picric acid. A fine golden yellow ppt of the picrate separates. Filter dry and determine the M.P

(C) Oxidation of side chain:

Make 2 cc of substituted aromatic hydrocarbon in a 100 cc R.B flask, add 2 cc of 2N alkali and boil under reflux with continuous periodic addition of 3% permanganate solution dioxide and pass sulphur dioxide or add potassium Meta bisulphite to the filtrate. benzoic acid is precipitated on cooling. Filter, recrystallize from water and find its M.P.

To 1 gm of the compound add 4 mL of conc. H_2SO_4 & 4 mL of conc. HNO_3 with shaking and cool the test tube in cold water. Heat the contents over a water bath at 5-60 °C for 15 min. Cool and pour the contents in ice water. Filter off the solid, wash with cold water, crystallize from alcohol & dry it.

HYDROCARBONS AND SUBSTITUTED HYDROCARBONS:

(1) Aldehydes: (a) Benzaldehyde (b) cinnamaldehyde	1.Oxidation 2.Phenyl hydrazone 3.Semi carbazone	1) Benzoic (121 °C), 2) cinnamic (133 °C) 1)158 °C 2) 168 °C 1) 224 °C 2) 211 °C
(2) Ketones: (a) Benzophenone (b) Acetophenone	1. Oxime 2.Phenyl hydrazone 3.Semi carbazone	1) 144 °C 2) 59 °C 1) 137 °C 2) 105 °C 1) 199 °C 2) 165 °C
(3)PHENOLS:		
1.(a) Phenol (b) Nitro phenol (c) chloro phenol	1) Nitration 2) Bromination	1)Picric acid (122 °C) 1) 95 °C 2)117 °C 1) 69 °C 2) 59 °C
2. *m* - cresol	1) Nitration	
4.5 drops of cresol dissolved in 2 cc of conc. H_2SO_4 is poured with stirring into a mixture of 3 cc of conc. HNO_3 in a boiling tube and heated for ten minutes on a boiling water bath. The contents are cooled and poured into ice water and the precipitate crystallized from water to which a few drops of conc. HCl have been added (106 °C)		
	2) Oxidation with Alk. $KMNO_4$ to m – Hydroxy Benzioic acid (200 °C)	
3. *o* - Cresol :	1) Oxidation to salicylic acid (159 °C) 2) Picrate derivative (88 °C) 3) Dibromo derivative (56 °C)	
4. *p*– Cresol :	1) Benzoate derivative 2) Bromo derivative	
CARBOHYDRATES:		
(1) (a) Glucose (b) Fructose (c) Sucrose	1) Osazone derivative (205 °C) 2) acetate 1)132 °C 2) 109 °C 3) 69 °C	
AMINES		
(1) (a) Aniline (b) Chloro aniline	1) Azo dye 2) Benzoyl derivative 1)132 °C 2)109 °C 3) 69 °C	
(2) N,N – Dimethyl Aniline Picrate (162 °C), P-Nitroso (85 -87 °C)		

ACIDS:		
(1) Benzoic acid	1) Nitration (140 °C) 2) Benzamide (128 °C)	
(2) Salicylic acid	1) Nitration (226 °C) 2) Benzoylation (68 °C) 3) acetylation (ASPRIN) 135 °C	
(3) Phthalic acid	1)	
To 0.2 gm of the contained in a test tube fitted with refluxing arrangement add 1 cc of aniline heat about 20 min. Boil the reaction product with 10 c.c. of alcohol (1:1) filter and recrystallize from alcohol.		
ESTERS (1) (a) Benzyl acetate (b) Ethyl cinnamate (c) Ethyl benzoate	Hydrolysis Amide	1) 121 °C, 2) 133 °C, 3)121 °C 1) 129 °C, 2) 147 °C, 3) 129 °C
Amide. (I) Benzamide	1) Hydrolysis (121 °C) 2) Anilide (160 °C)	

Sulphur Compounds:

(a) Thiourea (M.P. 175-177 °C)   (b) Sulphanilic acid (M.P.)

(c) Diphenyl thiourea(M.P.151 °C)   (d) Phenyl thiourea (M.P. 154 °C)

Report:

S.No.	Compound	M.P/B.P	Derivative 1	M.P/B.P	Derivative 2	M.P/B.P
1.						
2.						

Result Format: Unsaturated Aromatic Carbonyl or Acids, Basic, Neutral compounds etc.

References

1. Organic Analytical Chemistry, Theory and Practice, Jag Mohan, Narosa Publishing House Pvt.Ltd. New Delhi.
2. Analysis of binary Organic Mixture, Dr. B. Hari Babu, Own Publication, Guntur.
3. Some sources are collecting from internet website browser.