

Experiment VII. Identification of an unknown organic compound from physical properties, chemical reactivity and infrared spectroscopy.

Review the relevant mechanisms in any introductory organic chemistry textbook. See, for example, KPC Vollhardt and NE Schore, *Organic Chemistry*.

Introduction

Structure elucidation or identification of chemical compounds is one of the more challenging tasks a chemist will face. Many branches of chemical science are involved in identification of substances. Some examples are:

- a) Characterization of reaction products.
- b) Screening of new drug candidates from natural sources, i.e.; plants, animals, fungi or microorganisms.
- c) Analysis of deadly toxins in medicinal chemistry and forensic medicine.

The steps involved in structure elucidation or identification of an unknown compound make the process a logical puzzle. In order to solve this problem, it requires some problem solving skills, planning and preparation. The unknown you will be provided with is among the compounds listed in tables at the end of the manual. Some of these compounds are quite hazardous so use proper precautions.

You are required to perform a variety of chemical experiments to establish the identity of the unknown. Experiment VII will require you to use your own initiative and work individually. **You are therefore allowed to use this lab handout during the lab period and you don't need to copy the procedures to your lab notebook.** Your prelab should include a flowchart that will describe the possible routes for identifying the unknown. You are encouraged to perform enough tests to positively identify your unknown. There is of course a minimum amount of data required.

The identification process begins with classification of the compound based on its functional groups. The presence of a particular functional group can be deduced from solubility tests and an IR spectrum. In addition, specific chemical reactions (“chemical tests”) are used to reveal the presence of certain functional groups. The chemical tests are characterized by a visual change that indicates if a reaction took place. Common visual outcomes are color change, formation of precipitate or formation of bubbles. For example, for identifying an alcohol, we can react the unknown with chromic acid. If an oxidation reaction of the alcohol will occur, the color of the solution will change from orange to green. Therefore the change of color indicates that the unknown may be an oxidizable alcohol.¹

Once the functional group is identified, the specific identity of the compound can be achieved by comparing the melting point or boiling point of the unknown to literature values of known compounds. Several tables of possible unknowns are provided at the end of this manual. To further confirm the identity of the compound, a sample of the unknown is reacted with specific reagents to give a new compound (“derivative”). The derivatives are compounds that can be purified easily and have a well-defined melting point. The melting point of the derivative helps to further identify the compound. For example, let's assume that unknown sample was identified to be a ketone with a boiling point of 129°C. Looking at the table of possible ketones will reveal two possible candidates (2-hexanone and 5-Hexan-3-one) that have identical boiling points. However, when a derivative is prepared, the melting points of each derivative are different (122 and 102 respectively). Therefore the melting point of the derivative confirms the identity of the unknown.

¹ Aldehydes will also give a positive reaction.

Your Report: Your report should include the following:

1. The number of the unknown, the structure determined and the amount used.
2. Results from Physical and chemical tests for the unknown and the derivatives prepared.
3. A sample of the unknown and of each derivative prepared.
4. Discussion of the “logic puzzle” you deciphered that led you to the structural assignment.

Note: Remember that unknown compounds should be treated as possibly hazardous substances. Wear gloves since some organic compounds may be irritants. Be sure to dispose waste products properly. You will use many test tubes during this experiment. Clean all test tubes before disposing them. First drain the liquid and then rinse them with acetone. If you can not dissolve a chemical in the test tube, then place the test tube in a special designated box.

Part A: Physical properties.

1. Melting point or boiling point determination.

2. Solubility Tests

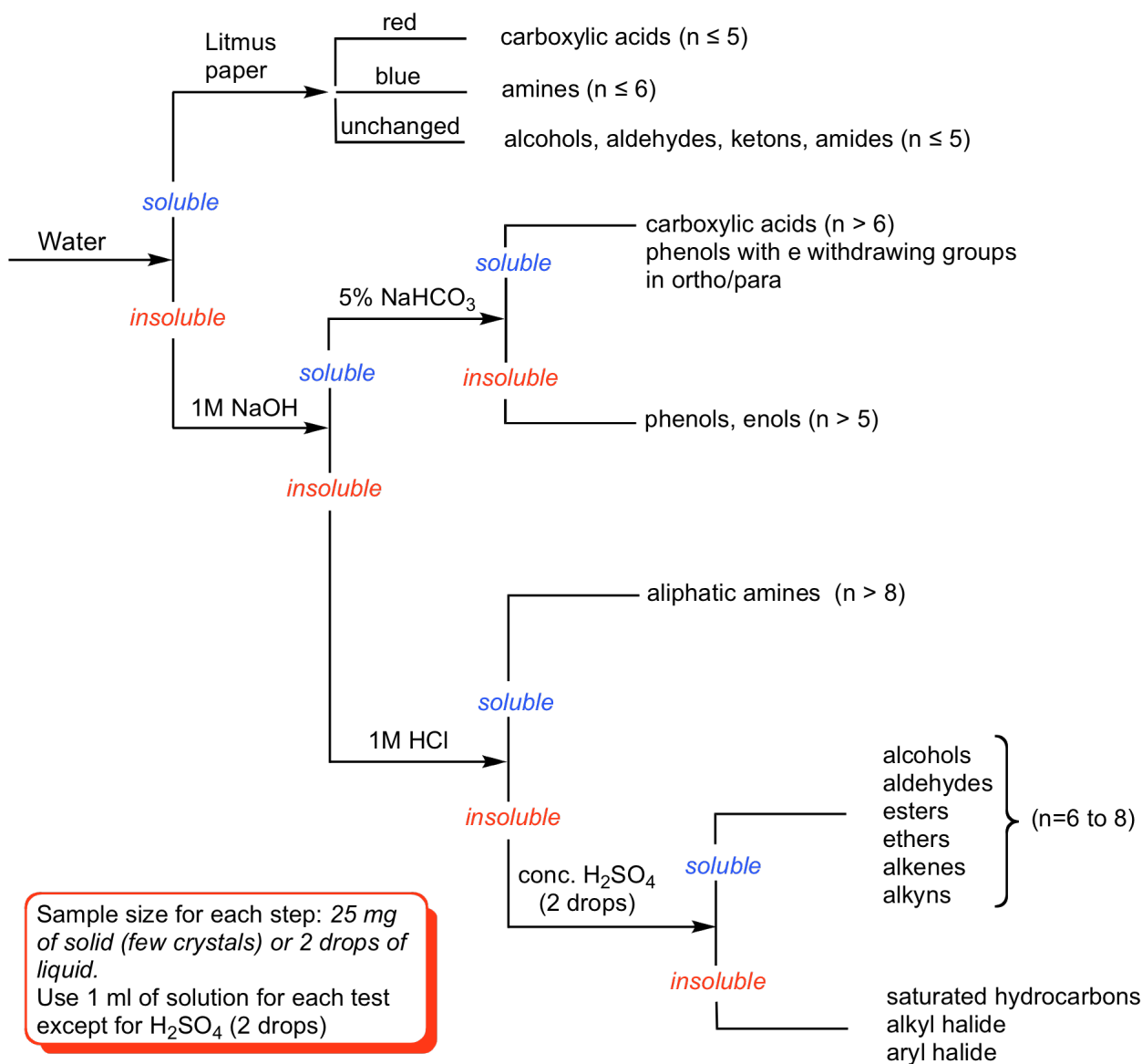
The solubility of an organic compound in water, dilute acid, or dilute base can provide useful evidence about the presence or absence of certain functional groups. The solubility reveals the presence of functional groups that can be protonated or deprotonated. Since various functional groups have different pKa, the solubility at a given pH is indicative of a particular group. A flowchart showing the sequence of solubility tests along with the appropriate conclusions is shown below. Make sure that you can correlate the solubility behavior with the reactivity of the group. For example, carboxylic acid will dissolve in both NaOH and NaHCO₃, while phenol that is less acidic will dissolve in NaOH. This reflects the different stability of the conjugate bases.

Remember that the solubility of a molecule in aqueous solution is influenced by the ratio between hydrophobic and hydrophilic groups. Therefore note that the solubility chart indicates also the number of carbons.

Procedure:

Follow the solubility chart. This flowchart is unusual, as each test requires a new sample. Place few crystals (~25 mg) or two drops of the unknown in a test tube. Crush the crystals with a spatula if necessary. Add about 1 mL of solution and gently mix. Clear solution indicates that the compound is completely soluble.

solubility tests flowchart



Sample size for each step: 25 mg of solid (few crystals) or 2 drops of liquid.
Use 1 ml of solution for each test except for H₂SO₄ (2 drops)

Part B: Infrared spectroscopic analysis.

Perform an Infrared spectral analysis of your unknown compound. For liquid samples use salt plates. Be careful with the salt plates as they are fragile and expensive. Do not use water or acetone in their handling and wash them with methylene chloride using the provided funnel. Why are water and acetone discouraged?

For solid samples form a KBr pellet:

1. Weigh 1-2 mg of sample and 70 mg of KBr. Place both in a clean agate mortar.
2. Grind the solids together using a pestle until a very fine powder is obtained and there is no evidence of crystallinity. This will take few minutes.
3. Place the powder inside the KBr holder and press the powder to form a pellet. Your TA will demonstrate the process

Part C: Chemical tests for the presence or absence of organic functional groups.

It is important to perform Classification Tests on known compounds as well as your unknown so that you can easily see the difference between a positive and negative result. This will also let you know if the reagents for the tests are behaving properly. Below are several chemical tests (reactions) that are used for determining the presence or absence of organic functional groups. The procedures for the chemical tests listed below are provided in Part E.

<u>Functional Group</u>	<u>Test</u>	<u>Derivative</u>
alcohol (1°, 2° or 3°)	Lucas Jones	3,5-Dinitrobenzoate
amine	Hinsberg Benzamide	Benzamide
aldehyde	2,4-DNP Jones	2,4-DNP Semicarbazone
ketone	2,4-DNP Iodoform	2,4-DNP Semicarbazone
carboxylic acid	Solubility in a base	Amide
ester	Hydroxamic acid test	3,5 dinitrobenzoate
halogen (R-X)	Beilstein	
phenol (Ar-OH)	Ferric Chloride	3,5-Dinitrobenzoate

WARNING! Most tests and derivative preparations require the use of *hazardous reagents*. Perform all of these procedures in a fume hood with *adequate personnel protective equipment*.

Part D: Derivatives of unknown organic compounds.

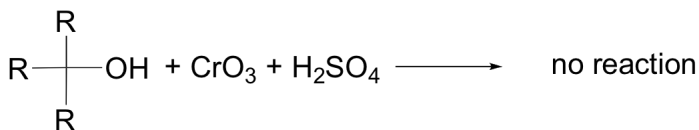
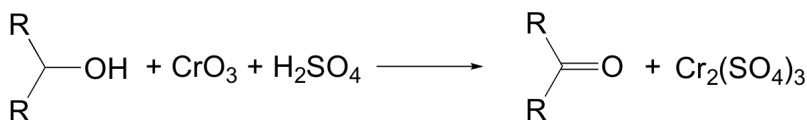
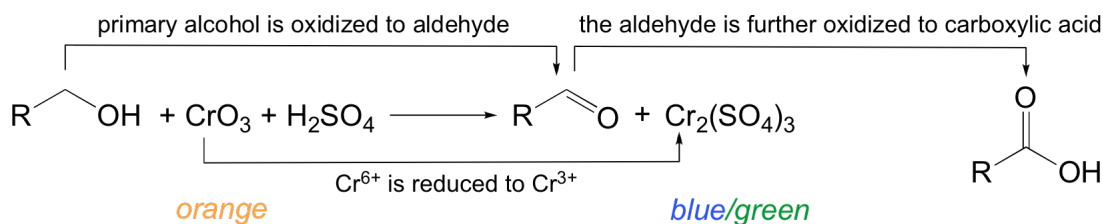
The presence of a functional group can also be confirmed by the preparation of a suitable solid derivative along with comparing the melting point obtained to that known for the derivative. A recrystallization is likely to be necessary to obtain an accurate melting point. Compare the melting point of the derivatives of known compounds to the melting point that you obtained for your derivative. The derivative types listed in the table above have been selected because; i) the conversion to the derivative is a relatively simple reaction, ii) these derivatives are known to be easier to purify via recrystallization, and iii) the melting points are known for many of the derivatives. If you are having difficulty in applying your specific unknown to the general instructions, please ask your TA for assistance. Include mechanisms of formation for any derivatives in your notebook and lab report. Use IR to prove that you obtained the correct derivative.

Part E: Procedures for chemical tests for organic functional groups.

Perform each test with three samples in parallel: your unknown, a known compound that carries the functional group that you are testing for (positive control) and a known compound that doesn't carry the functional group that you are testing for (negative control). This will ensure that you performed the tests accurately.

I. Identification of alcohol functional groups:

a) Jones oxidation test



Reagents:

Jones reagent (Chromic acid, in acid hood)

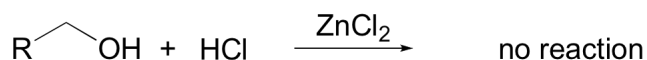
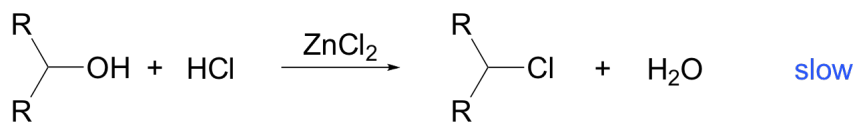
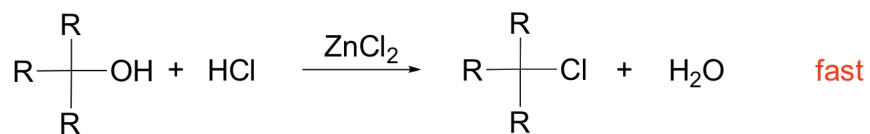
Acetone (spectral grade, in solvent hood)

Procedure:

Transfer one drop of the unknown (if a solid, dissolve 50 mg in a few drops of spectral grade acetone) to a small test tube and add two drops of Jones reagent. Stir the mixture for about 5 seconds and note any color changes. Primary and secondary alcohols are oxidized quickly by the Jones reagent. A reaction is apparent when the initial orange color of the Jones reagent turns to a blue-green color (a positive test) and provides an indication for the presence of a primary or secondary alcohol. Note: i) No color change (a negative Jones test) is observed for tertiary alcohols since they are not oxidized. ii) Color change (a positive test) is also observed for aldehydes since aldehydes are readily oxidized with the Jones reagent to the corresponding carboxylic acid.

NOTE: Amines can react with the Jones reagent to give a dark-brown-black heavy ppt., with heat, which is not a normal positive result.

b) *Lucas test*



Reagents:

Lucas reagent (10ml HCl/16g ZnCl₂ anhydrous, in acid hood)

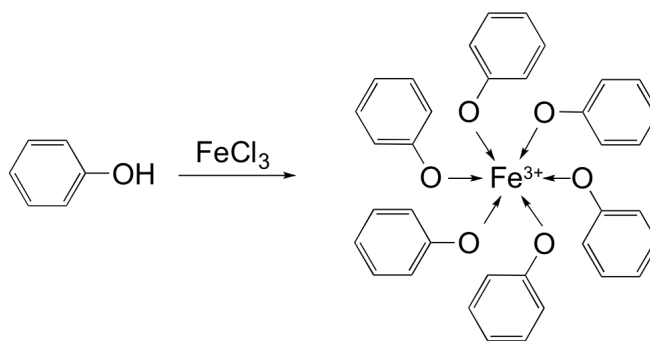
Procedure:

Transfer two drops of unknown to a small test tube and add ten drops of Lucas reagent. Shake or stir the mixture with a glass rod and note the time required for mixture to become cloudy or to separate into two layers. There will be an immediate cloudiness or formation of two layers if the unknown is a tertiary alcohol. A cloudy mixture should appear within 5 - 10 minutes if the unknown is a secondary alcohol. Hindered secondary alcohols may require gentle warming in a hot water bath. Primary alcohols are very slow to react and a cloudy mixture may not be observed.

NOTE: Amines can react violently with the Lucas test to give a white powdery ppt., with heat, which is not a normal positive result.

II. Identification of Phenols and Enols

a) *Ferric ion test*



Reagents:

1% ferric chloride aqueous solution (freshly prepared by student, FeCl₃ is located in the balance room).

Absolute ethanol (in solvent hood).

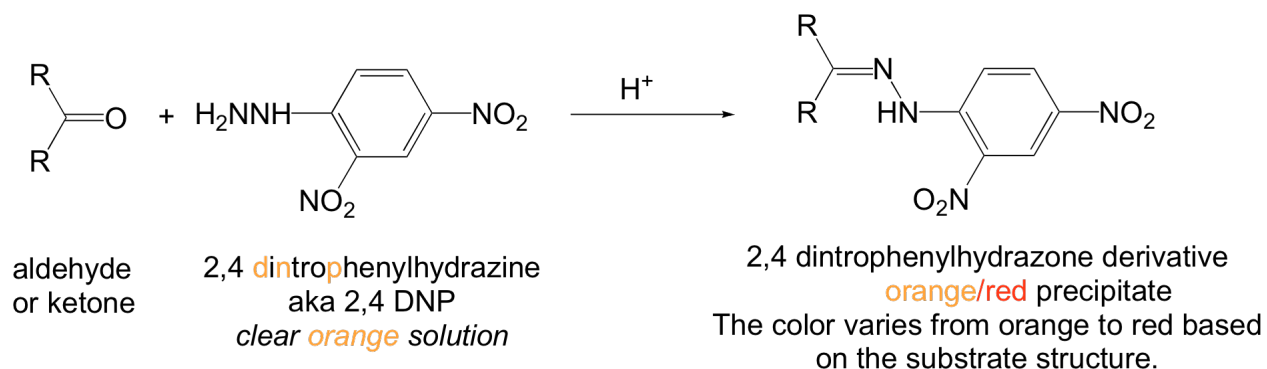
DI water

Procedure:

Transfer one drop of unknown (if a solid dissolve a few crystals in ethanol) to a small test tube containing 1ml freshly prepared 1% Ferric Chloride (aq) solution. The appearance of red, purple or blue color (positive test) indicates that the unknown is a phenol or an enol.

III. Identification of aldehyde and ketone functional groups

a) 2,4 Dinitrophenyl hydrazine test (DNP)



Reagents:

2,4 DNP reagent (1g 2,4 DNP/5ml H_2SO_4 /10ml H_2O /35ml EtOH in reagent hood)

Ethanol 95% (in solvent hood)

Procedure:

Transfer two drops of unknown (if a solid, dissolve a few crystals in ten drops of ethanol) to a small test tube and add 7 or 8 drops of 2,4 DNP reagent. Stir the contents with a thin glass rod and note any color changes. Formation of a red - yellow precipitate (a positive test) indicates the presence of an aldehyde or ketone functional group. Esters generally do not react.

NOTE: Amines can also react with the 2,4-DNP reagent and give a false positive.

b) Jones test

Reagents:

Jones reagent (Chromic acid, in acid hood).

Acetone (spectral grade, in solvent hood)

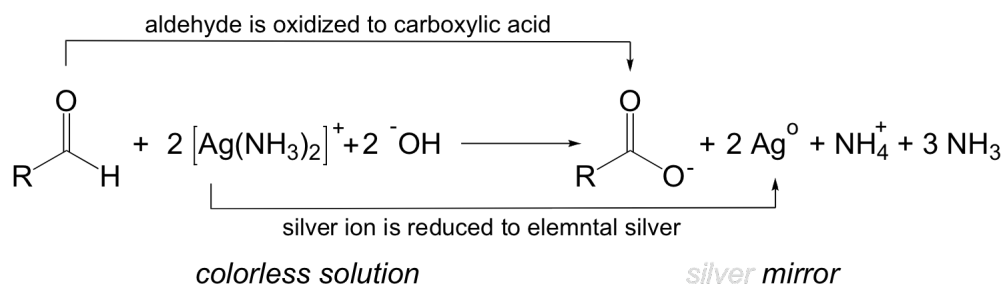
Procedure:

Transfer two drops of unknown (if a solid, dissolve a few crystals in ten drops of spectral grade acetone) to a small test tube and add a few drops of Jones reagent. A green precipitate of Chromous salt (III) is a positive test. Aliphatic and aromatic aldehydes give a precipitate within 30, and 30-90 sec. Note: the Jones reagent also reacts with primary and secondary alcohols (see I above).

NOTE: Amines can react with the Jones reagent to give a dark-brown-black heavy ppt., with heat, which is not a normal positive result.

IV. Distinguishing between aldehyde and ketone functional group.

a) Tollens test



Reagents:

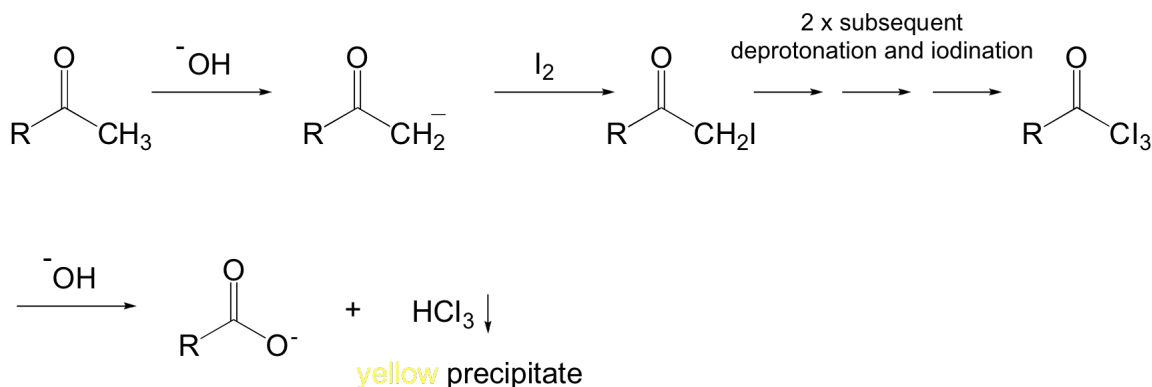
- 5% AgNO₃ aqueous solution (in acid hood)
- 10% NaOH aqueous solution (in base hood)
- conc. Ammonium Hydroxide (NH₄OH, in base hood)
- 95% Ethanol (in solvent hood)

Procedure (Ref: pp. 221-222):

Transfer ten drops of 5% AgNO₃(aq) and one drop of 10% NaOH(aq) to a test tube. A brown precipitate should form. With very thorough stirring add one drop of concentrated NH₃(aq). The brown precipitate should dissolve, if not add another drop of concentrated NH₃(aq) and stir thoroughly. No more than 3 drops of concentrated NH₃(aq) should be necessary to dissolve the brown precipitate. Avoid adding an excess of concentrated NH₃(aq). To this reaction solution add one drop of the unknown (if the unknown is a solid, use 50mg). If the unknown is insoluble in water, then dissolve 2 drops or 50 mg of solid unknown in 0.5 ml of 95% EtOH. Again, stir the contents thoroughly, and allow the reaction mixture to stand for 10 minutes at room temperature. The observation of a silver coating or lining of the glass sides of the test tube ("silver mirror") is a positive test for the presence of an aldehyde functional group. Ketones do not produce a "silver mirror". If no reaction has occurred, place the test tube in the sand bath (or warm water bath) and warm the reaction mixture to 40°C for 5 min. Observe the result. Note: Some sugars, acyloins, hydroxylamines, and substituted phenols give a positive Tollens test.

V. Distinguishing between a ketone and a methyl ketone functional group.

a) Iodoform test



Reagents:

- Iodoform reagent (3g KI/1g I₂/20ml H₂O, in acid hood)
- 10% NaOH (in base hood)
- 1-propanol (for dissolving solid sample, in solvent hood)
- Dioxane (in solvent hood)
- DI water

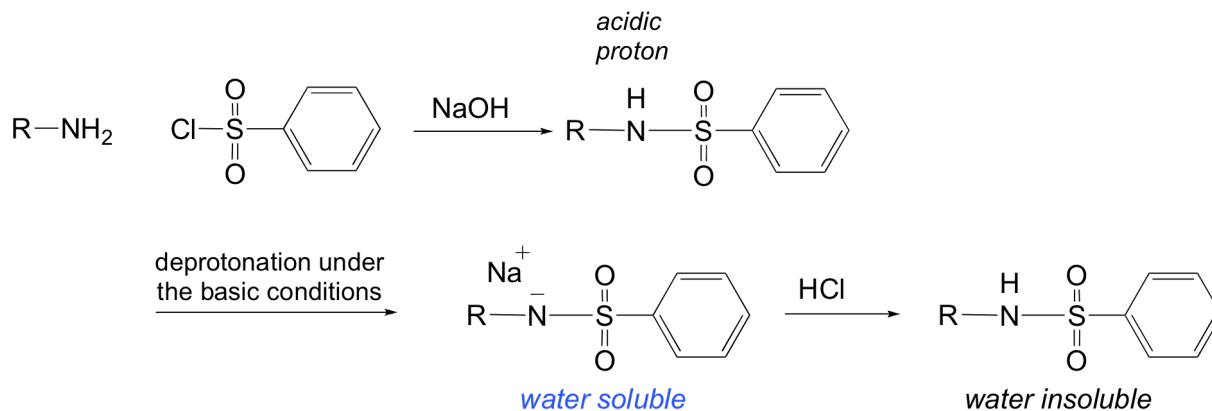
Procedure:

Transfer two drops of unknown (if a solid, dissolve few crystals in dioxane) to a small test tube and add five drops of 10% NaOH(aq). Stir or shake the contents thoroughly then add the Iodoform reagent drop wise until the dark iodine color persists. The presence of a yellow precipitate (CHI₃ namely, iodoform) is an indication (positive iodoform test) that a methyl ketone functionality is present. If a precipitate is not present within 3 to 5 minutes, warm the solution slightly (~60 °C); if the color fades, add more KI₃ until the color remains for 1-2 minutes. Then add 1-2 drops 10% NaOH to remove excess iodine (become colorless) and dilute the mixture with cold water. Note: The Iodoform reagent also reacts

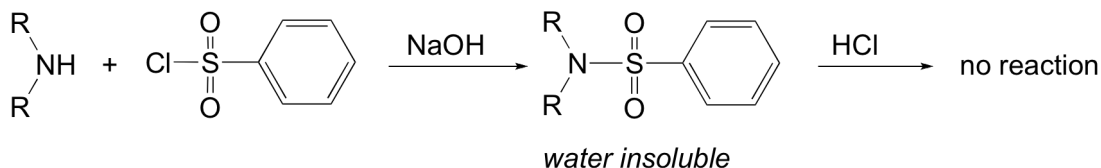
Transfer eight drops of 10% Copper Sulfate solution (aq) to a small test tube and add a drop of the unknown (or few crystals if a solid). The appearance of a blue-green coloration or precipitate (positive test) indicates the presence of an amine functional group. Note: ammonia gives a positive test.

b) *Hinsberg test*

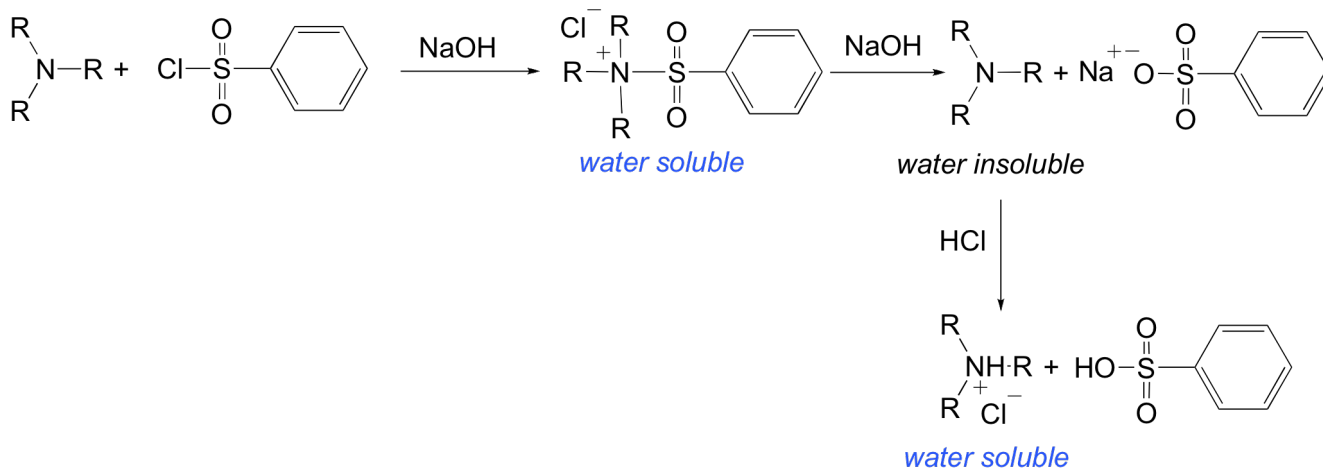
Primary amine



Secondary amine



Tertiary amine



Reagents:

Benzenesulfonyl chloride (in reagent hood)

10% NaOH (in base hood)

10% HCl (in acid hood)

DI water

Procedure: (perform these reactions in the hood!)

Transfer 0.1ml (~2 drops) of your unknown (or 100 mg if a solid) to a 25 ml Erlenmeyer flask and add 0.2 ml (4 drops) of Benzenesulfonyl chloride. Stir thoroughly for 1 minute and add 5 ml 10% NaOH (aq). Stir the reaction mixture very thoroughly for 5 minutes or longer until the oily sulfonyl chloride has reacted. Test the reaction mixture with litmus paper to ensure that the reaction contents are alkaline. Warm the reaction contents in a hot water bath for few minutes then cool the reaction mixture to room temperature and note whether or not a residue (oil) or precipitate is present in the reaction mixture.

If a precipitate or residue is not present in the reaction mixture, treat the reaction solution with 10% HCl (aq). The formation of a precipitate upon acidification of the reaction solution is an indication that the unknown is a primary amine.

If a precipitate or residue is present from the reaction of your unknown with Benzenesulfonyl chloride and NaOH(aq) then separate the residue or precipitate from the reaction mixture and test for the solubility of the residue or precipitate in 10% HCl (aq).

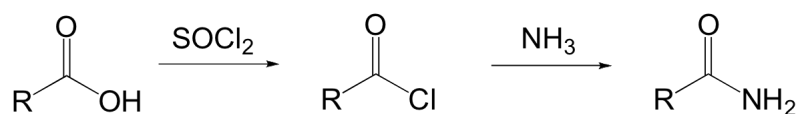
If the residue or precipitate is insoluble in 10% HCl (aq) then the unknown compound is a secondary amine.

If the residue or precipitate is soluble in 10% HCl (aq) then the unknown is a tertiary amine.

Part F: Procedures for the preparation of derivatives.

I. Preparing derivatives of carboxylic acids:

a) Preparation of an amide.



Reagents:

Thionyl Chloride (2ml/procedure; perform in the hood because HCl and SO₂ gases are generated. (in the reagents hood))

DMF (in solvent hood).

Methylene Chloride (10mlx3/procedure, in solvent hood).

Concentrated. Ammonium Hydroxide (10-15ml/procedure, in base hood).

Absolute Ethanol (10ml/procedure, in solvent hood).

Sodium Sulfate anhydrous (balance room).

Procedure:

Caution! This procedure (both parts) must be carried out inside the hood!

Part 1: Preparation of the intermediate acid chloride:

Transfer 0.4g of the unknown to a dry 5 mL conical vial containing spin vane or 2 boiling chips then add 2 mL of thionyl chloride (bp=78°C). Equip the conical vial with a reflux condenser and drying tube (CaCl₂ anhydrous). Stir at room temperature for 10 min and then heat the reaction contents to a gentle reflux using a sand bath. After 15 minutes of reflux, cool the reaction contents to room temperature and

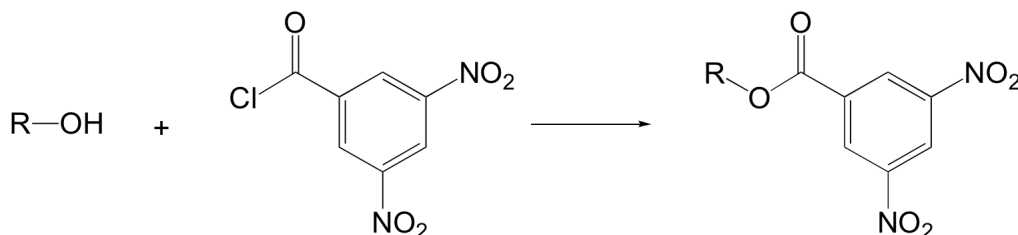
transfer the reaction mixture to a 100 mL beaker. Rinse the conical vial three times with 1 mL methylene chloride and transfer the rinses to the 100 mL beaker containing the reaction mixture.

Part 2: Preparation of the amide derivative.

Cool the reaction mixture above (100 ml beaker) to 0 °C with an ice bath. Similarly, cool 15 ml of concentrated ammonium hydroxide (NH₃ aq). Add the 15 ml of concentrated ammonium hydroxide **dropwise** with stirring to the acid chloride in the 100 ml beaker. **The addition will produce smoke and may produce some fizzing sounds. Don't panic, just add it slowly.** A precipitate (the amide) may form during this process. Following the addition, remove from ice bath, allow the reaction contents to come to room temperature and stir the mixture for an additional 5 minutes. Extract the product (amide) from the biphasic mixture with 10 mL of methylene chloride. If undissolved solids are present, stir the mixture to dissolve. If solids do not dissolve add a few more mLs of methylene chloride. Transfer the biphasic mixture to a separatory funnel and separate the methylene chloride layer from the aqueous layer. Extract the aqueous layer two more times with 10 ml of fresh methylene chloride. Combine the methylene chloride fractions and evaporate the solvent using a warm sand bath. Recrystallize the solid product remaining from the evaporation by adding 10 mL absolute ethanol with stirring and warming until all the crude amide is dissolved. Cool the solution in an ice bath. The crystals should appear within a few hours. Occasionally, the solution will need to sit overnight for crystal formation. Collect the crystals using the Hirsch funnel and wash with DI water. Dry the crystals and then determine the melting point and obtain an IR spectrum. Make the appropriate spectral assignments.

II. Preparing derivatives of alcohol and phenol

a) Preparation of 3,5-dinitrobenzoates:



Reagents:

3,5-dinitrobenzoyl chloride (0.5g/procedure, Keep it in desiccator! (in the hood)).

2% Na₂CO₃ (10ml/procedure, in base hood).

absolute ethanol (10-20ml/procedure (in solvents hood)).

diethyl ether (in solvent hood)

pyridine (3ml/procedure, (in solvent hood))

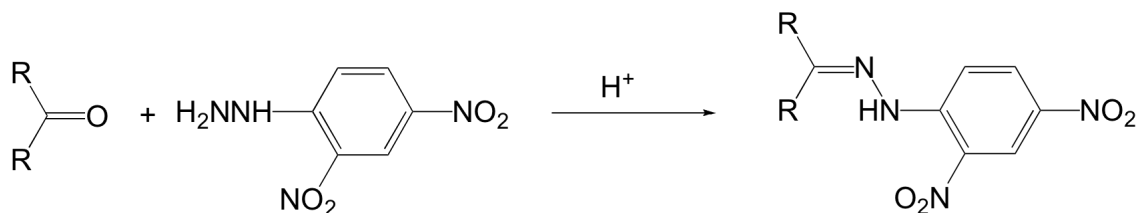
DI water

Procedure:

Dissolve 0.8g or 1ml unknown in 3ml of pyridine (bp = 115 °C) in a 25 ml Erlenmeyer flask. To this solution add 0.5g of 3,5-dinitrobenzoyl chloride, one or two boiling stones and warm the reaction mixture to boiling using a hot sand bath (125 -145 °C). Following a 5 minute boiling of the reaction contents, cool the reaction mixture to room temperature and slowly add 10 ml of DI water. Place the beaker in an ice bath to encourage crystallization. Vacuum filter and wash the product with 2% Na₂CO₃ (~5-10ml), then with 5-10ml DI H₂O. Recrystallize the product by dissolving the solid in absolute

ethanol while stirring and heating until all the solid is dissolved (~10-20 mL). Add DI water dropwise until the solution is just cloudy. Cool the turbid solution in an ice bath and collect the resulting crystals using a Hirsch funnel. Dry the product, determine the melting point and obtain an IR spectra. Make the appropriate spectral assignments.

III. Preparing derivatives of aldehydes and ketones.



Both derivatives are required.

a) Preparation of 2,4-dinitrophenylhydrazones:

Reagents:

2,4-dinitrophenylhydrazine reagent (50mg 2,4 DNP/1ml DMF (N,N, dimethyl formamide)

Absolute ethanol (2-3ml/procedure in solvent hood)

10% HCl (aq)

DI water

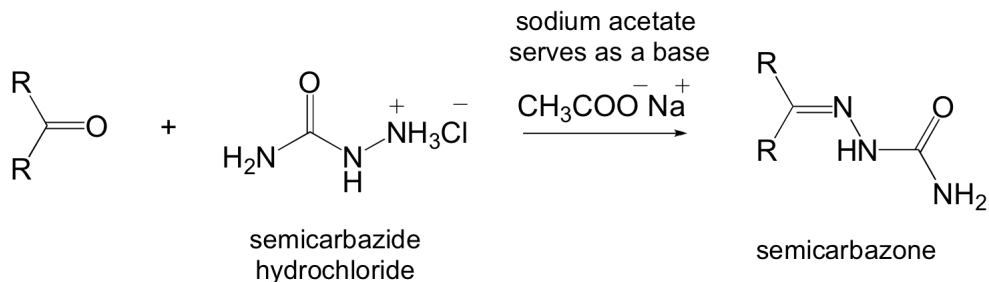
Procedure:

Note: if the aldehyde or ketone is a solid, prepare a solution by dissolving 0.5g of sample in 1ml of absolute ethanol. Use the solution for preparing the derivative.

Transfer 2ml of 2,4 DNP/in DMF reagent into a 10x130mm test tube. Add 10 drops of aldehyde or ketone (in liquid form or solution) while stirring the solution with a glass rod or a spatula. Add 8-10 drops of 10% HCl and continue stirring. A yellow/or orange/red precipitate is formed within few minutes. If a precipitate was not formed, add few more drops of 10% HCl. Cool the test tube to 0°C in an ice bath for few minutes to increase the yield of precipitation. Collect the precipitate by vacuum filtration using a 2" Buchner funnel with 2 pieces of filter paper #50 (4.25cm). Wash the precipitate with 1ml of 10% HCl (aq), followed by a second washing of the precipitate with 1ml of DI water.

The precipitate (2,4 DNP derivative) should be recrystallized from absolute ethanol. Transfer the solid into a small Erlenmeyer (30 ml) and add about 2 ml of absolute ethanol. Warm the suspension until boiling. If the solid is not completely dissolved, add more absolute ethanol, while stirring it, until all the solid is dissolved. Add dropwise DI water (~10 drops) while stirring the solution until precipitate appears, followed by cooling in an ice bath. Collect the crystals by vacuum filtration using a 2" Buchner funnel with 2 pieces of filter paper #50. Use 1ml DI water to wash the crystals. Dry the product in a desiccator and then record the melting point of the Derivative.

b) Preparation of semicarbazones:



Reagents:

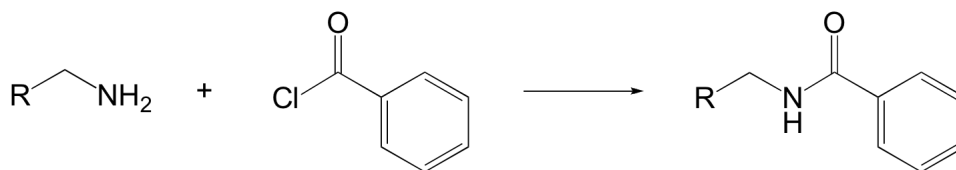
- semicarbazide hydrochloride (in balances room).
- sodium acetate (in balances room).
- 95% ethanol (in organic solvent hood).

Procedure:

In a 10x130mm test tube, dissolve 0.1g of semicarbazide hydrochloride and 0.15g of sodium acetate in 2ml of DI water. Transfer one ml of this reaction mixture to a small test tube containing 4 drops of the unknown (if a solid, dissolve 0.2 g of the unknown in 1ml of ethanol). Warm the resultant reactant mixture for 5 minutes on sand bath. Allow the reaction contents to cool to room temperature and then cool to 0°C to encourage crystallization. Vacuum filter the product using a Hirsch funnel and wash the product with 95% ethanol. Recrystallize the product from methanol. Dry the product, determine the melting point and obtain an IR spectra. Make the appropriate spectral assignments.

IV. Preparing derivatives of amines.

Preparation of Benzamide:



Reagents:

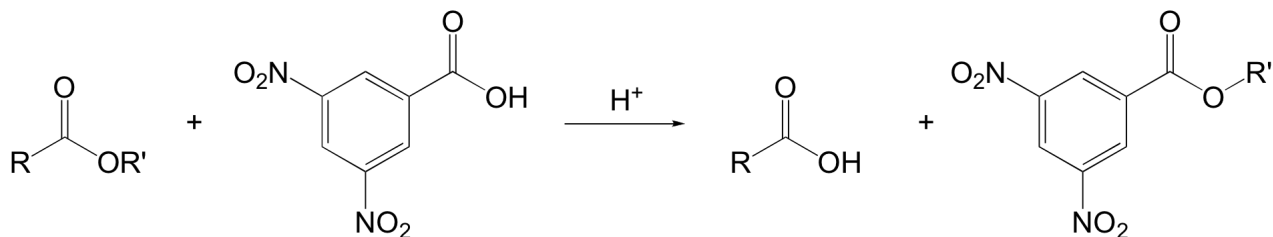
- benzoyl chloride (use in hood!, in reagent hood).
- 10% NaOH (10ml/procedure, in base hood).
- methylene chloride (in solvent hood).
- diluted HCl (1%, in acid hood).
- DI water.

Procedure:

Transfer ten drops of the unknown to a 25 ml Erlenmeyer flask followed by the addition of 10 mL of 10% NaOH(aq) and 1mL of benzoyl chloride. Stir the mixture for 10 minutes then vacuum filter the precipitate using a Hirsch funnel. Wash the precipitate (benzamide) with 2 mL 1% HCl(aq), followed by 2 mL DI water. Dry the product, determine the melting point and obtain an IR spectra. Make the appropriate spectral assignments.

V. Preparing derivatives of Esters

Preparation of 3,5 dinitrobenzoates:



Reagents:

3,5-Dinitrobenzoic Acid

Conc. Sulfuric Acid

TBME Anhydrous (15 mL/procedure)

5% Na₂CO₃ solution (20 mL/procedure, on base shelf)

Absolute ethanol (3 mL/procedure in solvent hood),

DI water

Procedure: (reference p.358 in SIOC by Shriner)

Transfer 1mL of liquid ester into a dry 5 mL conical vial containing a spin vane. Add 0.8 g of 3,5-dinitrobenzoic acid, and one drop of conc. sulfuric acid. Add a reflux condenser and heat the solution at 150-180°C for 30-60 minutes. The reaction time is dependent on how fast the 3,5-dinitrobenzoic acid dissolves. If the acid dissolves within 15 minutes heating at 150°C then 30 minutes of reflux is sufficient. Otherwise continue the reflux for an hour.

Extraction & neutralization: After refluxing is finished, cool down the reaction to room temperature. Transfer the mixture into a 60 mL separatory funnel and add 15 mL of tert-butyl methyl ether (tBME). Wash the solution with 10 mL of 5% sodium carbonate solution (for neutralizing the sulfuric acid and removing unreacted 3,5-dinitrobenzoic acid). Remove the aqueous layer and wash the ether layer with a second portion of 10 mL of 5% sodium carbonate. Wash with 5 mL of DI water 2-3 times until the washing water is neutral (use pH paper). Dry the organic layer over Na₂SO₄, filter the solid and evaporate the solvent. Dissolve the residue (usually is an oil) in 3 mL of boiling absolute ethanol and filter the solution. Add water dropwise until the solution begins to get cloudy. The mixture is cooled and stirred to induce crystallization of the derivative.

Use vacuum filtration to collect the solid, then transfer the crystal into a weighing paper. Place the paper in a desiccator overnight, then take melting point & IR.

Tables of possible unknowns and their derivatives

ACIDS

ACID			DERIVATIVE
<i>Compounds</i>	<i>Mp, °C</i>	<i>Bp, °C</i>	<i>Amide</i>
			<i>Mp, °C</i>
Acetic		118	82
Acetylanthranilic	185		171
o-Anisic (methoxybenzoic)	100		128
p-Anisic	184		162
Benzoic	122		128
o-Bromobenzoic	150		155
Butanoic		163	115
Chloroacetic	63		118
o-Chlorobenzoic	140		139
m-Chlorobenzoic	158		134
p-Chlorobenzoic	242		179
4-Chloro-3-nitrobenzoic	182		156
Cinnamic	133		147
Dichloroacetic		189	98
3,4-Dichlorobenzoic	208		133
Diglycolic (oxydiacetic)	148		135 (mono)
3,4-Dimethoxybenzoic	182		164
2,2-Dimethylsuccinic	140		
Diphenylacetic	146		167
p-Ethoxybenzoic	198		202
Glutaric	97		174
Hippuric (benzoylglycine)	187		183
p-Hydroxybenzoic	215		162
Itaconic	165 (d)		192 (di)
p-Methoxyphenylacetic	85		189
Methylpropanoic (isobutyric)		155	129
Methylsuccinic	115		165 (mono)
Naphthalene-1-acetic	133		181
1-Naphthoic	162		205
m-Nitrobenzoic	140		142
p-Nitrobenzoic	241		201
Phenylacetic	76		154
2-Phenylbutanoic	42		86
3-phenylpropanoic	48		82
5-Phenylpentanoic	60		109
Phthalic	208 (d)		149
Propionic		140	81
Salicylic (o-hydroxybenzoic)	158		139
Succinic	188		242 (mono)
o-Toluic	105		142
m-Toluic	111		97
p-Toluic	177		158
3,4,5-Trimethoxybenzoic	170		176

ALCOHOLS

ALCOHOL			DERIVATIVE <i>3,5-Dinitro-benzoate</i>
<i>Compounds</i>	<i>Bp, °C</i>	<i>Mp, °C</i>	<i>Mp, °C</i>
Benzyl alcohol	206		113
1-Butanol	117		64
2-Butanol	99		75
2-Buten-1-ol	122		
Cinnamyl alcohol	257	33	121
2-Chloroethanol	130		
1-Chloro-2-propanol	127		83
Cholesterol		148	
Cyclohexanol	161		112
Cyclopentanol	141		115
Diphenylmethanol		69	141
Ethanol	78		93
2-Ethyl-1-butanol	149		52
1-Heptanol	177		47
2-Heptanol	160		49
1-Hexanol	156		58
Methanol	65		108
4-Methoxybenzyl alcohol	260	25	
1-Methoxy-2-propanol	119		85
4-Methylbenzyl alcohol		60	118
2-Methyl-1-butanol	129		70
3-Methyl-1-butanol	132		61
3-Methyl-2-butanol	113		76
2-Methyl-3-buten-2-ol	98		
2-Methyl-1-pentanol	148		51
3-Methyl-2-pentanol	134		43
4-Methyl-2-pentanol	132		65
2-Methyl-1-propanol	108		87
1-Octanol	192		61
2-Octanol	179		32
1-Pentanol	138		46
2-Pentanol	119		61
3-Pentanol	116		101
2-Phenoxyethanol	237		
1-Phenylethanol	203		95
2-Phenylethanol	219		108
1-Phenyl-1-propanol	219		
2-Phenyl-2-propanol	202	34	
1-Propanol	97		74
2-Propanol	82		123
2-Propene-1-ol	97		48
2-Propyn-1-ol	115		

PHENOLS

PHENOL			DERIVATIVE <i>3,5-Dinitro- benzoate</i>
<i>Compounds</i>	<i>Mp, °C</i>	<i>Bp, °C</i>	<i>Mp, °C</i>
4-t-Butylphenol	100		
4-Chloro-3,5-dimethylphenol	115		
o-Chlorophenol		176	
p-Chlorophenol	43		186
o-Cresol (methylphenol)		190	138
m-Cresol		202	165
p-Cresol	36		189
2,4-Dichlorophenol	45		142
3,5-Dichlorophenol	68		
2,4-Dimethylphenol	27	212	165
2,5-Dimethylphenol	75		137
2,6-Dimethylphenol	49		159
3,4-Dimethylphenol	62		182
3,5-Dimethylphenol	68		195
4-Ethylphenol	47		132
o-Hydroxyphenol (catechol)	104		152 (di)
m-Hydroxyphenol (resorcinol)	110		201 (di)
p-Hydroxyphenol (hydroquinone)	169		317 (di)
2-Isopropyl-5-methylphenol (thymol)	51		103
2-Isopropylphenol		212	
4-Isopropylphenol	61		
2-Methoxyphenol	30	205	141
4-Methoxyphenol	56		
4-Methyl-2-nitrophenol	34		
5-Methyl-2-nitrophenol	53		
1-Naphthol	94		271
2-Naphthol	122		210
o-Nitrophenol	45		155
p-Nitrophenol	114		186
Phenol	42	180	146

ALDEHYDES

ALDEHYDE			DERIVATIVES, Mp, °C	
<i>Compounds</i>	<i>Bp, °C</i>	<i>Mp, °C</i>	<i>Semicarbazone</i>	<i>2,4-Dinitrophenylhydrazone</i>
o-Anisaldehyde (o-methoxybenzaldehyde)	246	38	215	254
p-Anisaldehyde	247		210	254
Benzaldehyde	179		222	237
Butanal	75		106	123
2-Butenal	103		199	190
o-Chlorobenzaldehyde	208		225	207
p-Chlorobenzaldehyde	214	47	230	270 (d)
Cinnamaldehyde	252		215	255
Citral	228		164	116
Citronellal	206		82	77
2,5-Dimethoxybenzaldehyde		52	---	---
3,4-Dimethoxybenzaldehyde		44	177	263
p-Dimethylaminobenzaldehyde		74	222	325
o-Ethoxybenzaldehyde	248		219	
2-Ethylbutanal	116		99	134
Furfural	161		202	230
Heptanal	156		109	108
Hexanal	131		106	104
o-Hydroxybenzaldehyde (salicylaldehyde)	197		231	248
p-Hydroxybenzaldehyde		115	224	280 (d)
2-Methylbutanal	93		103	120
3-Methylbutanal	92		107	123
a-Methylcinnamaldehyde	270		208	
5-Methylfurfural	187		211	212
1-Naphthaldehyde	292	34	221	
p-Nitrobenzaldehyde		106	221	
o-Nitrobenzaldehyde		44	256	250
Phenylacetaldehyde	194		156	121
Piperonal (3,4-methylenedioxybenzaldehyde)	264	36	230	266
o-Tolualdehyde	200		212	195
p-Tolualdehyde	204		215	234

KETONES

KETONE			DERIVATIVES, Mp, °C	
<i>Compounds</i>	<i>Bp, °C</i>	<i>Mp, °C</i>	<i>Semicarbazone</i>	<i>2,4-Dinitrophenylhydrazone</i>
Acetone	56		187	126
2-Acetonaphthone		54	234	262
Acetophenone	200		198	250
Benzophenone		48	167	239
p-Bromoacetophenone		51	208	235
Butanone	80		146	117
Butyrophenone	230		187	190
Chloroacetone	119		164	125
p-Chloroacetophenone	232		201	231
p-Chloropropiophenone		36	176	
Cyclohexanone	156		167	162
Cyclopentanone	131		203	146
3,3-Dimethyl-2-butanone	106		158	125
2,4-Dimethyl-3-pentanone	125		160	95
Fluorenone		83		283
2-Heptanone	151		127	89
3-Heptanone	148		103	
4-Heptanone	145		133	75
Hexane-2,5-dione	188		220 (di)	255 (di)
2-Hexanone	129		122	110
5-Hexen-3-one	129		102	108
4-Hexen-3-one	139		157	
p-Hydroxypropiophenone		148		229
Isobutyrophenone	222		181	163
p-Methoxyacetophenone		38	197	220
p-Methoxypropiophenone		28		
p-Methylacetophenone	226	28	205	258
3-Methyl-2-butanone	94		113	120
2-Methylcyclohexanone	163		195	137
4-Methylcyclohexanone	169		199	130
5-Methyl-3-heptanone	160		102	
6-Methyl-3-heptanone	160		132	
5-Methyl-2-hexanone	145		147	95
Methylcyclohexyl ketone	180		177	140
4-Methyl-2-pentanone	119		135	95
4-Methyl-3-penten-2-one	130		164	203
m-Nitroacetophenone		81	257	228
p-Nitroacetophenone		80		
2-Octanone	173		123	58
2,4-Pentadione	139		122 (mono)	209
2-Pentanone	102		112	144
3-Pentanone	102		139	156
Phenylacetone	216		198	156
4-Phenyl-2-butanone	235		142	
4-Phenyl-3-buten-2-one		41	187	
Propiophenone	218		174	191

AMINES

AMINE			DERIVATIVES, Mp, °C		
<i>Compounds</i>	<i>Bp, °C</i>	<i>Mp, °C</i>	<i>Acetamide</i>	<i>Benzamide</i>	<i>Phenylthiourea</i>
Aniline	183		114	160	154
Benzylamine	184		60	105	156
N-Benzylaniline		37			
o-Bromoaniline	229		99	116	146
p-Bromoaniline		66	167	204	148
n-Butylamine	77			42	65
iso-Butylamine	69			57	82
sec- Butylamine	63			76	101
tert-Butylamine	46			134	120
o-Chloroaniline	207		87	99	156
m-Chloroaniline	230		72	120	124
p-Chloroaniline		70	179	192	152
Cyclohexylamine	134		104	149	148
Di-n-butylamine	160				86
2,4-Dichloroaniline		63	145	117	
2,5- Dichloroaniline		50	132	120	
Diethylamine	55			42	34
Di-n-propylamine	110				69
Di-iso-propylamine	86				
p-Ethoxyaniline	250		137	173	136
Ethyl p-aminobenzoate		89	110	148	
N-Ethylaniline	205		54	60	
o-Ethylaniline	216		111	147	
n-Hexylamine	128			40	77
o-Methoxyaniline	225		87	84	
p-Methoxyaniline		58	128	155	154
2-Methoxy-5-methylaniline		50	110		
4-Methoxy-2-methylaniline		30	134		
N-Methylaniline	196		102	63	87
o-Nitroaniline		71	92	94	142
m-Nitroaniline		114	155	155	160
p-Nitroaniline		147	210	199	
α-Phenylethylamine	185		57	120	
β-Phenylethylamine	198		114	116	135
Piperidine	105			48	101
o-Toluidine	199		112	143	136
m-Toluidine	203		65	125	94
p-Toluidine		45	153	158	141

ESTERS

ESTER		DERIVATIVES
<i>Compounds</i>	<i>Bp, °C</i>	<i>Mp, °C</i>
Phenyl acetate	197	146
Methyl benzoate	199	108
Octyl formate	199	62