ISSN 2394-7446

INTERNATIONAL JOURNAL OF
APPLIED PHARMACEUTICAL SCIENCES

IDENTIFICATION METHODS OF UNKNOWN

Review Article

Dr. Nagham Mahmood Aljamali
Assist. Professor ,Chemistry Department .,College of Education ,IRAQ

(To corresponding : E-mail :dr.nagham_mj@yahoo.com)

Abstract
To identification of unknown organic compound and the establishing of its molecular and structural formula. There are two methods : spectroscopic methods or via chemical methods. Chemical methods: Involve the examination of the physical properties of the unknown and classification by solubility and elemental analysis by sodium fusion classification tests for functional groups and synthesis of solid derivatives .,spectroscopic methods: Involve using I.R, Mass Spectrometry,
H NMR, C NMR.
Keywords: **:** unknown , test, melting point , identification, functional group.

Introduction:

To identify an unknown organic sample the first thing to do is to check the purity of the Sample. (Normally we give you a pure sample), but if not
You need to make sure that the sample is pure otherwise you learn nothing definitive from any test carried out an impure compound.

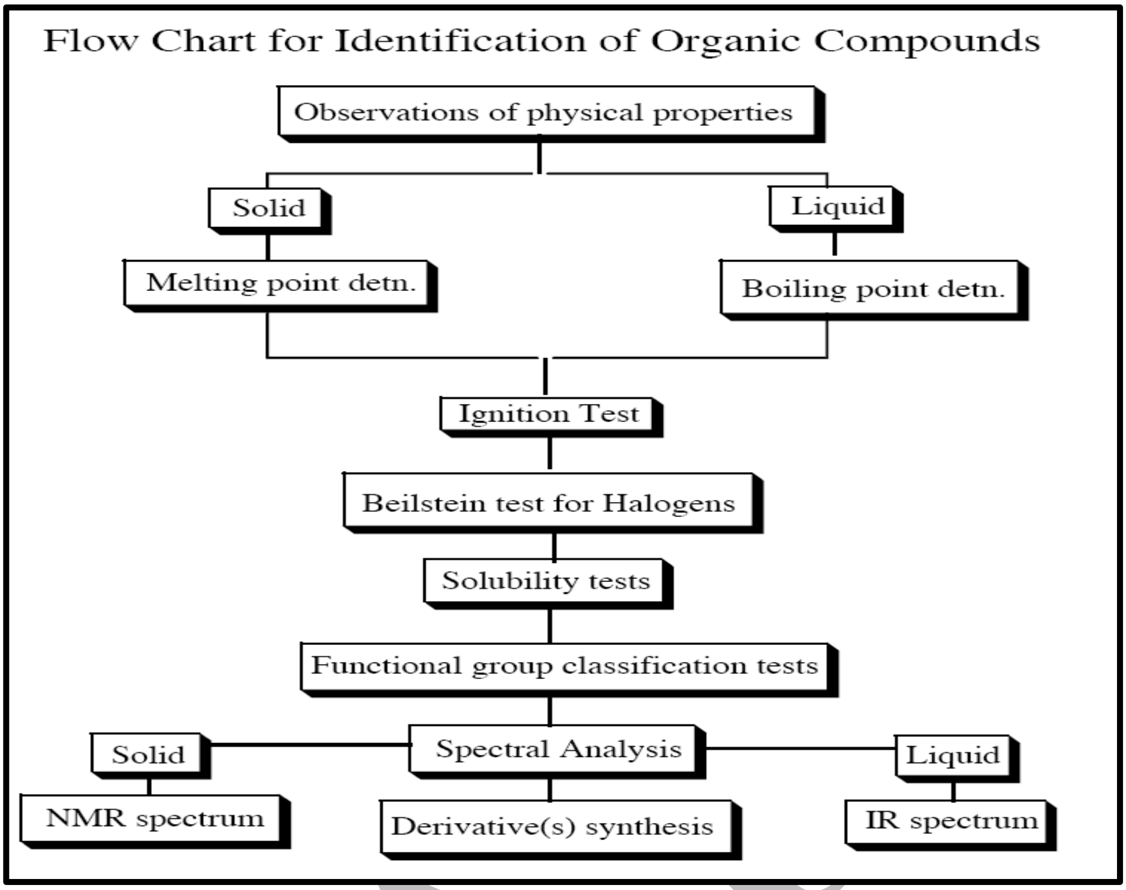
Experimental and Materials :

How to check the purity of your sample ?The best techniques are:
1-Melting Point for solid sample
2- Boiling Point for liquid sample
3- Thin layer chromatography TLC for both liquid and solid samples.
The melting point (mp) :of a substance is one of the physical properties that chemists use to identify a substance and/or to check the purity of a substance.

The melting point is the temperature at which a substance changes from a

solid to a liquid state. Pure crystalline organic compound usually has a sharp and characteristic melting point range of 0.5 to 1°C

The melting point range is determined by recording the temp at which melting first begins and the temp at which melting is complete. So, if your sample gave you Sharp M.P. that means it's a pure sample.



The physical appearance :of an unknown will be your first datum in the search to discover its identity Simply knowing that the compound is a solid rather than a liquid at room temperature narrows the search considerably.

A few solids have characteristic bright colors that may be of great significance in reaching a final answer The color of a liquid sample must be interpreted more cautiously, because many liquid compounds oxidize when they are stored for a long time.

Colour: Many liquid and solid organic compounds are coloured. They are coloured because of the presence of chromophoric groups in the molecules.

Chromophore :A chemical group capable of selective light absorption resulting in the coloration of certain organic compounds. Chromophores are generally groups of atoms having delocalized electrons. For example;

C=N, C=S, NO2, N=N,

The more conjugated a compound is the more the absorption is, as the conjugation in a molecule make the absorption to appear at higher wavelength

Odor : Many organic compounds have a characteristic

Odor. Generally specking the odor is more clear for Compounds with lower molecular weight. The following compounds are common in the lab and

They have characteristic odor.You will be able to recognised their odour Easley.

Benzaldehyde has the odor of bitter almond

Esters have nice odor Another examples are Alcohol, acetone and diethyl ether

Melting and Boiling points:

In the previous slides we have seen the importance of

Mp and bp in the determination of the compounds purities.

Now let us look at another importance of them in identifying an organic compounds

if you can be sure that the boiling point of a liquid alcohol

is 132° (+,-) 2°C, you have narrowed the choice to only

three or four possibilities from more than 40 liquid alcohols

Likes dissolve likes is our rule of thumb. It means that

Polar compounds dissolve in polar solvents and non polar Compounds dissolve in non- polar solvents.

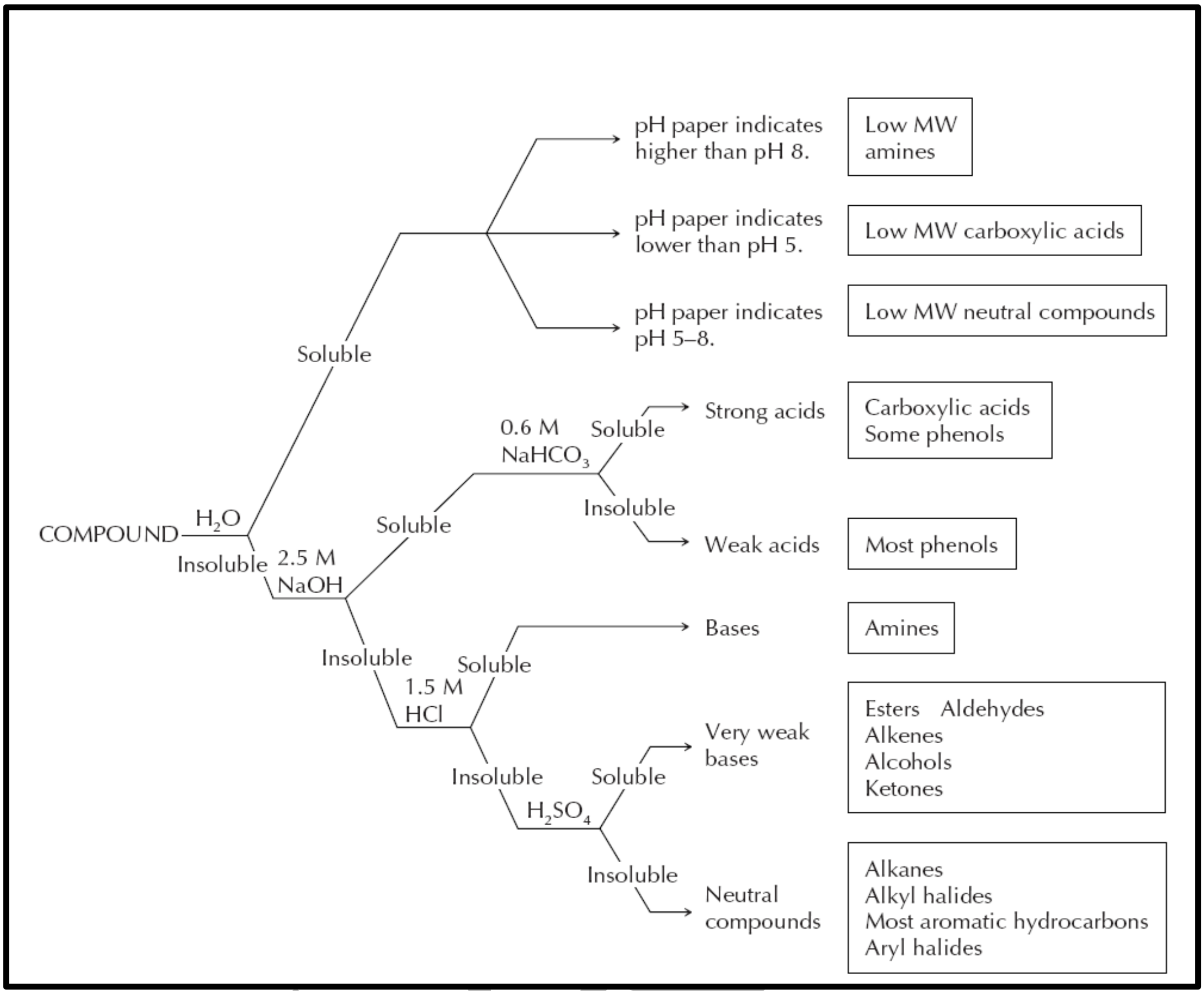
In general; low molecular weight organic compounds containing polar functional groups are soluble in water, and in polar solvents like MeOH , EtOH, etc

As the chain length increases, the solubility decreases.

For two isomeric structure, the one with the more branched structure will be more soluble in a given solvent.

A compound is soluble if it dissolves to the extent of about 30 mg of solid or 1 drop pf liquid in 1 ml of solvent

Solubility :



Solubility in 2.5 M (9%) NaOH Solution

Organic acids, which are insoluble in water, normally dissolve in a 2.5 M (9%) NaOH solution. The pH of this solution is greater than 14, so any acid whose dissociation constant is greater than ($pK_a < 12$) is converted almost entirely to its conjugate base. The conjugate base of a carboxylic acid ($pK_a \sim 5$) is a carboxylate anion. The conjugate base of a phenol ($pK_a \sim 10$) is a phenoxide ion. Ionic carboxylate salts and phenoxide salts are quite soluble in water. Thus, water-insoluble carboxylic acids and phenols will both dissolve in a 2.5 M sodium hydroxide solution.

$$\mathrm{R\overset{O}{\overset{\|}{C}}OH + OH^- \rightleftharpoons R\overset{O}{\overset{\|}{C}}O^- + H_2O}$$

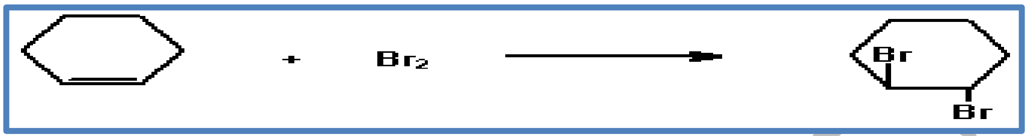
Water-soluble carboxylate ion

Two common types of unsaturated compounds :

Unsaturated compounds are alkenes and alkynes characterised by the carbon-carbon double and triple bond, respectively. The two common qualitative tests for unsaturation are the reactions of the compounds with

(a) bromine in carbon tetrachloride

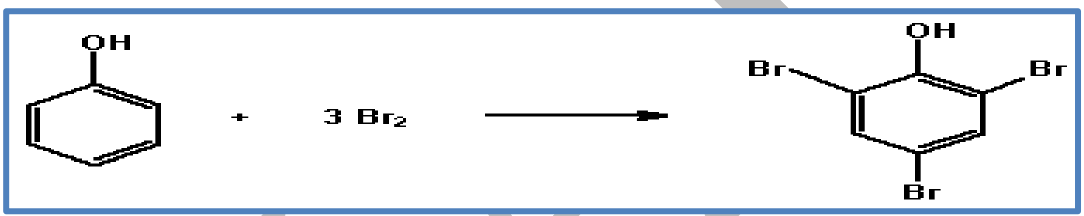
(b) potassium permanganate.



Rapid disappearance of the bromine colour to give

a colourless solution is a positive test for unsaturation

Phenols :
[Soluble in NaOH and produce no CO2 from NaHCO3]
(a)- Bromine water:
Phenols are generally highly reactive towards electrophilic reagents and are readily brominated by bromine water.



A white precipitate of the bromophenol may form

b)- Ferric chloride test:

Most phenols react with iron (III) chloride FeCl3 to form coloured complexes. The colours vary - red, purple, blue or green - depending on various factors, e.g. the phenolic compound used, the solvent, concentration. Since some phenols do not give colours, a negative test must not be taken as significant without supporting information

$$3\ ArOH \xrightarrow[3\ pyridine]{FeCl_3} Fe(OAr)_3 + 3\ pyridinium\ hydrochloride$$

colored complex

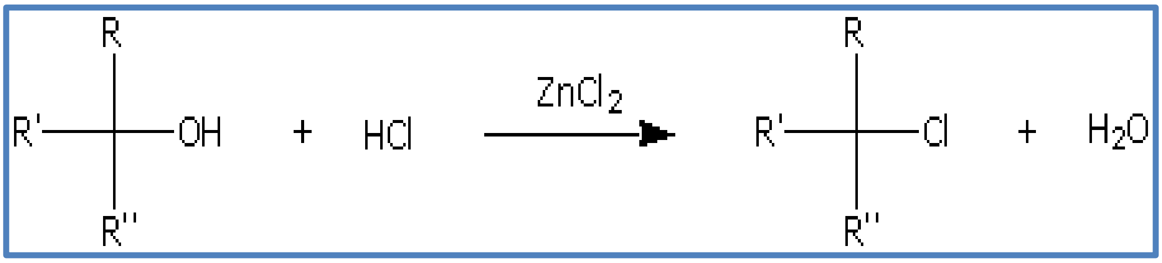
The appearance of blue, violet, purple, green, or red-brown colour is a positive test

Lucas Test (Alcohols)

Primary Alcohols :dissolve in reagent giving clear solution.

Secondary Alcohols: produce cloudiness after about 3-5 minutes. May need to heat slightly.

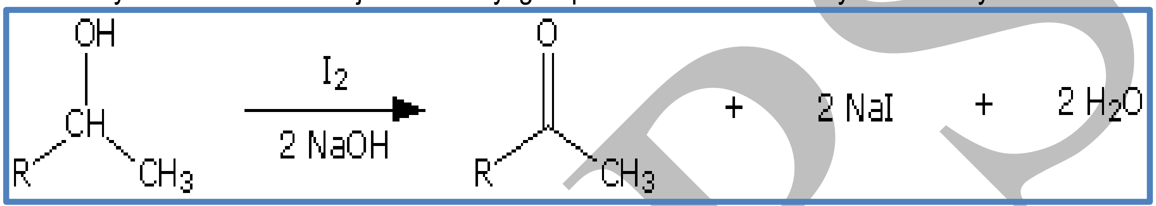
Tertiary: Benzylic, and Allylic alcohols produce immediate cloudiness; eventually, an immiscible Alkyl Halide separates into a separate layer.



The test applies only to those alcohols soluble in the reagent (mono functional alcohols lower than hexyl and some poly functional alcohols).

Iodoform Test:

Secondary alcohols with an adjacent methyl group are oxidized to methyl ketones by iodine.



Identify Functional Groups:

Water: Short-chain molecules (< 5 C) or molecules with polar groups that can hydrogen bond

HCl: Amines

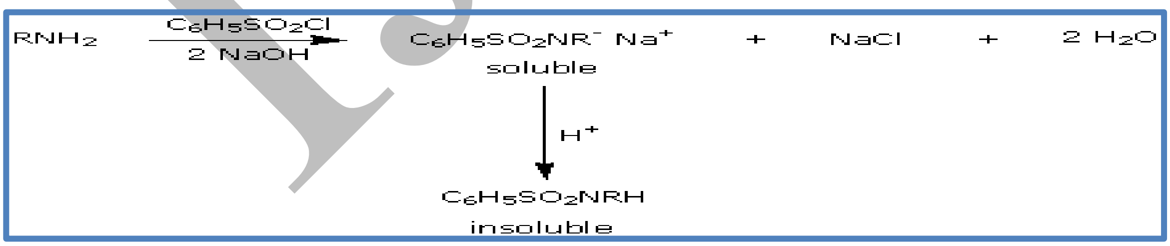
NaOH: Phenols and carboxylic acids

$NaHCO_3$: carboxylic acids

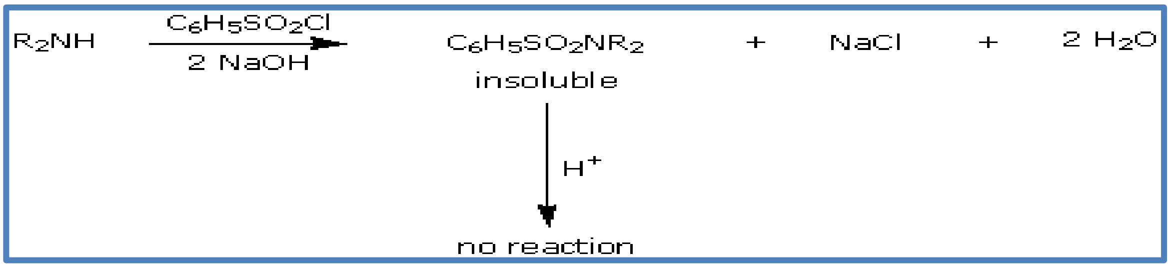
H_2SO_4: everything that has oxygens or nitrogens

Amines Hinsberg Test:

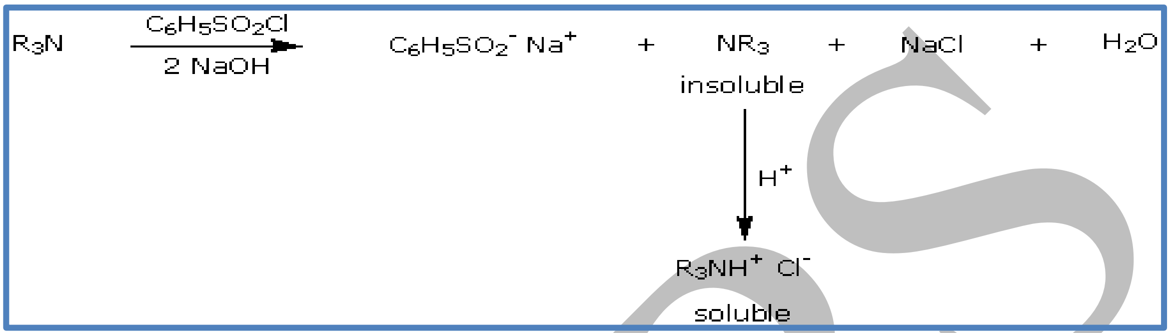
dissolves in base and precipitates from acid is (+) test



precipitates from base and no change from acid is (+) test **Result** :



Result :precipitates from base and dissolves in acid is (+) test



<u>**Chromic Acid (Jones Oxidation)**</u>

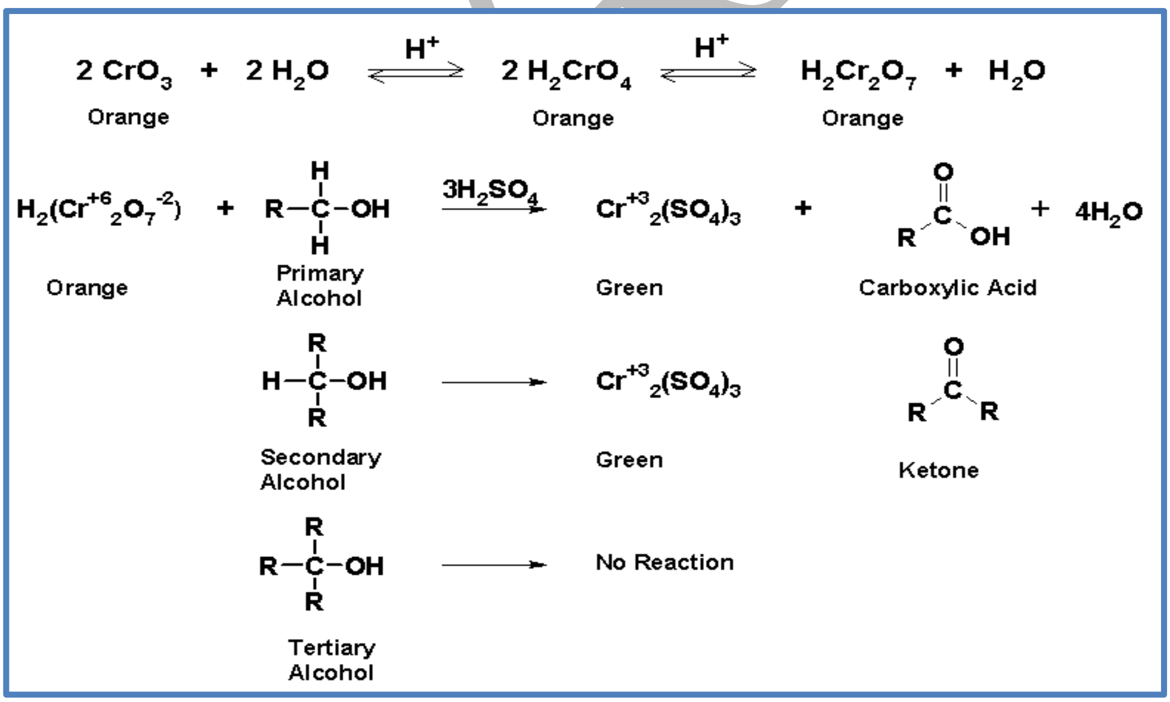
Distinguish Primary & Secondary Alcohols from Tertiary Alcohols.

Chromic Acid (Cr^{+6}) oxidizes Primary and Secondary Alcohols to Carboxylic Acids and Ketones, respectively.

Result:

Chromium (+6) - orange– is reduced to Chromium (+3) – green.

Tertiary Alcohols do not react with Chromic Acid.

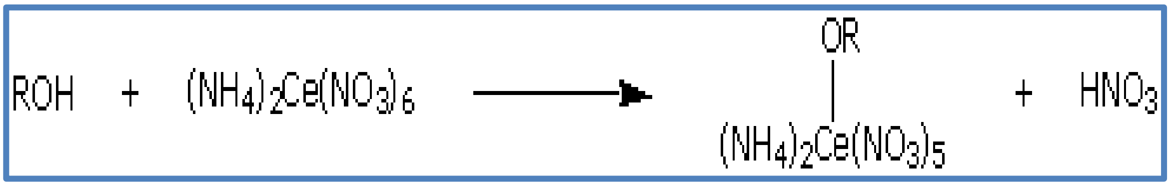


<u>**Alcohols Functional Groups:**</u>

i) Alcohols are neutral substances towards litmus:- the colour of blu or red litmus does not change when alcohol is added to it.

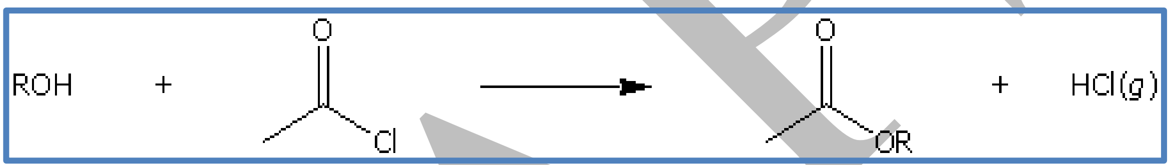
ii) Ceric ammonium nitrate test:-

When few drops of this reagent are added to the given compound or its solution if colour changes from yellow to red the compound contains a hydroxyl group.



Result ((Positive Test))
Phenols give a brown colour or precipitate as a positive test.
iii) Sodium metal test: - A small piece of sodium metal is added to the compound or its solution. Evolution of hydrogen gas indicates the presence of –OH group in the organic compound.
iv) Acylation test:- acetyl chloride or benzoyl chloride is

added to the given compound or its solution, if hydrogen chloride is evolved, it shows that the organic compound is an alcohol.



Alcohols and phenols produce esters indicated by the formation of a top layer in the flask. which precipitate.

References:

1- S . George . , "Organic Chemistry" Mosby-Year Book . 1995 , Chp.14 , p. 589-649 (1995).
2- P. Sykes ; "Agide Book to Mechanism in Organic Chemistry" , 5th Ed ., Longman, (1974) .
3- R . E . Brewster , W. E. McEwen ; "Organic Chemistry" , Ch . 30ed Ed ., p.638 , (1971) .
4-- B.A. Marry ; "Organic Reaction Mechanism" , Ch . 1, Jon Willey sons , (2005) .
5- L.F. Fieser and K.L. Eilliamson , "Organic Experiment" 5th Ed ., DC . Heath and company Toronto , Canada , p. 270 . (1983) .
6- F. A.Carey and R. J. Sundberg "Advanced Organic Chemistry" part A:strures and Mechanisms, 2nd ed ., Plenum Press. New York, p. 243, (1983).
7- Nagham M Aljamali ., As. J. Rech., 2014 , 7 ,9 , 810-838.
8--C.O.Wilson and O. Givold, "Text book of Organic Medicinal and pharmaceutical Chemistry", 5th Ed ., Pitman Medical Publishing Co. LTD, London coppy right. Cby. J. B. Lippin Cott Company (1966) .
9- Nagham M Aljamali ., As. J. Rech., 2014 , 7 ,11.
10 - Nagham M Aljamali., Int. J. Curr.Res.Chem.Pharma.Sci. 1(9): (2014):121–151.
11- Nagham M Aljamali., Int. J. Curr.Res.Chem.Pharma.Sci. 1(9): (2014):88- 120.
12- Y. Ju, D. Kumar, R. S. Varma, *J. Org. Chem.*, 2006, *71*, 6697-6700.
13 - N. Iranpoor, H. Firouzabadi, B. Akhlaghinia, R. Azadi, *Synthesis*, 2004, 92-96.
14 - Y. Liu, Y. Xu, S. H. Jung, J. Chae, *Synlett*, 2012, 2663-2666.
15 - D. S. Bhalerao, K. G. Agamanchi, *Synlett*, 2007, 2952-2956.
16- Gung, B.W., Taylor, R.T.; 2004. J. Chem. Ed., 81, 1630.
17- Decelles, C.; 1949, J. Chem. Ed., 26, 583.