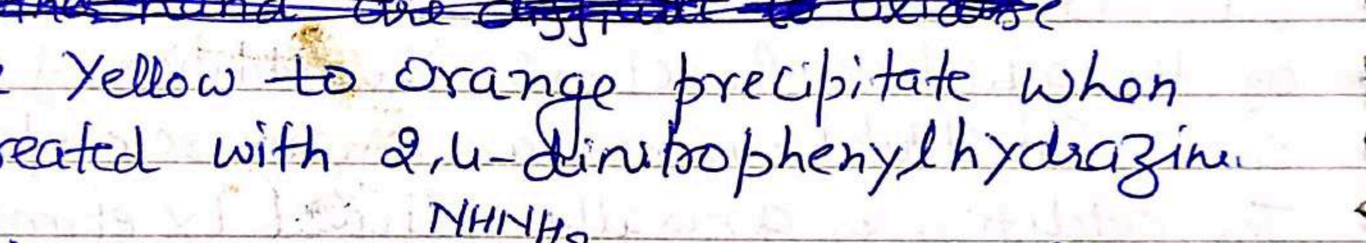
This difference in their reactivity on the basis of for distinction between aldehydes and ketones.
The following qualitative test may be performed for identification of aldehydes and ketones:

① <u>Reaction with 2,4-DinitroPhenyl Hydrazine:</u>
Aldehydes and Ketones ~~on the other hand are difficult to oxidise~~
give Yellow to orange precipitate when treated with 2,4-dinitrophenylhydrazine.



2,4-dinitrophenyl hydrazone
Yellow to orange solid

<u>Procedure</u> – Dissolve the Carbonyl Compounds 100 mg or 1-2 drops) in ethanol (2-3 ml) Now add an alcoholic Solution of 2,4-dinitro Phenylhydrazine (2ml) and Shake the mixture well. A Yellow to orange PPt indicates the Compound to be an aldehyde or Ketone.
An orange PPt is obtained, from Carbonyl

Compounds in which C=O gp. is Conjugated with C=C.

Tollen's test → Tollen's test (Reagent) Consists of Silver ammonia Complex in ammonia Solution. Aldehydes give a grey black Precipitate or Silver mirror when treated with a freshly prepared. Tollen's reagent Aldehydes are oxidised to the Corresponding acid and silver in tollen's reagent is reduced from +1 oxidation state to elemental form. Ketones do not reduce Tollen's reagent

$$RCHO + 2[Ag(NH_3)_2]OH \rightarrow RCOONH_4 + 3NH_3 + H_2O + 2Ag$$

Procedure — Take 1 ml tollens reagent, add solution of aldehyde (50 mg or 2 drops) dissolved in aldehyde free alcohol (2-3 ml) and warm the Solution in a hot water bath. Formation of a grey black precipitate or Silver mirror indicates the presence of an aldehyde.

Schiff's test –

Procedure – To a solution of the aldehyde (1-2 drops or 50 mg in 2-3 ml of aldehyde) add the Schiff's reagent (2-3 drops). Instant appearance of a violet or a purple colour indicates the presence of an aldehyde.

Test with chromic acid – Aldehydes give a green or a blue precipitate when treated with chromic acid. Ketones do not react.

Procedure – Add the carbonyl compounds to chromic acid reagent (1ml). Appearance of a green blue precipitate indicates the presence of an aldehyde.

p

Fehling test ⇒ Fehling solution contains complex of Cu^{+2}. When treated with an aldehyde, Cu^{+2} is reduced to Cu^{+1} (as a red PPt of Cu_2O) and an aldehyde is oxidised to the acid. Aromatic aldehydes do not reduce the Fehling solution

(d) Phenols

Hydroxy derivatives of aromatic compounds are known as phenols. Phenols are weaker acids than carboxylic acids, and hence dissolve in dilute sodium hydroxide and are generally insoluble in dilute sodium bicarbonate solution. Some phenols (like 2, 4, 6-trinitrophenol, 2, 4-dinitrophenol etc.) which contain strong electron withdrawing groups are stronger acids and dissolve even in sodium bicarbonate. Phenols undergo easy electrophilic substitution reactions, e.g. they decolourise bromine solution at room temperature forming a polybromo substituted phenol. Some phenols like catechol and hydroquinone are powerful reducing agents, because they are easily oxidised to the corresponding quinones.

Following tests may be performed for showing the presence of a phenolic group.

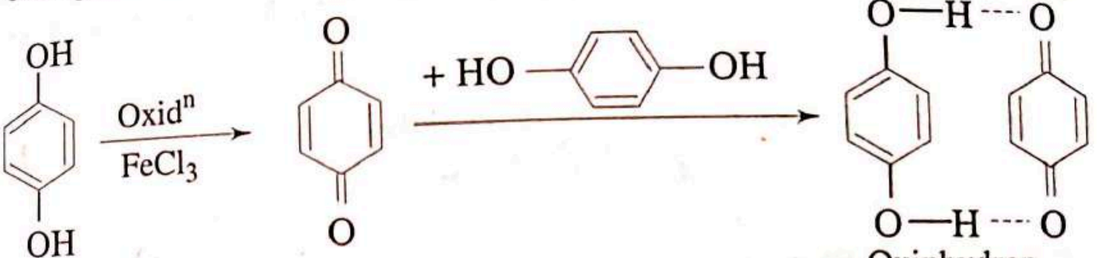
(i) Solubility in sodium hydroxide. Most phenols are soluble in dilute sodium hydroxide but insoluble in sodium bicarbonate solution.

(ii) Ferric chloride test. Most phenols and enols give a dark coloured solution (blue, green, purple etc.) on reaction with a neutral solution of ferric chloride, e.g. simple phenol reacts with $FeCl_3$ as follows:

$$6\ C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Purple}}{H_3\,[Fe(OC_6H_5)_6]} + 3\ HCl$$

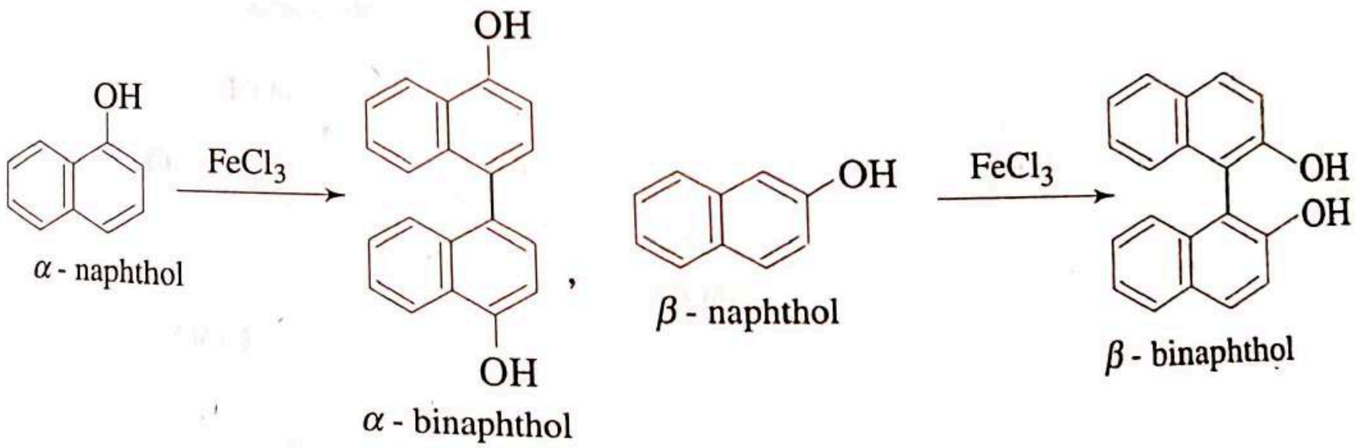
This test should be performed using a dilute solution of the phenol, observation should be made as the added $FeCl_3$ mixes with the phenol solution. Some phenols do not give this test and so a negative test must not be taken as an indication of the absence of phenol without supporting information (e.g. solubility in dilute sodium hydroxide, Br_2 test, Liebermann nitroso reaction and phthalein test).

Some phenols react in a different way with ferric chloride, e.g. Hydroquinone is oxidised to quinone which forms a dark green solid of quinhydrone with unreacted hydroquinone.



Quinhydron
Dark green solid

α-and β-Naphthol undergo oxidative coupling in the presence of excess of $FeCl_3$.



Procedure Dissolve the given compound (20 mg) in water (4-5 ml) and add a neutral solution of $FeCl_3$ slowly (several drops, dropwise) and observe the change in colour. A red, blue, green or purple colouration indicates the presence of a phenol. Enols produce a red, violet or tan colour.

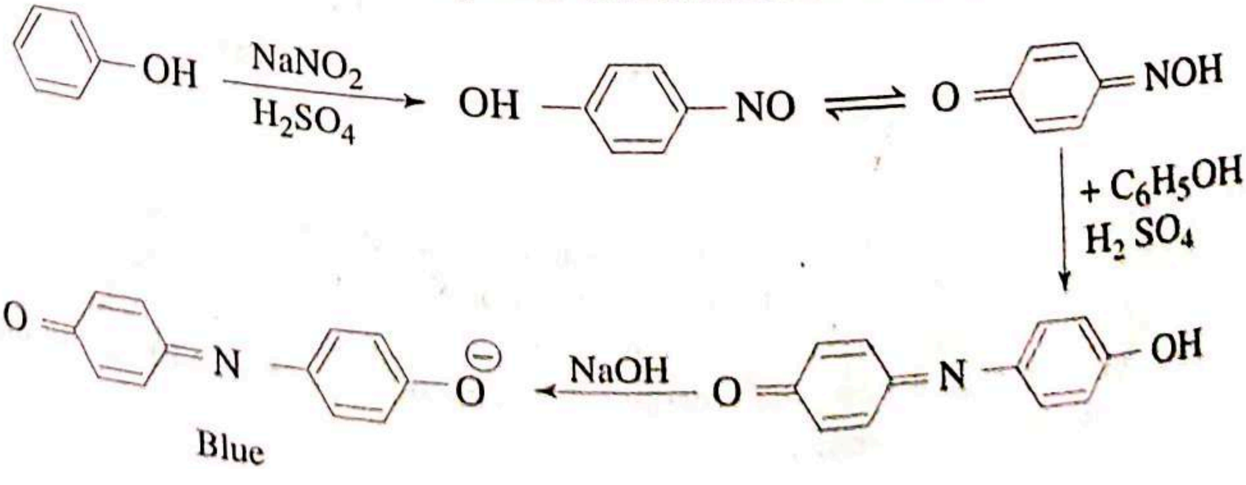
Note 1. Use alcohol if the compound is insoluble in water.

2. Phenols can be distinguished from enols by the following test:

Take the given compound (50 mg) and treat it with a solution of mercurous nitrate in nitric acid. Formation of an immediate grey precipitate shows the presence of an enol. Phenols do not give this test.

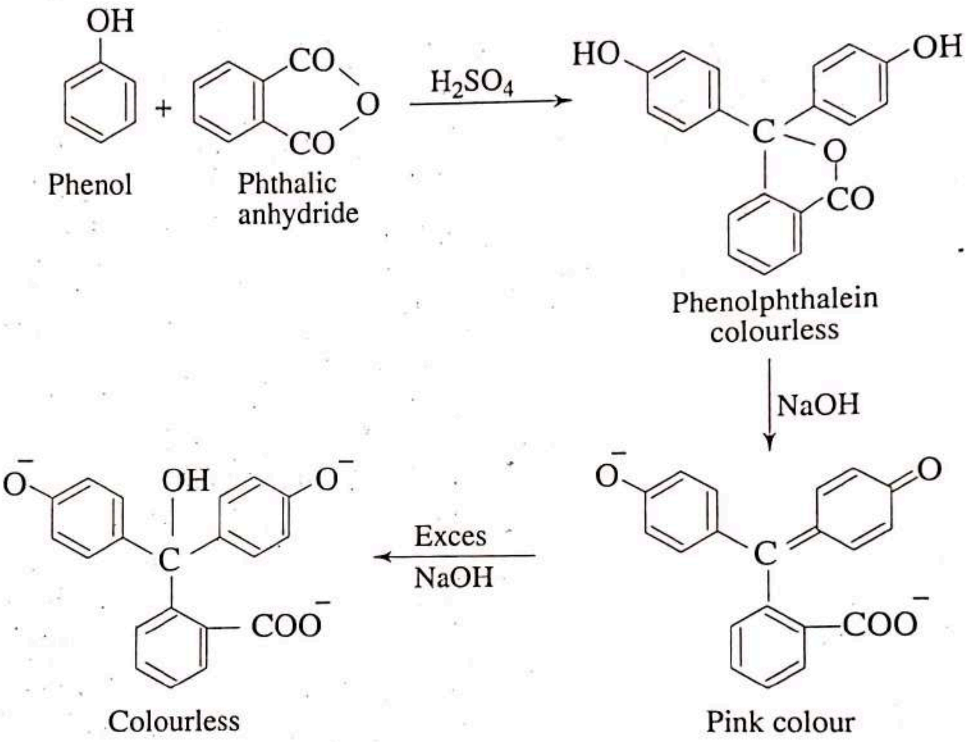
(iii) Liebermann Nitroso Reaction. Phenols having a free para-position undergo this reaction.

Phenol on heating with concentrated Sulphuric acid and sodium nitrite undergoes the following reaction.

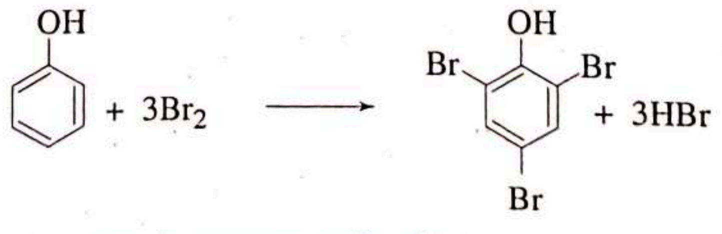


Procedure Take the compound (100 mg) in a dry test tube, add sodium nitrite (few crystals) and concentrated sulphuric acid (1 ml), mix well and heat gently. A blue colour is obtained. The solution turns red on dilution with water and blue on basification with a dilute solution of sodium hydroxide.
(iv) Phthalein test. A number of phenols having a free p-position respond to this test. On heating with phthalic anhydride in presence of concentrated sulphuric acid, phenols produce condensation compounds which give a characteristic colour in alkaline solution.

Phenol gives phenolphthalein and resorcinol produces a fluorescent compound called fluorescein.



Procedure In a dry test tube, heat the given compound (100 mg) with an equal amount of phthalic anhydride and concentrated sulphuric acid (2-3 drops), for 1-2 minutes. Cool and pour into a beaker containing dilute sodium hydroxide solution. Appearance of a pink, blue, green, red etc. colour indicates the presence of a phenol. However, the colour disappears on addition of large excess of concentrated sodium hydroxide solution.
(v) Bromine test. Phenols are readily brominated by bromine forming polybromo-substituted phenols. For examples.



The rate of bromination is greater in water or acetic acid than in carbon tetrachloride solution. Hydrogen bromide is liberated due to substitution reaction but this is not observed when water is used as a solvent.
Procedure Dissolve the given compound (100 mg) in glacial acetic acid or water. Add to this, a saturated solution of bromine in water or acetic acid. (dropwise). The disappearance of the orange colour of bromine indicates the presence of phenol.

(f) Alcohols

Alcohols are very weak acids and react only with very reactive metals like sodium to form alkoxides. The relative acidity is teritary < secondary < primary < methanol. The following tests can be performed.

for detection of an -OH group and distinction between a primary, secondary and a teritary alcohol. Alcoholic —OH is also present in carbohydrates and other natural compounds like steroids.

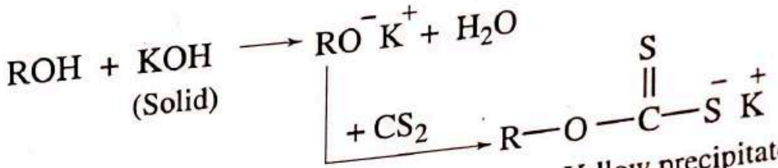
(i) Ceric ammonium nitrate test. Alcohols replace the nitrate ion of ceric ammonium nitrate, changing the colour of the solution from yellow to red.

$$\underset{\text{Yellow}}{(NH_4)_2\,[Ce(NO_3)_6]} + ROH \longrightarrow \underset{\text{Red}}{(NH_4)_2\,[Ce\,(OR)\,(NO_3)_5]} + HNO_3$$

Procedure Dissolve the given organic compound (50 mg) in water (1-2 ml) or dioxane and add ceric ammonium nitrate solution (few drops). Observe the colour change immediately. Appearance of a red colour shows the presence of an alcoholic group.

Note 1. Use freshly prepared ceric ammonium nitrate.
2. A blank test should be performed if dioxane has been used as a solvent.
3. Some alcohols given only a transient red colouration, so look for red colour on mixing.
4. Some amines and phenols also give various colours in this test.

(ii) Xanthate test. Alcohols produce a yellow precipitate of xanthate on treatment with CS_2 in presence of an alkali.



Yellow precipitate

Procedure Warm the compound (0.1g) with solid potassium hydroxide (one pellet) until it dissolves. Cool, wash with a little ether, decant the ether and add carbon disulphide (2-3 drops). Shake well. The formation of a yellow precipitate indicates the presence of an alcohol.

(iii) Sodium metal test. Reactive metals like sodium liberate hydrogen from alcohols.

$$2\,ROH + 2Na \longrightarrow 2RONa + H_2 \uparrow$$

Procedure In a dry test tube take the dry compound (1 ml of liquid or a few crystals of solid dissolved in dry benzene). To this add a very small piece of clean, dry sodium. Dissolution of sodium with brisk effervescence indicates the presence of an —OH group.

Note 1. A dry sample of the compound should be used.
2. Sodium should be handled carefully.
3. Excess of unreacted sodium should not be discarded in the sink or dust bin. It should be decomposed carefully by adding a small amount of alcohol.
4. A blank test should be performed if the given compound has been dissolved in a solvent.
5. Many other compounds like acetone, acids etc. also give this test.

(iv) Test with Chromic acid in acetone. This test is helpful in identifying the presence of the hydroxy group, provided other easily oxidisable groups like—CHO, carbohydrate etc. are absent. Tertiary alcohols do not answer the te

Both primary and secondary alcohols give a positive test.

(for experimental details, see page 21).

(v) Iodoform test. Alcohols which contain CH_3 CHOHR group are oxidised to CH_3CO— group during the reaction, and give a positive iodoform test (For experimental details, see page 21)

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$$ROH + \underset{\text{(Solid)}}{KOH} \longrightarrow RO^-K^+ + H_2O$$

$$RO^-K^+ \xrightarrow{+CS_2} \underset{\text{Yellow precipitate}}{R—O—\overset{\overset{\displaystyle S}{\|}}{C}—S^-\ K^+}$$

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(v) Iodoform test. Alcohols which contain CH_3 CHOHR group are oxidised to CH_3CO— group during the reaction, and give a positive iodoform test (For experimental details, see page 21)

$$CH_3CH_2OH \longrightarrow CH_3CHO \xrightarrow[NaOH]{I_2} CHI_3$$

$$CH_3CHOH\ CH_3 \longrightarrow CH_3COCH_3 \longrightarrow CHI_3$$

(vi) Lucas test. This test is used for distinction between primary, secondary and tertiary alcohols. The three types of alcohols can be distinguished by reacting with Lucas reagent (anhydrous zinc chloride in concentrated hydrochloric acid). Zinc chloride, itself being a strong Lewis acid, increases the acidity of the solution. Alcohols react with Lucas reagent at different rates, e.g.

$$\underset{\text{primary}}{RCH_2OH} + HCl \xrightarrow{ZnCl_2} \text{No reaction}$$

$$\underset{\text{secondary}}{R_2CHOH} + HCl \xrightarrow{ZnCl_2} R_2CHCl + H_2O$$

$$\underset{\text{Tertiary}}{R_3COH} + HCl \xrightarrow{ZnCl_2} R_3Cl + H_2O$$

Alcohols are soluble in Lucas reagent but the formed alkyl chlorides are insoluble.

Procedure Add Lucas reagent (3-4 ml) to the given organic compound (1 ml) in a test tube. Shake well and note the time required for the separation of two distinct layers.

Tertiary alcohol	–	layers separate immediately
Secondary alcohol	–	layer separation takes 5—10 minutes
Primary alcohol	–	A clear homogeneous solution is obtained

Lucas test is applicable to only those alcohols which are soluble in the reagent, as it is based on the appearance of alkyl halides as a second liquid phase.

(vii) Oxidation. A primary alcohol gives an aldehyde and a secondary alcohol a ketone on oxidation with chromic acids. Tertiary alcohols do not oxidise under these conditions.

$$RCH_2OH \longrightarrow RCHO,\ R_2CHOH \longrightarrow R_2CO$$

Procedure Mix the given compound (1 g), water (5 ml), chromic acid (1 g) and concentrated sulphuric acid (1 ml) in a small distillation flask. Distil the mixture and collect the distillate. Test for the presence of an aldehyde or a ketone (page 20) in the distillate. Positive test with 2.4 DNP indicates the presence of a primary or a secondary alcohol.

(viii) Spectroscopy. IR—The characteristic absorption peaks present in alcohols are due to the O—H and C—O stretch. The absorption due to the O—H stretch is broad and highly variable depending mainly on the concentration of the alcohol.

In very dilute solutions, in a non-polar solvent, OH is unassociated (free or non-hydrogen bonded) and shows a sharp absorption band between 3650–3580 cm^{-1}.

Intermolecular hydrogen bonding increases with an increase in the concentration resulting in an absorption due to O—H shifting to a lower frequency, i.e. 3550–3200 cm^{-1}. The absorption due to the associated O—H is broad. Generally, both the peaks, i.e. at 3650–3580 cm^{-1} and 3550–3200 cm^{-1} are observed in the IR spectrum of an alcohol. If the O—H is intramolecularly associated, then the absorption