Classification Tests

1. Classification Tests For Alcohols

a) Metallic Sodium:

$ROH + Na \rightarrow RONa + H_2(g)$

Positive Test evolution of gas

Other Functional groups that give positive Test:

R_2NH, RSH, $RC \equiv C\text{-}H$, RCO_2H,

b) Ceric Ammonium Nitrate Oxidation

$R_2CHOH + Ce(IV) \rightarrow R_2C{=}O + Ce(III)$

Positive Test: Color changes form yellow to red first then to colorless solution.(1 min. to 12 hrs)

Very good test for 1^o, 2^o alcohol

Slow for 3^o alcohol

Note:Phenols gives brown or black products.

c) **Jones Oxidation** (CrO_3)

Good for 1^o, and 2^o alcohols but not 3^o alcohol.

Pos. Test: Orange solution changes to opaque suspension with green to blue color.

Result in 2 sec.

Note: Aldehydes give positive result.

d) **Lucas Test** ($HCl/ZnCl_2$)

shows the existence of OH group

$ROH + HCl\ (ZnCl_2) \rightarrow RCl + H_2O$

Pos. Test: Formation of insoluble layer or emulsion in 5-10 min.

Note:Primary alcohols do not give positive Result.

e) **Periodic Acid** (HIO_4) Test for detection of Vicinal Diols.

Pos. Test: White ppt upon addition of $AgNO_3$

2. Classification Tests For Aldehydes and Ketones

a) **2,4-Dinitrophenyl Hydrazine**

Pos. Test indicate: formation of yellow, orange or red ppt.

b) **Phenyl hydrazine and p-Nitrophenylhydrazine**.

Pos. Test indicate formation of yellow ppt.

c) **Hydroxylamine Hydrochloride**

In the presence of orange color indicator =) Orange color changes to red.

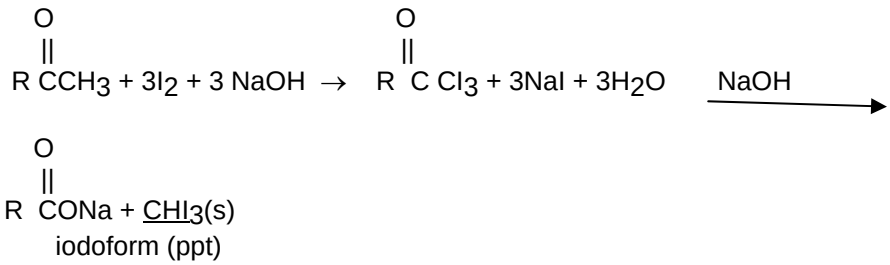
d) **Sodium Bisulfite** ($NaHSO_3$)

Pos. Test: formation of ppt

good for aldehydes , all give ppt

Only some ketones give positive results (ppt)

e) **Iodoform Test_** (For methyl Ketones)

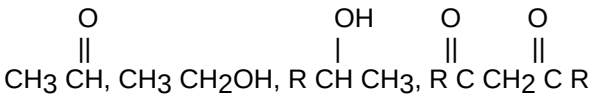


$$R\,CCH_3 + 3I_2 + 3\,NaOH \rightarrow R\,C\,CI_3 + 3NaI + 3H_2O \xrightarrow{NaOH} R\,CONa + CHI_3(s)$$

iodoform (ppt)

Pos. Test: Yellow ppt for methyl kekones

Disadvantages:: Some compounds that can be easily oxidized to methyl ketones give also positive results e.g.



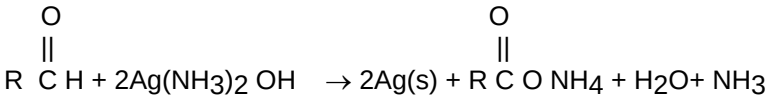
$$CH_3\,CH,\ CH_3\,CH_2OH,\ R\,CH\,CH_3,\ R\,C\,CH_2\,C\,R$$

3. Tests that give positive results with aldehydes and negative results with Ketones

(a) CrO_3 (**Jones Oxidation**)

See alcohols part C.

(b) **Tollens Reagents** ($Ag(NH_3)_2\,OH$)



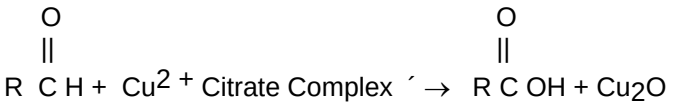
$$R\,C\,H + 2Ag(NH_3)_2\,OH \rightarrow 2Ag(s) + R\,C\,O\,NH_4 + H_2O + NH_3$$

Positive Test. Formation of silver mirror. (ppt)

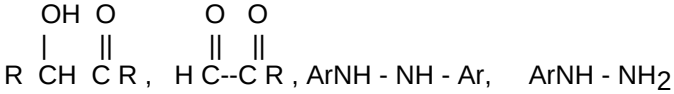
(c) **Fuchsin Reagent**:

$$R\,C\,H + \text{colorless} \rightarrow \text{violet-purple solution dye}$$

(d) **Bendicts solution**

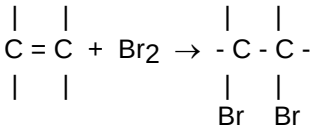


Positive Test ==> yellow or yellowish green ppt.
All aldehydes give positive result except Aromatic aldehydes give negative result. Other compounds that give positive result are



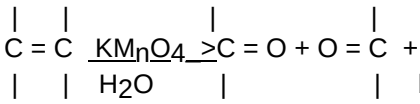
4. Classification Tests for Unsaturation "alkenes & alkynes"

(a)**Bromine in CCl_4**



Pos. Test: Bromine color discharged without evolution of gas (HBr)
alkenes & alkynes give positive results
If HBr evolved ==> indicates enols & phenols.

(b) **Baeyer Test** ($KMnO_4$ aqueous)

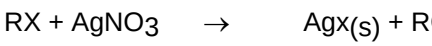


Pos. Test: Purple color discharges. and brown color PPT (MnO_2) appears

Note: Aldehydes and alcohols also give positive result.

5. Tests for Alkyl Halides

(a) **Ethanolic Silver Nitrate**



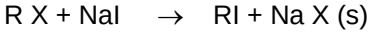
Pos. Test: formation of ppt.

Indicates: 2^{o} and 3^{o} RX

1^{o} RX , Ar-X, and vinyl halides give negative Result.

Note alkylic and benylic RX give Pos. Result

(b) **Sodium Iodide in Acetone**



X = Cl, Br

Pos. Test: ppt forms

Indications: 1^{o} , 2^{o} RX , allylic and benzylic halides.

Not good for ArX , vinyl halides ,$HCCl_3$, and 3° RX

6. Tests for amines

(a) **Acid chloride**

Pos. Test: Heat evolves and formation of ppt when added to H_2O

Indications. 1^{o} & 2^{o} amines give both heat & ppt 3^{o} amines give only heat

Note: ROH give also pos. result (heat).

(b) **Nitrous Acid**

1. Primary amines (a) $RNH_2 + HNO_2 \rightarrow R\text{-}N2^{+} \rightarrow R+ + N_2(g)$

(b) RN_2^{+} + b-naphthol $\rightarrow$ orange - red dye

Pos. Test: gas evolution and formation of orange-red dye when reacted with ß-naphthol.

2. Secondary amines: should give yellow oil or solid

$R_2NH + HONO \rightarrow R_2N\text{-}NO$

(c) **Hinsberg Test**

$ArSO_2Cl + RNH_2 + NaOH \rightarrow ArSO_2NHR$

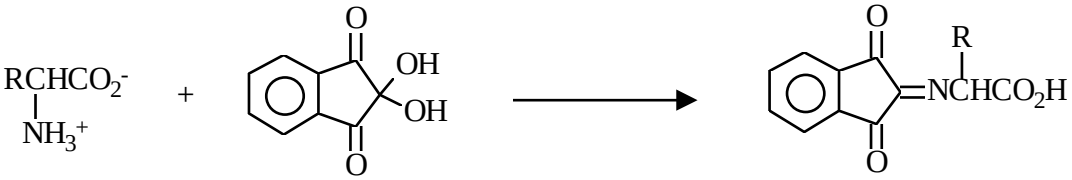
1- Primary amines: give solution that produce ppt after addition of HCl.

2- Secondary amines: give ppt not soluble in NaOH or HCl.

3- Tertiary amines : Give ppt (starting material) soluble in HCl (no reaction).

7. Tests for Amino Acids

(a) **Ninhydrin Test**:



Pos. Test: blue or blue-violet color for amino acids.

8. Tests for Aromatics

(a) **Fuming Sulfuric Acid**

This test is good for aromatics with no other functional group present .

Pos. Test: soluble in H_2SO_4 (Fuming)

(b) **Chloroform and Aluminum Chloride**

Aromatics give colored solution or powder.

Pos. Test(Orange, red, blue, purple, green)

non aromatics give yellow color (Neg.result)

9. Tests for Ethers

(a) **Hydroiodic Acid** (Zeisel's, Alkoxyl method)

ROR' + 2HI $\rightarrow$ RI + 'RI + H_2O

Pos. Test: Orange or Orange-red color

Indication: ether with R equal to 3 carbons or less.

Note: Ethyl and methyl esters give also pos. result.

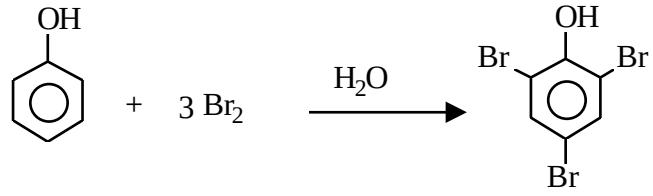
(b) **Bromine water**

Pos. Test:decolorization of Bromine

Indicates:Aromatic ethers and some aliphatic ethers.

10. Tests for Phenols

(a) **Bromine water**



Pos. Test: decolorization of bromine.

This is good for water soluble phenols

(b) **Ferric Chloride/Pyridene**

Pos. Test: Production of blue, violet, purple, green, or red-brown colors

good for all types of Ar-OH.

11. Test For Nitro compounds

(a) **Ferrous Hydroxide Reduction**

$RNO_2 + 6Fe(OH)_2 + 4H_2O \rightarrow RNH_2 + 6Fe(OH)_3$

Pos. Test indicated by formation if red, brown to brown ppt

Note: Nitroso Compounds, quinones, hydroxylomines alkyl nitrates give also pos. results

(b) **Zinc and ammonium chloride reduction**

$$RNO_2 + \frac{Zn}{NH_4Cl} \rightarrow RNHOH + H_2O$$

Test the solution with Tollens Reagent

Pos. Test $\rightarrow$ formation of metallic silver