Classification Tests

1. Classification Tests For Alcohols

a) Sodium Metal:

 $\text{ROH} + \text{Na} \rightarrow \text{RONa} + \text{H}_2(\text{g})$

<u>Positive Test:</u> evolution of gas – the rate is highly variable and depends upon the alcohol structure Other Functional groups that give positive Test:

 R_2NH , RSH, $RC \equiv C-H$, RCO_2H ,

b) Ceric Ammonium Nitrate Oxidation

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

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

Postive for alochols of 10 or fewer carbons

Very good test for 1° , 2° alcohol

Slow for 3 $^{\circ}$ alcohol

Note: Phenols gives brown or black products.

c) Jones Oxidation (CrO₃)

Good for 1 °, and 2 ° alcohols but not 3 ° 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/ZnCl₂)

shows the existence of OH group

 $\text{ROH} + \text{HCI} \ (\text{ZnCl}_2) \rightarrow \quad \text{RCI} + \text{H}_2\text{O}$

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

Note: Primary alcohols do not give positive Result.

e) Periodic Acid (HIO₄) Test for detection of Vicinal Diols.

Pos. Test: White ppt upon addition of AgNO3

(f) Acetyl Chloride (ROH & ArOH)

Pos. Test: Evolution of heat and HCl gas - ester formation in the top layer of the flask.

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 (NaHSO₃)

Pos. Test: formation of ppt

good for aldehydes , all give ppt

Only some ketones give positive results (ppt)

e) Iodoform Test_ (For methyl Ketones)

 $\begin{array}{cccc} O & & O \\ II \\ RCCH_3 + 3 I_2 + 3 NaOH \longrightarrow & RCCI_3 + 3 NaI + 3 H_2O \xrightarrow{NaOH} & O \\ II \\ RCONa + CHI_{3 (s)} \\ iodoform (ppt) \end{array}$

Pos. Test: Yellow ppt for methyl kekones

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

0		OH	0 0
CH ₃ CH	CH ₃ CH ₂ OH	RCHCH ₃	$\ \ \ $ RCCH ₂ CR

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

(a) CrO₃ (Jones Oxidation)

See alcohols part C.

(b) Tollens Reagents (Ag(NH₃)₂ OH)

$$\begin{array}{c} O \\ \parallel \\ \text{RCH} + 2 \text{ Ag}(\text{NH}_3)_2 \text{OH} \end{array} \longrightarrow 2 \text{ Ag}_{(s)} + \begin{array}{c} O \\ \parallel \\ \text{RCONH}_4 + H_2 O + \text{NH}_3 \end{array}$$

Positive Test. Formation of silver mirror. (ppt)

Fuchsin Reagent: (c) 0 Ш colorless violet-purple solution dye RCH + (d) **Bendicts solution** Ο 0 $R\ddot{C}H + Cu^{2+}$ Citrate Complex RCOH $+ Cu_2O$ <u>Positive Test</u> ==> yellow or yellowish green ppt. All aldehydes give positive result except Aromatic aldehydes give negative result. Other compounds that give positive result are 0 0 \mathbf{O} 11

RCH-CR HC-CR ArNH-NH-Ar ArNH-NH₂

4. Classification Tests for Unsaturation "alkenes & alkynes"

(a) Bromine in CCl₄



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

(b) Baeyer Test (KMnO₄ aqueous)



<u>Pos. Test</u>: Purple color discharges. and brown color PPT (MnO₂) appears **Note:** Aldehydes and alcohols also give positive result.

5. Tests for Alkyl Halides

(a) Ethanolic Silver Nitrate

 $RX + AgNO_3 \rightarrow Agx_{(s)} + RONO_2$

Pos. Test: formation of ppt.

Indicates: 2 $^{\circ}$ and 3 $^{\circ}$ RX

 $1\,^{\circ}\,\text{RX}$, $\,\text{Ar-X},$ and vinyl halides give negative Result.

Note alkylic and benzylic RX give Pos. Result

(b) Sodium lodide in Acetone

 $\begin{array}{lll} R \; X + Nal & \rightarrow & Rl + Na \; X \; (s) \\ X = Cl, \; Br \\ \underline{Pos. \; Test}: \; ppt \; forms \\ Indications: \; 1^{\,\circ} \, , \; 2^{\,\circ} \; RX \;\; , \; allylic \; and \; benzylic \; halides. \\ Not \; good \; for \; \; ArX \, , \; vinyl \; halides \; , HCCl_3 \, , \; and \; \; 3^{\,\circ} \; RX \end{array}$

6. Tests for amines

(a) Acid chloride

 $\begin{array}{c} O & O \\ II \\ RCC1 + 2 'RNH_2 \longrightarrow RNHCR + 'RN^+H_3 CI^- \end{array}$

<u>Pos. Test</u>: Heat evolves and formation of ppt when added to H_2O <u>Indications.</u> 1° & 2° amines give both heat & ppt 3° amines give only heat **Note**: ROH give also pos. result (heat).

(b) Nitrous Acid

1. Primary amines (a) RNH2 + HNO2 \rightarrow R-N2⁺ \rightarrow R+ + N2(g)

(b) $RN_2^+ + \beta$ -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

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

(c) Hinsberg Test

 $\text{ArSO}_2\text{Cl} \ + \text{RNH}_2 \ + \text{NaOH} \ \rightarrow \ \text{ArSO}_2\text{NHR}$

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

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

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

7. Tests for Amino Acids

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 . <u>Pos. Test</u>: soluble in H_2SO_4 (Fuming)

(b) Chloroform and Aluminum Chloride

Aromatics give colored solution or powder.

<u>Pos. Test</u>(Orange, red, blue, purple, green) – dependent upon the functional groups on the aryl ring. non aromatics give yellow color (Neg.result)

9. Tests for Ethers

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

 $\text{ROR'} + 2\text{HI} \ \rightarrow \ \text{RI} + \text{`RI} + \text{H}_2\text{O}$

<u>Pos. Test</u>: 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

<u>Pos. Test</u>:decolorization of Bromine Indicates:Aromatic ethers and some aliphatic ethers.

10. Tests for Phenols



<u>Pos. Test</u>: decolorization of bromine. This is good for water soluble phenols

(b) Ferric Chloride/Pyridene

<u>Pos. Test</u>: 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

 $\mathsf{RNO}_2 + \mathsf{6Fe}(\mathsf{OH})_2 + \mathsf{4H}_2\mathsf{O} \rightarrow \ \mathsf{RNH}_2 + \mathsf{6Fe}(\mathsf{OH})_3$

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

 $\text{RNO}_2 + \frac{\text{Zn}}{\text{NH}_2\text{Cl}} \rightarrow \text{RNHOH} + \text{H}_2\text{O}$

Test the solution with Tollens Reagent

 $\underline{\text{Pos. Test}} \ \rightarrow \ \text{formation of metallic silver}$