CHAPTER-07
DISTINCTION BETWEEN PAIRS & COMPOUNDS

UNSATURATION TEST

(A) Double/Triple bonded Compounds (C=C)/(C≡C) + Br_2 in CCl_4 (Brown colour) → Colourless compound.

- $R–C=CH–R + Br_2 \xrightarrow{CCl_4} R–\underset{Br}{\overset{|}{C}}H–\underset{Br}{\overset{|}{C}}H–R$

  (Alkene) (Brown) (Colourless)

- $R–C\equiv C–R + Br_2 \xrightarrow{CCl_4} R–\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{C}}}}–\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{C}}}}–R$

  (Alkene) (Brown) (Colourless)

(b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) → Brown precipitate

- $R–CH=CH–R + KMnO_4 \longrightarrow R–\underset{OH}{\overset{|}{C}}H–\underset{OH}{\overset{|}{C}}H–R + MnO_2$

  (Alkene) (Brown) (Colourless) (Brown ppt)

- $R–C\equiv C–R' + KMnO_4 \longrightarrow MnO_2 + RCOOH\ R'COOH$

  (Hot, dilute) (Brown)

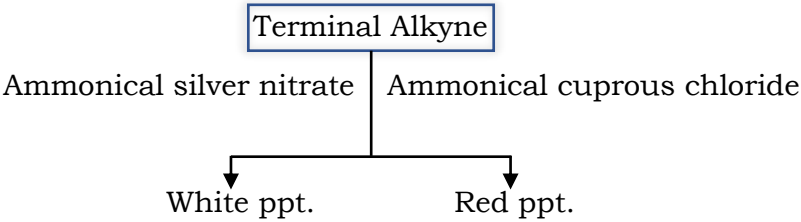
- $R–C\equiv C–H + KMnO_4 \longrightarrow MnO_2 + RCOOH + CO_2 + H_2O$

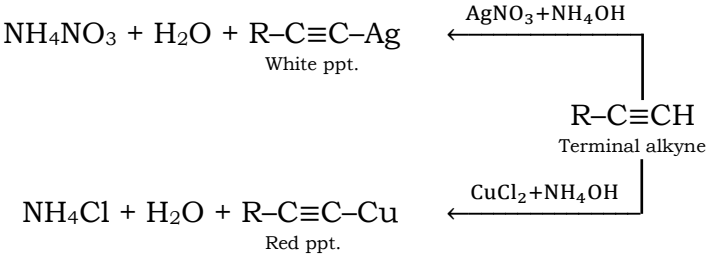
  (Alkyne) (Hot, dilute) (Brown ppt) (Colourless)

Bayer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

Notes: The above test are not given by Benzene. Although it has unsaturation.

Test for Terminal Alkyne





Nature of X-Group in C-X Bond

$$R\text{–}X + \text{aqueous KOH} \longrightarrow R - OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{(Precipitate)}}{AgX}$$

If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

Distinction Between 1°, 2° & 3° Alcohol

- $R - \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}} - OH \xrightarrow[\text{Room temerature}]{\text{Lucas reagent}} R - \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}} - Cl$

  Tertiary alcohol — Cloudiness appears immediately

- $\underset{\text{Secondary alcohol}}{R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OH} \xrightarrow[\text{Room temerature}]{\text{Lucas reagent}} \underset{\substack{\text{Cloudiness appears}\\ \text{within five minutes}}}{R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-Cl}$

- $\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow[\text{Heat}]{\text{Lucas reagent}} \underset{\substack{\text{Cloudiness appears}\\ \text{after 30 minutes}}}{R-CH_2-Cl}$

Lucas reagent is anhydrous $ZnCl_2$ + Conc. HCl.

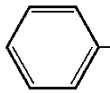
- $H_3C-\overset{\overset{OH}{|}}{CH}-R$ type of alcohols give iodoform test.

- $H_3C-\overset{\overset{OH}{|}}{CH}-R + I_2 \xrightarrow[\text{Iodoform}]{NaOH} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + RCOONa$

Phenol

Phenol + Ferric Chloride ⟶ Violet Colouration

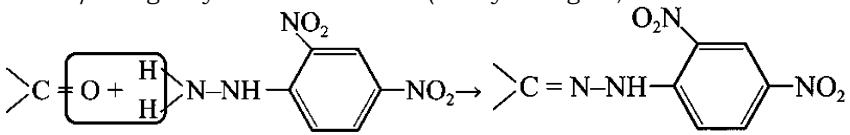
(neutral)

6  $OH + FeCl_3 \longrightarrow 3H^+ + \underset{\text{Violet colouration}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$

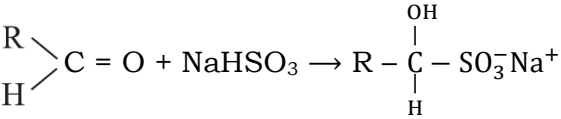
Carbonyl Group

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine →

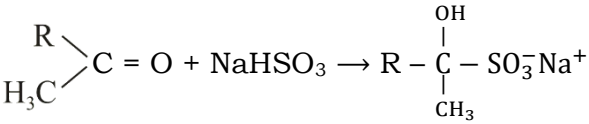
Yellow/orange crystal (Brady's reagent)



- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite.



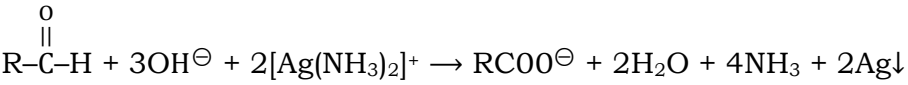
Aldehyde



Methyl ketone

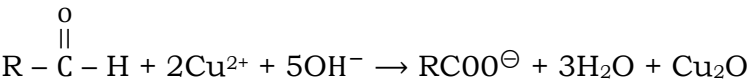
Aldehyde Group

- Aldehyde + Tollen's reagent → Silver mirror



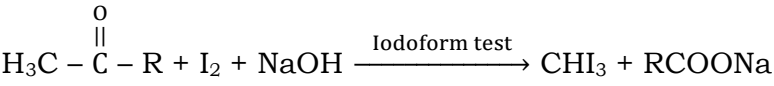
(silver mirror)

- Aldehyde + Fehling's solution → Reddish brown precipitate



(Reddish brown ppt)

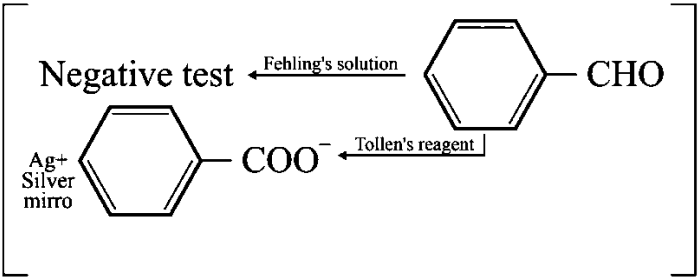
- $H_3C-\overset{O}{\overset{\|}{C}}-$ group also give iodoform test



Iodoform
(Yellow ppt.)

Aromatic Aldehyde Group

- Aromatic aldehyde + Tollen's reagent → Silver mirror
- Aromatic aldehyde + Fehling's solution → Negative test

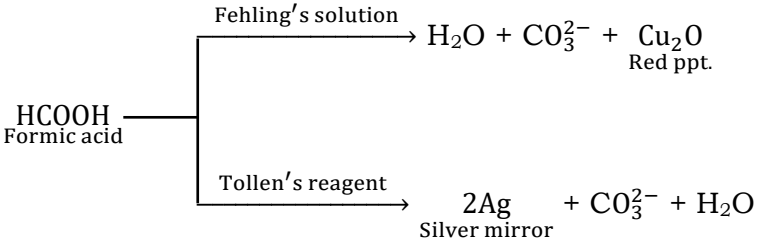


Carboxylic Group

Carboxylic acid + Sodium bicarbonate → effervescence

$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$

FORMIC ACID



AMINES (1°)

Primary amine + KOH + $CHCl_3$ $\xrightarrow{\text{Carbylamine reaction}}$ Isonitrile (Offensive smell)

Amines (1°, 2° and 3°) (Hinsberg's test)

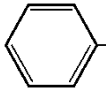
● Primary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ Soluble

● Secondary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ insoluble

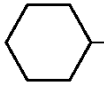
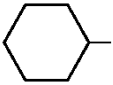
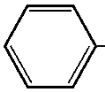
- Tertiary amine + Benzenesulphonyl chloride → No reaction

Notes: Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and Chlorobenzene

- $C_2H_5–Cl + aq.\ KOH \xrightarrow{Boil} C_2H_5–OH + KCl \xrightarrow[AgNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$
-  $+ aq.\ KOH \xrightarrow[AgNO_3,\ HNO_3]{Boil}$ No reaction

Chlorocyclohexane and chlorobenzene

-  $+ aq.\ KOH \xrightarrow{Boil}$  $+ KCl \xrightarrow[AgNO_3,\ HNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$
-  $+ aq.\ KOH \xrightarrow[AgNO_3,\ HNO_3]{Boil}$ No reaction

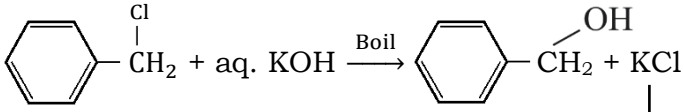
Chlorocyclohexane and Bromoethane

- $C_2H_5–Cl + aq.\ KOH \xrightarrow{Boil} C_2H_5 – OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$

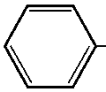
  (Chloroethane) White ppt.
- $C_2H_5–Br + aq.\ KOH \xrightarrow{Boil} C_2H_5 – OH + KBr \xrightarrow[AgNO_3]{HNO_3} AgBr$

  (Bromoethane) Yellow ppt.

Benzyl Chloride & Chlorobenzene

- 
(Benzyl chloride)

$$\xrightarrow[HNO_3,\ AgNO_3]{} AgCl \text{ White ppt.}$$

-  + aq. KOH $\xrightarrow[HNO_3,\ AgNO_3]{\text{Boil}}$ No reaction

(Chlorobenzene)

Ethyl Chloride & Vinyl Chloride

- $C_2H_5 - Cl$ + aq. KOH $\xrightarrow{\text{Boil}}$ $C_2H_5 - OH + KCl$
(Ethyl chloride)

$$\xrightarrow[AgNO_3]{HNO_3} AgCl \text{ White ppt.}$$

- $H_2C{=}CH{-}Cl$ + aq. KOH $\xrightarrow[HNO_3,\ AgNO_3]{\text{Boil}}$ No reaction
(Vinyl chloride)

n-Propyl Alcohol & Iso-Propyl Alcohol

- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$
No cloudiness at room temp.

- $H_3C{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$
Cloudiness within 5 minutes

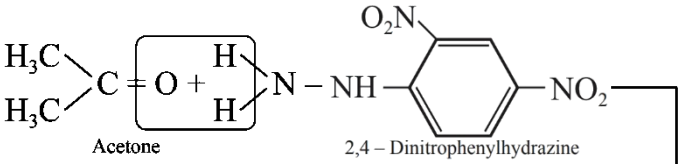
Ethyl Alcohol & Methyl Alcohol (Iodoform Test)

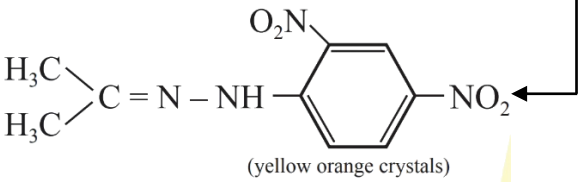
- $CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa$

Yellow ppt.

- $CH_3OH + 4I_2 + 6NaOH \longrightarrow$ No yellow ppt.

Ethyl Alcohol & Acetone (2,4-DNP)

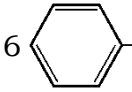
- 



- $C_2H_5OH \xrightarrow{2,4-DNP}$ No reaction

Phenol & Ethyl Alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride ⟶ Violet colouration



$$6\,\text{C}_6\text{H}_5\text{OH} + FeCl_3 \longrightarrow 3H^+ + \underset{\text{Violet colouration}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

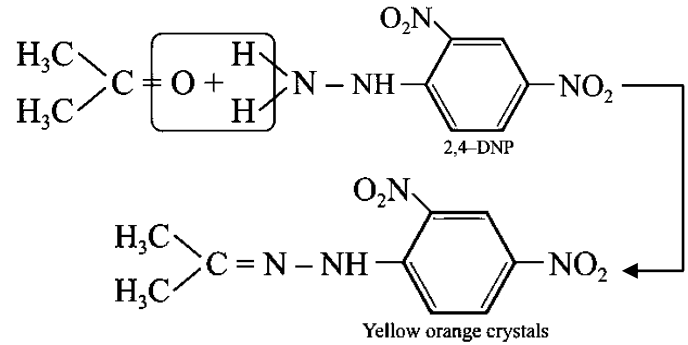
- CH_3CH_2OH + Neutral ferric chloride ⟶ No violet colouration

Benzoic Acid & Phenol ($NaHCO_3$)

- Benzoic acid + Sodium bicarbonate → effervescence
  $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$

- Phenol + Sodium bicarbonate → No effervescence
  (Phenol is less acidic than benzoic acid)

Propanone and propanol (2,4-DNP)



- Propanol + 2,4-Dinitrophenylhydrazine ⟶ No crystals

Ethanal & Propanal (Iodoform Test)

- $H_3C–\overset{\overset{O}{\|}}{C}–H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform}}{CHI_3} + HCOONa$

  Ethanal — (Yellow ppt.)

- $H_3C–CH_2–\overset{\overset{O}{\|}}{C}–H + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal & Propanone (Tollen's & Fehling Reagent)

- Propanal + Tollen's reagent ⟶ Silver mirror

$$H_3C–CH_2–\overset{\overset{O}{\|}}{C}H + 3OH^- + 2[Ag(NH_3)_2]^+$$

$$CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$

(Silver mirror)

- Propanal + Fehling's solution ⟶ Reddish brown precipitate

$$H_3C - CH_2 - CH + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2C00^- + 3H_2O + Cu_2O$$

(Reddish brown ppt.)

- Propanone → Fehling′s solution → Negative test
- Propanone → Tollen′s reagent → Negative test

Pentan-2-one & Pentan-3-one (Iodoform Test)

- $H_3C–CH_2–CH_2–\overset{\overset{O}{\|}}{C}–CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + CH_3CH_2CH_2COONa$

(Pentan-2-one)

Iodoform (Yellow ppt.)

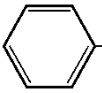
- $H_3C–CH_2–\overset{\overset{O}{\|}}{C}–CH_2–CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal & Benzaldehyde (Fehling Solution)

- Propanal + Fehling's solution ⟶ Reddish brown precipitate

$$H_3C–CH_2–\overset{\overset{O}{\|}}{C}–H + \underset{\text{Fehling′s solution}}{2Cu^{2+}} + 5OH^- \longrightarrow CH_3CH_2C00^- + 3H_20 + Cu_20$$

- Benzaldehyde + Fehling's solution ⟶ No precipitate



$-CHO + 2Cu^{2+} + 5OH^- \longrightarrow$ No reaction

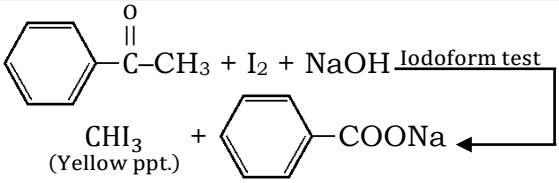
Methanoic Acid & Ethanoic Acid (Tollen's and Fehling Solution)

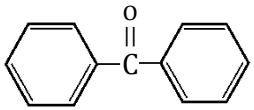
- $\underset{\text{Methanoic acid}}{HCOOH}$
  - Fehling's solution → $H_2O + CO_3^{2-} + Cu_2O$
  - Tollen's reagent → $2Ag\downarrow + CO_3^{2-} + H_2O$
- Ethanoic Acid
  - Fehling's solution → No brown ppt.
  - Tollen's reagent → No silver mirror

Ethanal & Methanal (Iodoform Test)

- $\underset{\text{(Ethanal)}}{CH_3CHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3} + HCOONa$
- $\underset{\text{(Methanal)}}{HCHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Acetophenone & Benzophenone (Iodoform Test)

- 

- 

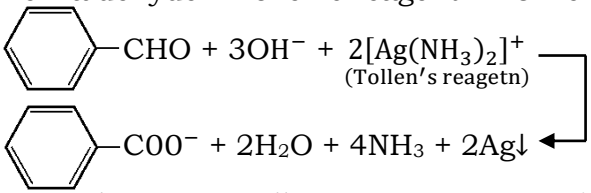
Benzoic Acid & Ethylbenzoate

- $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + \underset{\text{(effervescence)}}{CO_2\uparrow} + H_2O$

- Ethyl benzoate + Sodium bicarbonate ⟶ No effervescence

Benzaldehyde & Acetophenone (Tollen's Test)

- Benzaldehyde + Tollen's reagent ⟶ Silver mirror



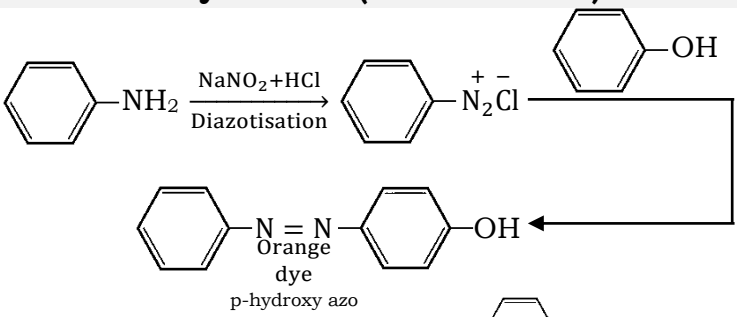
- Acetophenone + Tollen's reagent ⟶ No silver mirror

Methyl Amine & Dimethyl Amine (Isocyanide Test)

- $\underset{\text{Methyl amine}}{CH_3NH_2} + CHCl_3 + 3KOH \xrightarrow[\text{(alc.)}]{} \underset{\substack{\text{Methyl isocynaide}\\\text{(Offfensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$

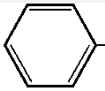
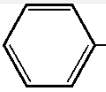
- $\underset{\text{Di-methyl amine}}{H_3C{-}\overset{\overset{CH_3}{|}}{N}H} + CHCl_3 + 3KOH \xrightarrow[\text{(alc.)}]{} \text{No offensive smell}$

Aniline & Ethyl Amine (Diazotisation)

- 

- $\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} \xrightarrow{NaNO_2+HCl} CH_3CH_2OH \xrightarrow{OH}$ No orange dye

Aniline & N-Methylaniline (Isocyanide Test)

- 
$NH_2 + CHCl_3 + 3KOH \xrightarrow[(alc.)]{} $ 
$NC + 3KCl + 3H_2O$

Aniline

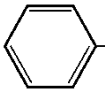
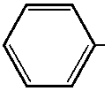
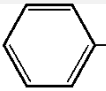
Phynyl icocyanide

(Offensive smell)

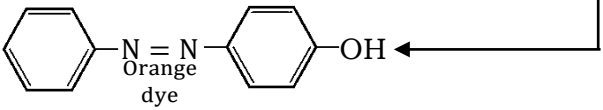
- 
$NH–CH_3 + CHCl_3 + 3KOH \xrightarrow[(alc.)]{} $ No offensive smell

N-Methylaniline

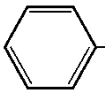
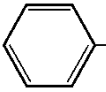
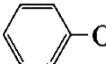
Aniline & Benzylamine (Diazotisation + Phenol)

- 
$NH_2 \xrightarrow[\text{Diazotisation}]{NaNO_2+HCl}$ 
N_2Cl 
OH

Aniline



Orange dye

- 
$CH_2–NH_2 \xrightarrow{NaNO_2+HCl}$ 
$CH_2–OH$ 
OH

No orange dye ←

Glucose & Fructose

- Glucose + $Br_2 + H_2O \longrightarrow$ Gluconic acid + 2HBr
(Brown colour) (Colourless)

- Fructose + $Br_2 + H_2O \longrightarrow$ Brown colour
(Brown colour) (No change in colour)

Glucose & Sucrose

- Glucose + Tollen's reagent ⟶ Silver mirror

- Sucrose + Tollen's reagent ⟶ No silver mirror

Glucose & Starch

- Glucose + Fehling's solution ⟶ Red ppt.
- Starch + Fehling's solution ⟶ No red ppt.

or

- Glucose + I_2 solution ⟶ No blue colour
- Starch + I_2 solution ⟶ Blue colour