CHAPTER 5

# DISTINCTION BETWEEN PAIRS OF COMPOUNDS

## UNSATURATION TEST

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

- $R-CH=CH-R + Br_2 \xrightarrow{CCl_4} R-\underset{Br}{\overset{Br}{CH}}-\underset{Br}{\overset{Br}{CH}}-R$
  (Alkene) (Brown) (Colourless)

- $R-C\equiv C-R + Br_2 \xrightarrow{CCl_4} R-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-R$
  (Alkyne) (Brown) (Colourless)

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

- $R-CH=CH-R + KMnO_4 \rightarrow R-\underset{OH}{\overset{OH}{CH}}-\underset{OH}{\overset{OH}{CH}}-R + MnO_2$
  (Alkene) (Cold, dilute) (Colourless) Brown ppt

- $R-C\equiv C-R' + KMnO_4 \rightarrow MnO_2 + RCOOH + R'COOH$
  (Hot, dilute) Brown ppt.

- $R-C\equiv C-H + KMnO_4 \rightarrow MnO_2 + RCOOH + CO_2 + H_2O$
  (Alkyne) (Hot, dilute) Brown ppt. (Colourless)

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

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

## TEST FOR TERMINAL ALKYNE

Terminal alkyne

- Ammonical silver nitrate → White ppt.
- Ammonical cuprous chloride → Red ppt.

$NH_4NO_3 + H_2O + R-C\equiv C-Ag \xleftarrow{AgNO_3 + NH_4OH} R-C\equiv CH$
White ppt. Terminal alkyne

$NH_4Cl + H_2O + R-C\equiv C-Cu \xleftarrow{Cu_2Cl_2 + NH_4OH} R-C\equiv CH$
Red ppt. Terminal alkyne

## NATURE OF X-GROUP IN C–X BOND

$R-X + \text{aqueous KOH} \rightarrow R-OH + KX \xrightarrow[AgNO_3]{HNO_3} AgX$
Precipitate

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

## DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS

- $R-\underset{R}{\overset{R}{C}}-OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R-\underset{R}{\overset{R}{C}}-Cl$
  Tertiary alcohol — Cloudiness appears immediately

- $R-\underset{H}{CH}-OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R-\underset{H}{CH}-Cl$
  Secondary alcohol — Cloudiness appears within five minutes

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

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

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

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

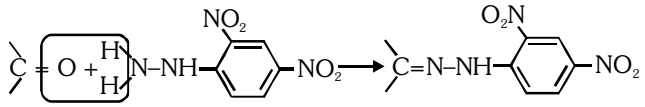
## PHENOL

Phenol + ferric chloride (neutral) ⟶ Violet colouration

$6\,C_6H_5OH + FeCl_3 \rightarrow 3H^+ + [Fe(OC_6H_5)_6]^{3-} + 3HCl$
Violet colouration

## 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.

$R-CH=O + NaHSO_3 \rightarrow R-\underset{H}{\overset{OH}{C}}-SO^-_3Na^+$
Aldehyde

$H_3C-C(=O)-R + NaHSO_3 \rightarrow R-\underset{CH_3}{\overset{OH}{C}}-SO^-_3Na^+$
Methyl ketone

## ALDEHYDE GROUP

- Aldehyde + Tollen's reagent ⟶ Silver mirror

$$R-\overset{O}{\overset{\|}{C}}-H+3OH^{\ominus}+2[Ag(NH_3)_2]^{+}\longrightarrow RCOO^{\ominus}+2H_2O+4NH_3+2Ag\downarrow$$

(silver mirror)

- Aldehyde+Fehling's solution → Reddish brown precipitate

$$R-\overset{O}{\overset{\|}{C}}-H+2Cu^{2+}+5OH^{-}\longrightarrow RCOO^{\ominus}+3H_2O+Cu_2O$$

(Reddish brown ppt)

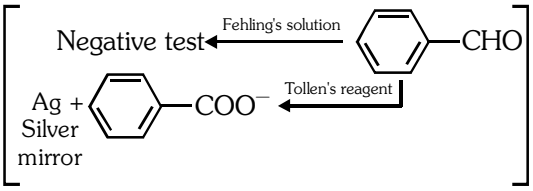
- $H_3C-\overset{O}{\overset{\|}{C}}-$ group also give iodoform test

$$H_3C-\overset{O}{\overset{\|}{C}}-R+I_2+NaOH\xrightarrow{\text{Iodoform test}}CHI_3+RCOONa$$

Iodoform
(Yellow ppt.)

## AROMATIC ALDEHYDE GROUP

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

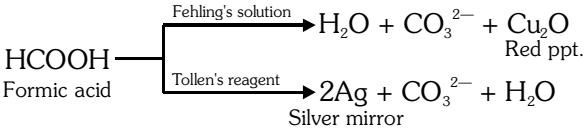



## CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence

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

## FORMIC ACID




## AMINES (1°)

$$\text{Primary amine}+KOH+CHCl_3\xrightarrow[\text{reaction}]{\text{Carbylamine}}\text{Isonitrile}$$

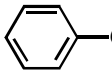
(Offensive smell)

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

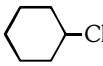
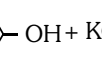
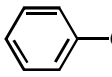
- Primary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ soluble
- Secondary amine + Benzenesulphonyl chlorid ⟶ Precipitate $\xrightarrow{KOH}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction

**Note :** Benzenesulphonyl chloride is called Hinsberg's reagent.

### Chloroethane and chlorobenzene

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

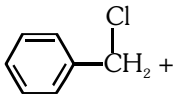
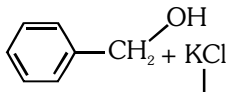
### Chlorocyclohexane and chlorobenzene

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

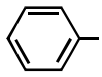
### Chloroethane and bromoethane

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

### Benzyl chloride and chlorobenzene

-  $+aq.\ KOH\xrightarrow{Boil}$  $+KCl$

  (Benzyl chloride)

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

  Chlorobenzene

### Ethyl chloride and vinyl chloride

- $C_2H_5-Cl+aq.KOH\xrightarrow{Boil}C_2H_5-OH+KCl$

  (Ethyl chloride)

  $AgCl\xleftarrow[AgNO_3]{HNO_3}$ (White ppt.)
- $H_2C=CH-Cl+aq.KOH\xrightarrow[HNO_3,\ AgNO_3]{Boil}$ No reaction

  Vinyl chloride

### n-Propyl alcohol and iso-propyl alcohol

- $CH_3CH_2CH_2OH+HCl\xrightarrow{ZnCl_2}CH_3CH_2CH_2Cl$

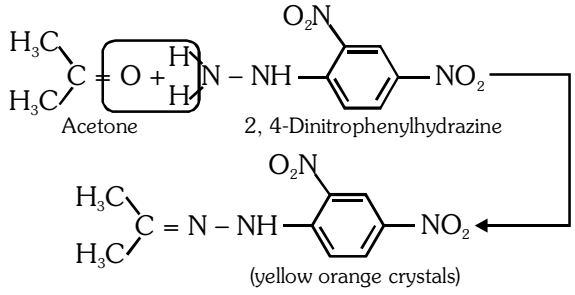
  No cloudiness at room temp.
- $H_3C-\underset{OH}{\underset{|}{CH}}-CH_3\xrightarrow[HCl]{ZnCl_2}H_3C-\underset{Cl}{\underset{|}{CH}}-CH_3$

  Cloudiness within 5 minutes

***Ethyl alcohol and 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 and acetone (2, 4 – DNP)***

- 


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

***Phenol and ethyl alcohol (Neutral $FeCl_3$)***

- Phenol + Neutral ferric chloride $\longrightarrow$ Violet colouration

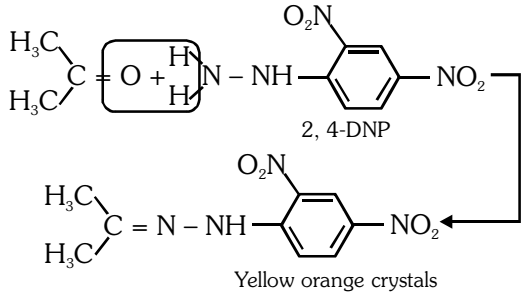
$$6\,C_6H_5OH + FeCl_3 \longrightarrow 3H^+ + [Fe(OC_6H_5)_6]^{3-} + 3HCl$$
Violet colouration

- $CH_3CH_2OH$ + Neutral ferric chloride $\longrightarrow$ No violet colouration

***Benzoic acid and phenol ($NaHCO_3$)***

- Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence
  $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
- Phenol + Sodium bicarbonate $\rightarrow$ No effervescence
  (Phenol is less acidic than benzoic acid)

***Propanone and propanol (2, 4 - DNP)***

- 


- Propanol + 2,4-Dinitrophenylhydrazine $\longrightarrow$ No crystals

***Ethanal and propanal (Iodoform test)***

- $H_3C-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + HCOONa$
  Ethanal → Iodoform (Yellow ppt.)
- $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  Propanal

***Propanal and propanone (Tollen's and Fehling reagent)***

- Propanal + Tollen's reagent $\longrightarrow$ Silver mirror

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$
(Silver mirror)

- Propanal + Fehling's solution $\rightarrow$ Reddish brown precipitate

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$
(Reddish brown ppt.)

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

***Pentan-2-one and pentan-3-one (Iodoform test)***

- $H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + CH_3CH_2CH_2COONa$
  (Pentan-2-one) → Iodoform (Yellow ppt.)
- $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  Pentan-3-one

***Propanal and benzaldehyde (Fehling solution)***

- Propanal + Fehling's solution $\rightarrow$ Reddish brown precipitate

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$
Fehling's solution

- Benzaldehyde + Fehling's solution $\rightarrow$ No precipitate

$$C_6H_5CHO + 2Cu^{2+} + 5OH^- \longrightarrow \text{No reaction}$$

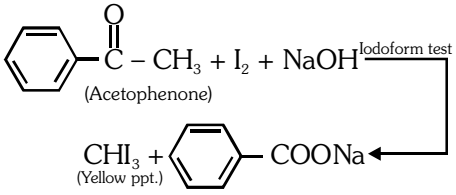
***Methanoic acid and ethanoic acid (Tollen's & Fehling solution)***

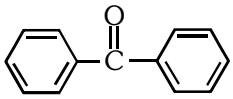
- HCOOH (Methanoic acid)
  - Fehling's solution → $H_2O + CO_3^{2-} + Cu_2O$
  - Tollen's reagent → $2Ag\downarrow + CO_3^{2-} + H_2O$
- Ethanoic acid
  - Fehling's solution → No brown ppt.
  - Tollen's reagent → No silver mirror

## Ethanal and methanal (Iodoform test)

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

## Acetophenone and benzophenone (Iodoform test)

- 

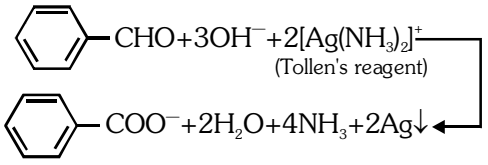
-  $+I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No ppt.
  (Benzophenone)

## Benzoic acid and ethylbenzoate

- $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
  effervescence
- Ethyl benzoate + Sodium bicarbonate → No effervescence

## Benzaldehyde and acetophenone (Tollen's test)

- Benzaldehyde + Tollen's reagent → Silver mirror



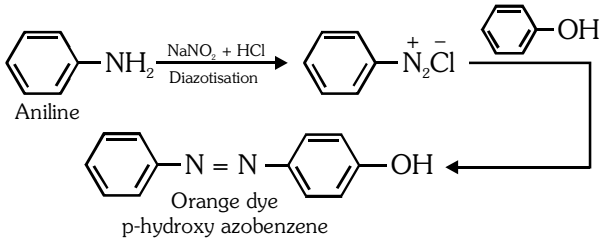

- Acetophenone + Tollen's reagent ⟶ No silver mirror

## Methyl amine and dimethyl amine (Isocyanide test)

- $CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$
  Methyl amine — (alc.) — Methyl isocyanide (Offensive smell)

- $H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{N}}H + CHCl_3 + 3KOH$ (alc.) ⟶ No offensive smell
  Di-methyl amine

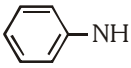
## Aniline and ethyl amine (Diazotisation)

- 

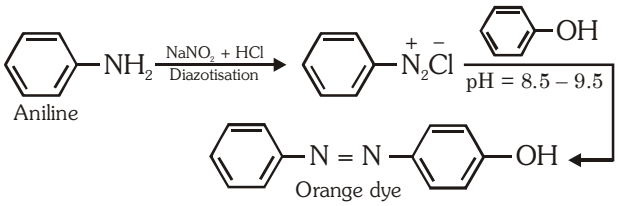

- $CH_3CH_2NH_2 \xrightarrow{NaNO_2 + HCl} CH_3CH_2OH \xrightarrow{OH}$ No Orange dye
  Ethyl amine

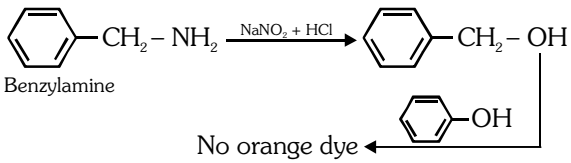
## Aniline and N-methylaniline (Isocyanide test)

- $NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{(alc.)}]{} NC + 3KCl + 3H_2O$
  Aniline — Phenyl isocyanide (Offensive smell)

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

## Aniline and Benzylamine (Diazotisation + phenol)

- 


- 


## Glucose and fructose

- Glucose + $Br_2$ + $H_2O$ ⟶ Gluconic acid + 2HBr
  (Brown colour) — (Colourless)
- Fructose + $Br_2$ + $H_2O$ ⟶ Brown colour
  (Brown colour) — (no change in colour)

## Glucose and sucrose

- Glucose + Tollen's reagent ⟶ Silver mirror
- Sucrose + Tollen's reagent ⟶ No silver mirror

## Glucose and 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