CHAPTER 22

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.

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

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

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

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

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

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

Baeyer'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

Terminal alkyne

Ammonical silver nitrate | Ammonical cuprous chloride

White ppt. | Red ppt.

$AgNO_3 + NH_4OH$

$R - C \equiv CH$ (Terminal alkyne) → $NH_4NO_3 + H_2O + R{-}C{\equiv}C{-}Ag$ (White ppt.)

$CuCl_2 + NH_4OH$

$R - C \equiv CH$ (Terminal alkyne) → $NH_4Cl + H_2O + R{-}C{\equiv}C{-}Cu$ (Red ppt.)

NATURE OF X-GROUP IN C-X BOND

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

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

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOL

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

  Tertiary alcohol → Cloudiness appears immediately

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

  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

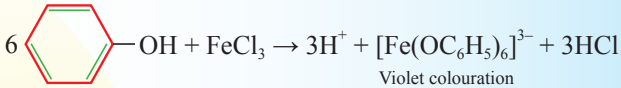
Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

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

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

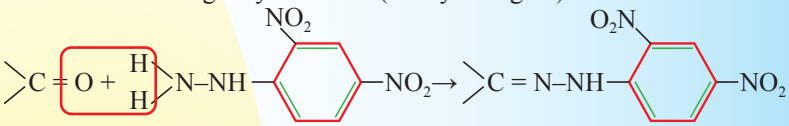
PHENOL

Phenol + ferric chloride → Violet colouration
(neutral)

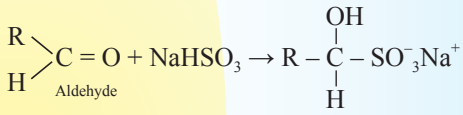


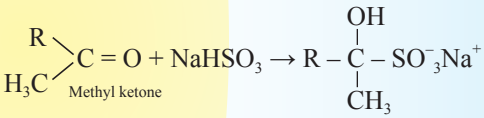
CARBONYL GROUP

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine →
  Yellow/orange crystal (Brady's reagent)



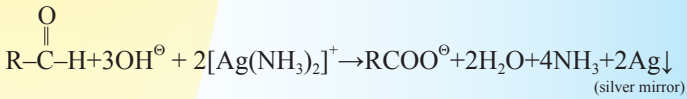
- All aldehydes and only aliphatic methyl ketones
  + $NaHSO_3$ → White crystalline bisulphite.



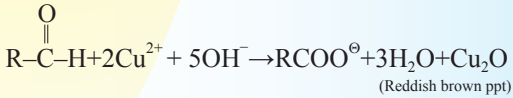


ALDEHYDE GROUP

- Aldehyde + Tollen's reagent → Silver mirror



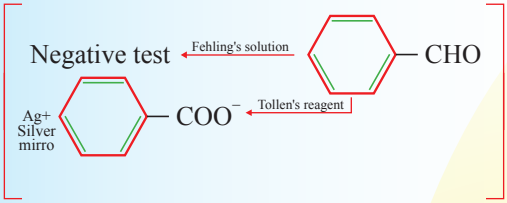
- Aldehyde + Fehling's solution → Reddish brown precipitate



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

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

$$HCOOH \text{ (Formic acid)} \xrightarrow{\text{Fehling's solution}} H_2O + CO_3^{2-} + Cu_2O \text{ (Red ppt.)}$$

$$HCOOH \text{ (Formic acid)} \xrightarrow{\text{Tollen's reagent}} 2Ag + CO_3^{2-} + H_2O \text{ (Silver mirror)}$$

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 chloride → Precipitate $\xrightarrow{KOH}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction.

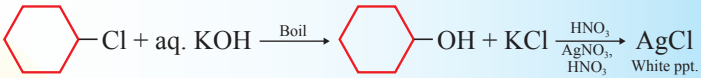
NOTES

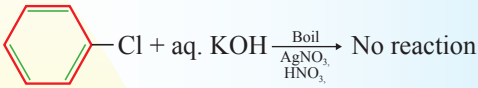
Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and Chlorobenzene

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

Chlorocyclohexane and chlorobenzene

- 

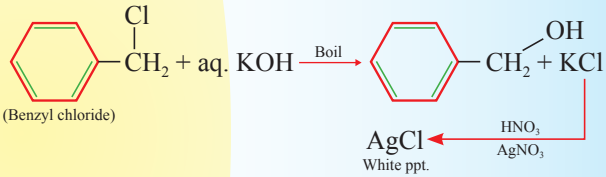
- 

Chlorocyclohexane and bromoethane

- C_2H_5–Cl + aq. KOH $\xrightarrow{\text{Boil}}$ C_2H_5–OH+KCl $\xrightarrow[AgNO_3]{HNO_3}$ AgCl (White ppt.)
  (Chloroethane)

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

Benzyl chloride and chlorobenzene

- 

  (Benzyl chloride)

- 

  Chlorobenzene

Ethyl chloride and vinyl chloride

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

  AgCl (White ppt.) $\xleftarrow[AgNO_3]{HNO_3}$

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

n-Propyl alcohol and iso-propyl alcohol

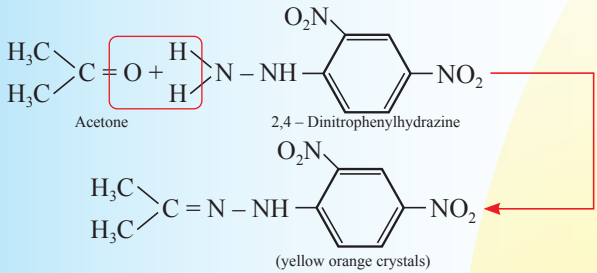
- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$
  No cloudiness at room temp.

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

Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa$
- $CH_3OH + 4I_2 + 6NaOH \rightarrow$ No yellow ppt.

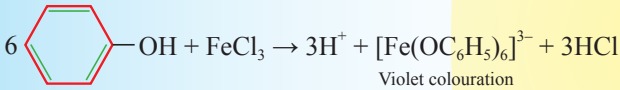
Ethyl alcohol and acetone (2,4 – DNP)

- 

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

Phenol and ethyl alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride → Violet colouration



- CH_3CH_2OH + Neutral ferric chloride → No violet colouration

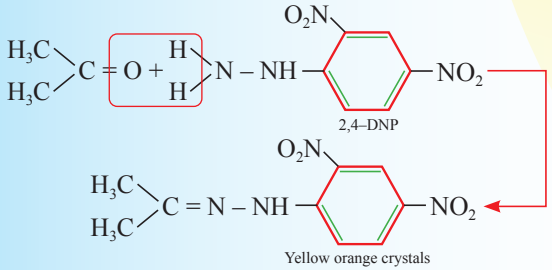
Benzoic acid and phenol ($NaHCO_3$)

- 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 and propanal (Iodoform test)

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

Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent → Silver mirror

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

(Silver mirro)

- Propanal + Fehling's solution → Reddish brown precipitate

$$H_3C-CH_2-\overset{\overset{O}{\|}}{C}H + 2Cu^{2+} + 5OH^- \rightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

(Reddish brown ppt.)

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

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

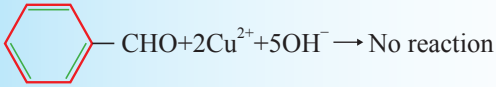
- $H_3C-CH_2-CH_2-\underset{\text{(Pentan-2-one)}}{\overset{\overset{O}{\|}}{C}}-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\(\text{Yellow ppt.})}}{CHI_3} + CH_3CH_2CH_2COONa$
- $H_3C-CH_2-\underset{\text{Pentan-3-one}}{\overset{\overset{O}{\|}}{C}}-CH_2-CH_3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

Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution → Reddish brown precipitate

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

- Benzaldehyde + Fehling's solution → No precipitate



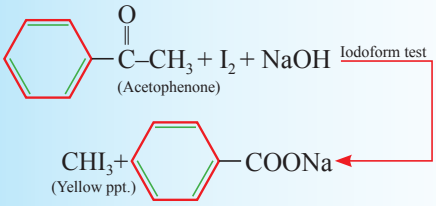
Methanoic acid and ethanoic acid (Tollen's & Fehling solution)

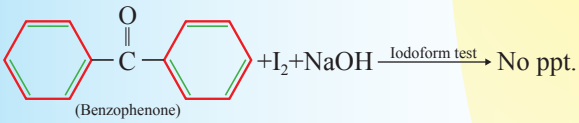
- HCOOH (Methanoic acid)
  - Fehling's solution → $H_2O + CO_3^{2-} + Cu_2O$
  - Tollen's reagent → $2Ag\downarrow + CO_3^{2-} + H_2O$
- Ethanoic acid
  - Fehling's solution → No brown ppt.
  - Tollen's reagent → No silver mirror

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)

- 

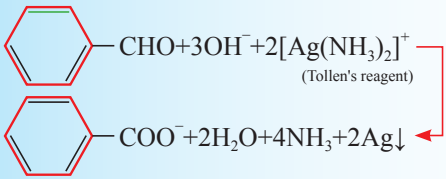
- 

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)

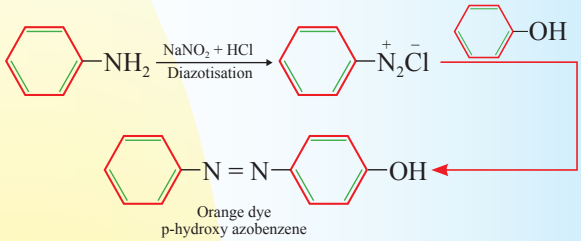
- $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$

  Methyl amine (alc.) Methyl isocyanide (Offensive smell)

- $H_3C-\underset{\underset{CH_3}{|}}{N}H + CHCl_3 + 3KOH(alc.) \rightarrow$ No offensive smell

  Di-methyl amine

Aniline and ethyl amine (Diazotisation)

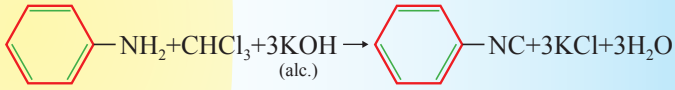
- 

  Orange dye
  p-hydroxy azobenzene

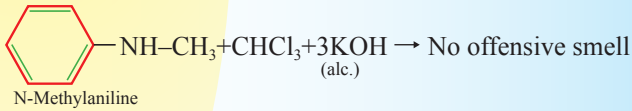
- $CH_3CH_2NH_2 \xrightarrow{NaNO_2+HCl} CH_3CH_2OH \xrightarrow{-OH}$ No Orange dye

  Ethyl amine

Aniline and N-methylaniline (Isocyanide Test)

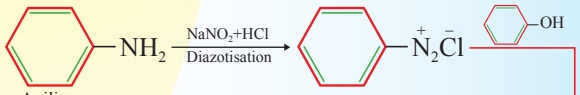
- 

  Aniline Phenyl isocyanide (Offensive smell)

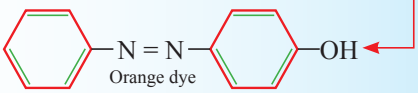
- 

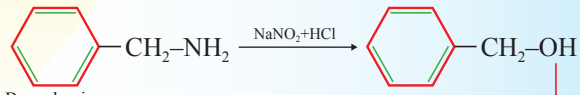
  N-Methylaniline

Aniline and Benzylamine (Diazotisation + phenol)

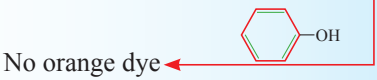
- 

  Aniline



- 

  Benzylamine



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

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