

FTOC P. 100

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EXPERIMENT

2

# ACETYLATION

(Preparation of Acetyl Salicylic Acid)

Date : \_\_\_\_\_

**Aim**

Preparation of acetyl salicylic acid by acetylation of salicylic acid.

**Chemicals**

Salicylic acid, acetic anhydride,  $H_2SO_4$ .

**Principle**

Phenols, Alcohol's and primary amines react readily with acetic anhydride on warming to yield mono acetyl derivatives. On prolonged heating with excess of acid anhydride, diacetyl derivative also forms. When the product is crystallised from an aqueous solvent like dilute alcohol, only the mono acetyl derivative is obtained.

Formation of diacetyl derivative is overcome by the acetylation is conducted in aqueous solution.

Acetylation with acetic anhydride is expensive and hence inexpensive glacial acetic acid may be used.

Phenols unlike amines can not be acetylated satisfactorily in aqueous solution. Acetylation is carried with acetic anhydride in the presence of a little concentrated Sulphuric Acid as catalyst.

**Preparation of Acetyl Salicylic Acid (Asprin)**

5 grams of dry Salicylic Acid is mixed with 7.0 ml of redistilled acetic anhydride in a 100 ml conical flask and 2 - 3 drops of conc  $H_2SO_4$  is added. The mixture is swirled for uniform mixing and warmed on a water bath at about 50 - 60° C with occasional stirring using a thermometer for about 15 minutes. The mixture is cooled with occasional stirring. 75 ml distilled water is added to the cooled solution and filtered using suction pump.

The crude acetyl salicylic acid is dissolved in 15 ml hot ethanol and poured the solution into 40 ml warm water. The mixture is warmed if necessary to dissolve any solid formed and then cooled slowly. Beautiful needle like crystals of Asprin *i.e.*, acetyl salicylic acid are formed.

M.P. 128 - 135° C with decomposition

Yield 5-9 gram.

# BENZOYLATION

(Preparation of Benzylidene Aniline)

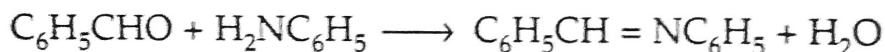
Date : \_\_\_\_\_

## Aim

To Prepare benzylidene aniline

## Principle

Primary amines condense with aldehyde to form Schiff's base



## Procedure

4.0 ml of pure benzaldehyde and 4.0 ml of redistilled aniline are mixed in an evaporating dish and heated on a water bath for about 20 minutes. The mixture is stirred with a glass rod frequently during heating. When water drops are observed on the surface of the oil, the evaporating dish is cooled in water with stirring. When the oily liquid started crystallisation it is transferred into a conical flask and recrystallised from methylated spirit as follows.

The solid is mixed with 40-50 ml methylated spirit and heated on a water bath until all crystals are dissolved. The hot solution is filtered through hot fluted filter paper. On cooling, colourless crystals of benzylidene aniline formed.

M.P 52° C

Yield 5 gms

**BENZOYLATION OF PHENOL***(Preparation of Phenyl Benzoate)*

Date : \_\_\_\_\_

**Aim**

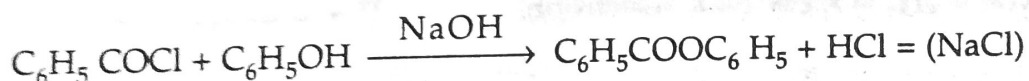
Preparation of Phenyl Benzoate

**Chemicals**

Phenol, NaOH, Benzoyl chloride.

**Principle**

Benzoylation of aromatic compound has less application than acetylation. The process is used for the identification of aromatic Hydroxy compounds and amines. Benzoyl chloride is the reagent and the benzoylation is carried in aqueous medium. This reaction is called **Schotten - Baumann method of Benzoylation**. Phenol reacts with Benzoyl chloride in the presence of NaOH as below

**Procedure**

2.5 gms of phenol is dissolved in 38 ml of 10% NaOH solution in a 100 ml conical flask. 4.5 ml of benzoyl chloride is added, the conical flask is stoppered tightly and the mixture is vigorously shaken for about 10 minutes. When the reaction is complete solid ester appeared. It is filtered by suction arrangement. The precipitate is washed with water and recrystallised from methylated spirit as below.

Hot methylated (below 60°) spirit is added twice the required volume and when the ester is completely dissolved the mixture is evaporated at 60° C to half its volume. When crystallisation started the hot solution is quickly filtered through Buchner funnel. On cooling the solution colourless crystals of phenyl Benzoate separated. The crystals are dried upon filter paper.

Yield 4.1 gm

M.P 69° C

# NITRATION

(Preparation of Nitrobenzene)

Date : \_\_\_\_\_

## Aim

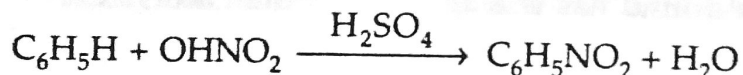
To prepare nitro benzene from benzene by aromatic electrophilic substitution

## Chemicals

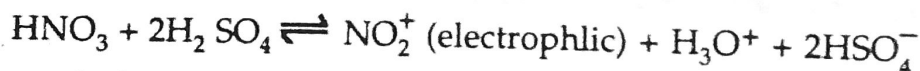
Benzene, nitric acid, sulphuric acid, anhydrous  $\text{CaCl}_2$

## Principle

Aromatic hydrocarbons undergo electrophilic substitution easily; The 'H' atoms can be easily replaced by Nitro group with concentrated nitric acid in the presence of concentrated sulphuric acid.



Sulphuric acid acts as a strongly acid medium and as a dehydrating agent. It also converts nitric acid into highly reactive nitronium ion.



Nitration at comparatively low temperature produces nitro benzene.

## Procedure

17.5 ml of conc  $\text{HNO}_3$  is taken into a 250 ml round bottomed flask and 20 ml of concentrated  $\text{H}_2\text{SO}_4$  is slowly added in portions keeping the mixture cool during the addition of the acid by immersing the flask in cold water. 15 ml of benzene liquid is added in portions of 1 ml each time shaking the flask well after each addition. The temperature is maintained below  $55^\circ\text{C}$  throughout. When all the benzene is added a reflux condenser is fixed to the flask and it is heated on a water bath at  $60^\circ\text{C}$  for about 15 minutes, with occasional vigorous shaking. Finally the mixture is poured into a 250 ml beaker and shaken very well with cold water. Nitrobenzene liquid settled at the bottom of the beaker. The upper layer of acid is drained out carefully and again washed with cold water. The process is repeated 2, 3 times and the residual liquid is transferred into a separatory funnel. The heavy liquid is filtered through fluted filter paper and transferred into 250 ml round bottomed flask provided with Claisen condenser. The liquid is heated to  $206-211$  and the distillate is collected below  $214^\circ\text{C}$ .

B.P  $210^\circ\text{C}$

Yield 16 gms

# HALOGENATION

(Preparation of *p* - bromoacetanilide)

Date : \_\_\_\_\_

## Aim

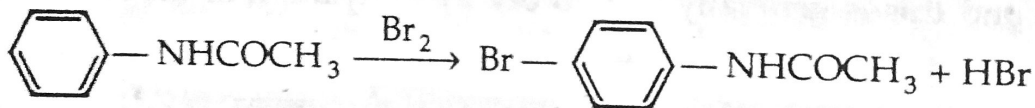
To prepare *p* - bromoacetanilide by the electrophilic bromination of Acetanilide.

## Chemicals

Acetanilide, glacial acetic Acid, liquid Bromine, 10% sodium bisulphite solution.

## Principle

Bromination of aromatic primary amine is carried only by protecting the  $\text{NH}_2$  group by acetylation.



## Procedure

7 gram of finely powdered acetanilide is dissolved in 25 ml glacial acetic acid in a 250 ml conical flask. 2.7 ml of Bromine liquid is dissolved in 12.5 ml glacial acetic acid and transferred into a burette. The bromine solution is now slowly added to acetanilide solution drop by drop with constant shaking. When it is observed that the conical flask is getting heated it is kept in a beaker of cold water for some time. Bromine solution is added till the resulting mixture appeared orange coloured. The mixture is allowed to stand at room temperature for about 15 minutes with occasional shaking. The reaction mixture is poured into 200 ml water in a 250 beaker. The conical flask is rinsed with 50 ml water and the rinsings are taken into the beaker. It is stirred well and 10% sodium bisulphite solution is added drop by drop to remove the orange colour. The crystals are filtered through Buchner funnel, washed thoroughly with water. The precipitate is pressed with a wide glass stopper. The substance is recrystallised from methylated spirit.

Yield of *p* - bromoacetanilide = 8.5 gm

M.P. 167° C

EXPERIMENT

9

**BROMINATION***(Preparation of 2, 4, 6 tribromophenol)*

Date : \_\_\_\_\_

**Aim**

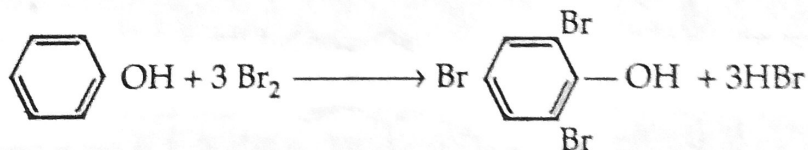
To prepare 2, 4, 6 tribromophenol.

**Chemicals**

Phenol, bromine liquid, glacial acetic acid sodium bisulphite.

**Principle**

Phenol reacts with bromine liquid or Bromine water to give 2, 4, 6 tribromophenol finally.

**Procedure**

7 gm of Phenol is dissolved in 10-15 ml glacial Acetic Acid in a 250 ml conical flask. In a separate beaker 3 - 4 ml of bromine liquid is taken and 10-15 ml glacial acetic acid is added slowly keeping the beaker in a fume chamber. The bromine solution is transferred in to a separatory funnel or burette and it is added drop by drop to the phenol solution with continuous stirring. Bromine is added till the reaction mixture becomes orange red. The mixture is allowed to stand at room temperature for about 15 minutes and then poured into a beaker containing 100 ml water. It is shaken well. The conical flask is rinsed with 25 ml of water and the washings are also taken into the beaker. Now 10% sodium bisulphite solution is added drop by drop till the orange solution becomes colourless. This operation is carried to remove excess of Bromine. Now the mixture is filtered through and a Buchner funnel, the crystal are washed with water the washings are drained out and finally the precipitate is recrystallised from methylated spirit.

# DIAZOTISATION AND COUPLING

(Preparation of phenyl azo- $\beta$ -naphthol)

Date : \_\_\_\_\_

### Aim

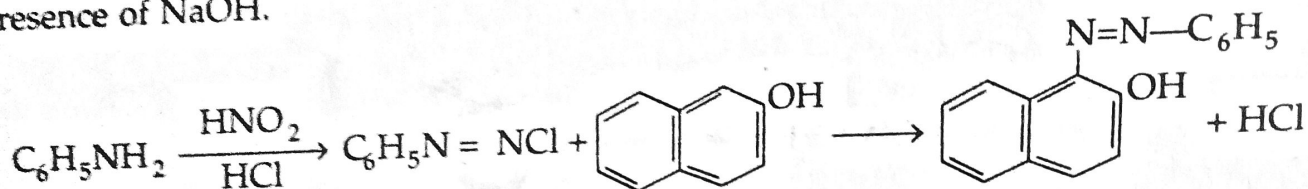
To prepare phenyl azo- $\beta$ -naphthol by diazotisation and coupling.

### Chemicals

Aniline, con HCl,  $\text{NaNO}_2$ ,  $\beta$  naphthol, 10 % NaOH, ice, glacial Acetic Acid.

### Principle

Azo compounds are prepared by the interaction of a diazonium salt with  $\beta$  - naphthol in the presence of NaOH solution. Aniline is diazotised and then treated with  $\beta$  - naphthol in the presence of NaOH.



### Procedure

**A** 2.45 ml of pure aniline is taken into a 250 ml beaker and dissolved in Con HCl and 8 ml of water. The temperature is maintained below  $5^\circ\text{C}$  by keeping in ice and an aqueous solution of sodium nitrite (2 gm  $\text{NaNO}_2$  dissolved in 10 ml water) is added in small quantities. It is allowed to stand for 3, 4 minutes. Aniline is now converted to diazonium chloride.

**B** 3.9 gm of pure  $\beta$  - naphthol is dissolved in 22.5 ml of 10 percent NaOH in a 250 ml beaker. The solution is cooled in an ice bath to  $5^\circ\text{C}$ . The naphthol solution is thoroughly shaken and cold diazonium solution is added drop by drop very slowly. Red coloured solution and red crystals of phenyl azo  $\beta$  - naphthol separated immediately. After the addition of all the diazonium salt solution, the mixture is kept in ice bath for 10 minutes with occasional stirring.

The solution is filtered using Buchner funnel with gentle suction. The precipitate is washed with water; excess of water is drained out and the crystals are pressed with a wide glass stopper and recrystallised from 30-35 ml glacial acetic acid. Finally the crystals are washed with methylated spirit to eliminate acetic Acid.

M.P.  $131^\circ\text{C}$

Yield 6 gm



**OXIDATION***(Preparation of Benzoic Acid from Benzoylchloride)*

Date : \_\_\_\_\_

**Aim**

To prepare Benzoic Acid from Benzyl Chloride by Oxidation process.

**Chemicals**

Benzyl chloride, NaOH,  $\text{KMnO}_4$

**Principle**

Benzyl chloride reacts with sodium hydroxide to give benzyl alcohol. This on oxidation with  $\text{KMnO}_4$  solution produces benzoic acid.

**Procedure**

10 ml benzyl chloride is taken into a 250 ml round bottomed flask; 5 ml of 2 N NaOH are added and refluxed with 5%  $\text{KMnO}_4$  solution on a wire gauge stand for about 20 minutes. Small amounts of  $\text{KMnO}_4$  are added, when needed so that the colour of the solution persisted. Finally the  $\text{MnO}_2$  precipitated is filtered off by filtering through Buchner funnel;  $\text{SO}_2$  gas is passed through the solution to remove excess of  $\text{KMnO}_4$ . Benzoic Acid crystallised slowly. It is recrystallised from hot water.

M.P. :  $121^\circ\text{C}$

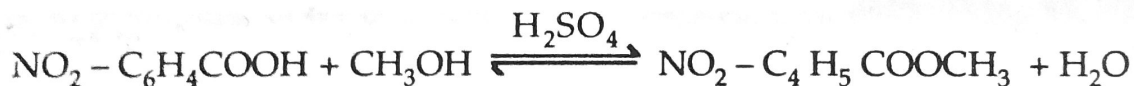
Yield : 8 gm

**ESTERIFICATION***(Preparation of methyl p-nitrobenzoate from p-nitrobenzoic acid)*

Date : \_\_\_\_\_

**Aim**To prepare methyl *P*-nitro benzoate from *P*-nitro benzoic acid.**Chemicals***p*-nitro benzoic acid, Conc H<sub>2</sub>SO<sub>4</sub>, methanol.**Principle**

The aromatic acid is refluxed with a large excess of methyl alcohol in the presence of a small proportion of concentrated sulphuric acid (acid catalysis).

**Procedure**

10 grams of *p*-nitrobenzoic acid is taken into a 250 ml round bottomed flask and 34 ml of absolute methyl alcohol is added to it. 0.9 ml of con H<sub>2</sub>SO<sub>4</sub> is added and then few porcelain chips. The mixture is boiled gently for about 10 minutes. Excess of alcohol is distilled off on a water bath. The residue is shaken with 85 ml of water and taken into a separatory funnel. 5 ml of carbon-tetrachloride is added and shaken well. The ester dissolved in CCl<sub>4</sub> and formed heavy layer. The lower layer is separated carefully and it is shaken with concentrated solution of NaHCO<sub>3</sub> to neutralise the excess of acid. It is then washed with water and dried over anhydrous magnesium sulphate. The product is shaken thoroughly and filtered through a fluted filter paper. The excess of CCl<sub>4</sub> is removed by raising the temperature in a distilling flask and the product is collected.

**Note :** The procedure adopted for the preparation of methyl benzoate is adopted using *p*-nitrobenzoic acid, yield is about 8.9 gm.

## METHYLATION

(Preparation of  $\beta$  - naphthylmethylether)

Date : \_\_\_\_\_

## Aim

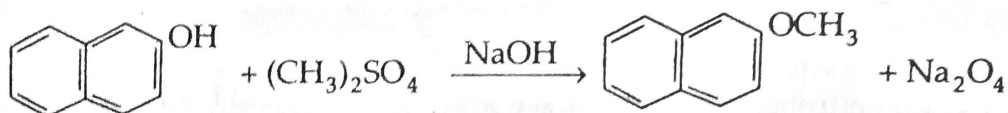
Preparation of  $\beta$  - naphthylmethylether by the methylation of  $\beta$  - naphthol.

## Chemicals

 $\beta$  - naphthol, NaOH, dimethyl sulphate+  $\text{Na}_2\text{O}_4$ 

## Principle

Phenol under suitable condition reacts with methyl compound to form an ether.



## Procedure

5 grams of pure finely ground  $\beta$  - naphthol is taken into 100 ml round bottom flask and it is dissolved in a solution of sodium hydroxide prepared by dissolving 4 grams in 50 ml water. 4 ml dimethyl sulphate is added drop by drop by through shaking and also cooling the flask under tap water. The flask is arranged with air condenser and heated on a water bath for about 30 minutes and then cooled.  $\beta$  - naphthyl methyl ether separated as white crystalline solid. The substance is filtered in a Buchner funnel and then washed well with water. The solid is pressed with a wide glass stopper. The substance is recrystallised from methylated spirit.

M.P.  $72^\circ\text{C}$ 

Yield 5.5 gm