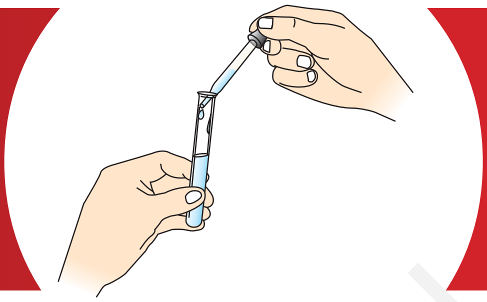
UNIT-10

PREPARATION OF ORGANIC COMPOUNDS



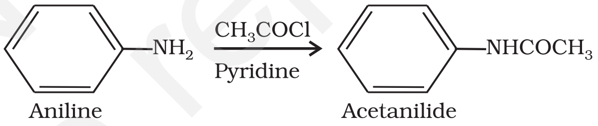
EXPERIMENT 10.1

Aim

To prepare acetanilide.

Theory

The replacement of one hydrogen atom of the — NH_2 group of aniline by CH_3CO– group in the presence of glacial acetic acid. Gives acetanilide. In the laboratory, acetylation is usually carried out with acetic anhydride. Acetyl chloride may also be used for the purpose of acetylation if acetic anhydride is not available. Acetylation with CH_3COCl is usually carried out in the presence of pyridine.



Material Required

• Funnel	:	One
• Round bottomed flask (100 mL)	:	One
• Beaker (250 mL)	:	One
• Air condenser	:	One
• Sand bath	:	One
• Clamp and iron stand	:	One
• Pumice stone	:	As per need
• Melting point assembly	:	One

• Aniline	:	5 mL
• Acetic anhydride / Acetyl chloride	:	5 mL
• Acetic acid / Pyridine	:	5 mL

Procedure

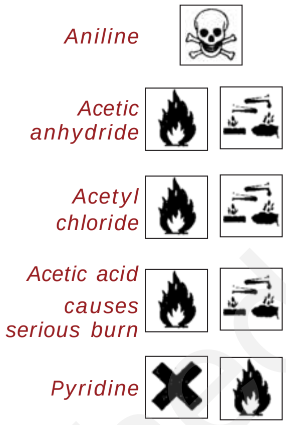
(i) Take 5 mL of aniline in a 100 mL round bottom flask and add acetylating mixture containing 5 mL acetic anhydride and 5 mL glacial acetic acid. Alternatively, you can use 5 mL of acetyl chloride and 5 mL of dry pyridine as the acctylating mixture.

(ii) Fit an air condenser on the mouth of the round bottom flask after adding a few pumice stones and reflux the mixture gently for 10-15 minutes on a sand bath.

(iii) Cool the reaction mixture and pour it slowly in 150-200 mL of ice cold water with stirring.

(iv) Filter the solid, wash it with cold water and recrystallise a small amount of sample from hot water containing a few drops of methanol or ethanol.

(v) Report the yield and the melting point of the compound.



Result

(a) Yield of acetanilide _______ g.

(b) Melting point of acetanilide is _______ °C.

Precautions

(a) Handle acetic anhydride and acetyl chloride carefully as they cause irritation to the eyes and acetyl chloride also strongly fumes in air.

(b) Store acetylchloride under dry conditions.

(c) Handle pyridine with extreme caution. Dispense it in an efficient fume cupboard and wear disposable glasses while using it.

(d) Distil pyridine before use because it absorbs mioisture and the reaction does not take place under moist conditions.

(e) Wash the solid 2-3 times with cold water till the filtrate is neutral to litmus.

(f) Determine the melting point of perfectly dried and recrystallised sample.

ALTERNATIVE METHOD FOR THE PREPARATION OF ACETANILIDE

If acetic anhydride or pyridine is not available then the following method can be used for the preparation of acetanilide.

Material Required

- Boiling tube : One
- Water bath : One
- Melting point assembly : One
- Funnel : One

- Aniline : 1 mL
- Glacial acetic acid : 1 mL
- Acetyl chloride : 1 mL

Procedure

(i) Take 1 mL of aniline in a dry boiling tube, add 1 mL of glacial acetic acid to it and mix the two thoroughly.

(ii) To the above mixture add 1 mL of acetyl chloride in lots (0.3 mL at a time). The mixture becomes warm. If the boiling tube becomes unbearable to touch, cool it under tap water.

(iii) After addition of whole amount of acetyl chloride, heat the mixture for five minutes in a boiling water bath.

(iv) Cool the boiling tube and add ice-cold water (~10 mL) into the tube with constant stirring.

(v) Filter the acetanilide separated as white powder and wash with water till filtrate is neutral to litmus.

(vi) Crystallise the crude acetanilide with hot water. White shining needle shaped crystals are obtained.

(vii) Report the yield and melting point of the compound.

Precautions

(a) If aniline sample is too much coloured, distill it before carrying out the experiment, because yield is lowered with impure aniline.

(b) Use perfectly dry apparatus.

(c) Do not inhale the vapours coming out during the addition of acetylchloride.

(d) Determine the melting point of perfectly dried and recrystallized sample.

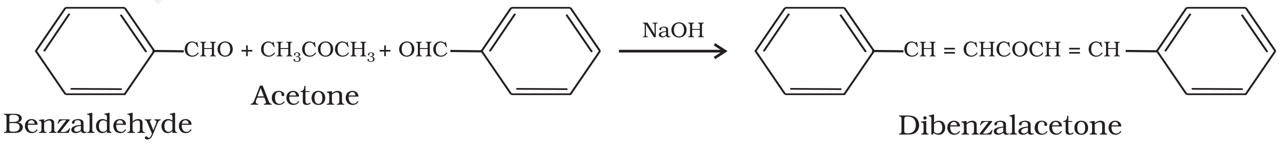
EXPERIMENT 10.2

Aim

To prepare dibenzalacetone (Dibenzylideneacetone)

Theory

α-Hydrogen atom of aliphatic aldehydes and ketones is acidic in nature, therefore, in the presence of dilute alkali, such an aldehyde or ketone condenses with an aromatic aldehyde to give α, β–unsaturated aldehyde or ketone. This reaction is called **Claisen - Schmidt reaction**. For example, benzaldehyde undergoes condensation with acetone in the presence of aqueous sodium hydroxide (NaOH) to give dibenzalacetone.



Material Required

Conical flask(250 mL)	:	One
Beaker(250 mL)	:	One
Funnel	:	One
Melting point assembly	:	One

Ethanol	:	25 mL
NaOH	:	3.15 g
Benzaldehyde	:	3.2 mL
Acetone	:	2.3 mL
Ice	:	As per need
Ethylacetate	:	As per need

Procedure

(i) Prepare a solution of 3.15 g sodium hydroxide in a mixture of 25 mL ethanol and 30 mL distilled water taken in a 250 mL beaker. Cool the beaker in an ice bath maintained at a temperature of about 20–25°C.

(ii) Prepare a mixture of 3.2 mL of benzaldehyde and 2.3 mL of acetone and add half of this mixture slowly in ice cooled NaOH solution prepared in step (i) with vigourous stirring. A fluffy precipitate is formed within 1-2 minutes. Stir the mixture gently for about fifteen minutes.

(iii) After 15 minutes add remaining mixture of benzaldehyde and acetone and stir for 30 minutes more.

(iv) Filter the pale yellow solid so obtained and wash with cold water. Dry it and recrystallise its small amount from ethanol or ethyl acetate.

(v) Report the yield and the melting point of the compound.

Ethanol

NaOH

Benzaldehyde

Acetone

Ethyl acetate

Result

(a) Yield of dibenzalacetone is ________g.

(b) Melting point of dibenzalacetone ______°C.

Precautions

(a) Maintain the temperature around 20°C while shaking the reaction mixture.

(b) Always use freshly distilled benzaldehyde or the sample from a freshly opened bottle.

EXPERIMENT 10.3

Aim

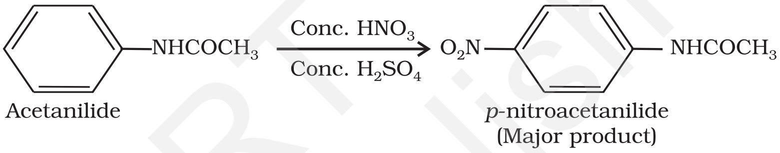
To prepare *p*-nitroacetanilide.

Theory

p-Nitroacetanilide is prepared by the nitration of acetanilide by using a mixture of conc. nitric acid and conc. sulphuric acid as nitrating reagent. The mixture of the two acids releases nitronium ion(NO_2^+), which acts as an electrophile in the reaction.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Nitronium ion attacks the benzene ring containing anilide group, mainly at the para position to give *p*-nitroacetanilide as a major product. This is an example of aromatic electrophilic substitution reaction.



Material Required

• Beaker (100 mL)	:	One
• Funnel	:	One
• Glass rod	:	One
• Ice bath	:	One

• Acetanilide	:	2 g
• Glacial acetic acid	:	2 mL
• Conc. H_2SO_4	:	5 mL
• Conc. HNO_3	:	1.5 mL
• Ice	:	As per requirement
• Ethanol / methanol	:	As per requirement

Acetic acid causes severe burns

Hazard Warning

- *Acetanilide may cause cyanosis.*

Procedure

(i) Dissolve 2 g of acetanilide in 2 mL of glacial acetic acid taken in a 100 mL beaker.

(ii) Add 4 mL of conc. H_2SO_4 gradually with stirring to the above mixture. The mixture becomes hot and clear solution is obtained. Cool the reaction mixture in an ice bath maintained at 0-5°C.

(iii) Add a cold mixture of 1.0 mL conc. HNO_3 and 1.0 mL conc. H_2SO_4 to the viscous reaction mixture drop by drop with constant stirring, so that the temperature of the mixture does not rise above 10°C.

(iv) Remove the beaker from the ice bath and allow the reaction mixture to attain room temperature. Let it stand at room temperature for about 30 minutes. Stir the reaction mixture continuously and pour it on 100g of crushed ice.

(v) Stir the mixture well and filter the compound so obtained.

(vi) Wash the compound with cold water and dry it.

(vii) Recrystallise a small amount of the pale yellow solid from alcohol. Colourless crystals of *p*-nitroacetanilide are obtained. Yellow ortho-nitroacetanilide formed in the small amount remains dissolved in the mother liquor.

(viii) Record the yield and melting point of the pure compound.

Result

(a) Yield of *p*-nitroacetanilide is _______ g.

(b) Melting point of *p*-nitroacetanilide is ______°C.

Precautions

(a) Do not allow the temperature of the reaction mixture to exceed 10°C during addition of nitrating mixture.

(b) Add mixture of concentrated nitric acid and sulphuric acid into the solution of acetanilide slowly and carefully.

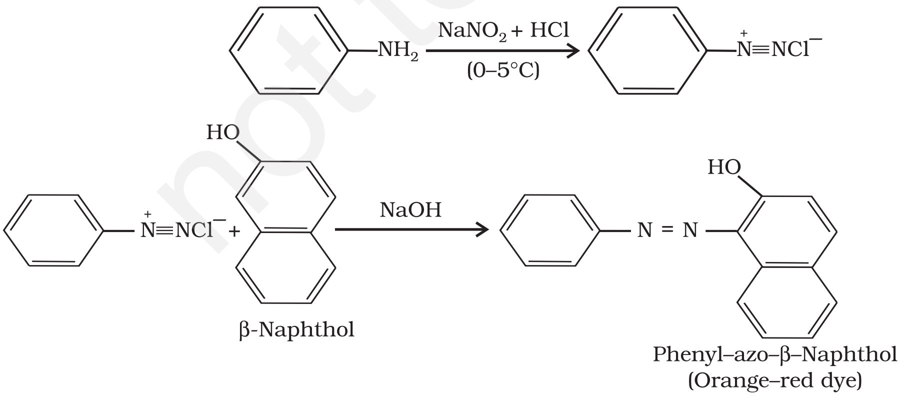
EXPERIMENT 10.4

Aim

To prepare phenyl–azo–β-naphthol (an azo dye).

Theory

Aniline is an aromatic primary amine. It forms diazonium salt when treated with nitrous acid at 0-5°C. Nitrous acid is generated *in situ* by the reaction of sodium nitrite with hydrochloric acid. The process is called **diazotisation**. The diazonium salt is coupled with an alkaline solution of β-naphthol to form an orange-red azo dye.



Material required

• Beaker (250mL)	:	One
• Conical flask (100mL)	:	One
• Glass rod	:	One
• Thermometer (210°C)	:	One
• Filter paper	:	As per need
• Funnel	:	One
• Melting point assembly	:	One

• Aniline	:	2 mL
• Conc. HCl	:	6.5 mL
• Sodium nitrite	:	1.6 g
• β-naphthol	:	3.2 g
• Sodium hydroxide	:	2.0 g
• Glacial acetic acid	:	12.0 mL
• Ice	:	As per need
• Distilled water	:	As per need

Aniline

HCl

Sodium nitrite

Sodium hydroxide

β-naphthol

Acetic acid causes severe burns

Procedure

(i) Take 6.5 mL of concentrated hydrochloric acid in a 100 mL beaker. Dilute it with 6.5 mL of water and dissolve 2 mL of aniline in it.

(ii) Cool the above mixture by placing the beaker in an ice bath maintained at 0-5 °C temperature.

(iii) Diazotise the above mixture by adding a solution of 1.6 g of sodium nitrite in 8 mL water.

(iv) Dissolve 3.2 g β-naphthol in 18 mL of 10% sodium hydroxide solution. Add about 25 g of crushed ice to it.

(v) Stir the β-naphthol solution well and add chilled diazonium chloride solution very slowly to it with constant stirring.

(vi) An orange red dye of phenyl-azo-β-naphthol is formed.

(vii) Allow the mixture to stand in the bath for 30 minutes with occasional shaking.

(viii) Filter the crystals obtained and wash them well with cold water.

(ix) Recrystallise about one-fourth of the crude product from glacial acetic acid.

(x) Filter the recrystallised sample, wash with a little alcohol to remove acetic acid. Dry the recrystallised sample between the folds of a filter paper.

(xi) Record the yield and the melting point of the compound.

Result

(a) Yield of phenyl–azo–β–naphthol is _____g and its

(b) Melting point of phenyl-azo-β-naphthol is ______ °C.

Precautions

(a) Maintain the temperature in the range of 0-5°C during diazotisation.

(b) Always add diazonium chloride solution in alkaline β-naphthol for dye formation and not vice versa.

(c) Dry the recrystallised sample perfectly for determining the melting point.

Note : *Azo-dye synthesis are mostly so nearly quantitative that one should use amounts of reactants closely agreeing with equations. Any excess of certain reactants may cause decomposition of unused material and tar may appear.*

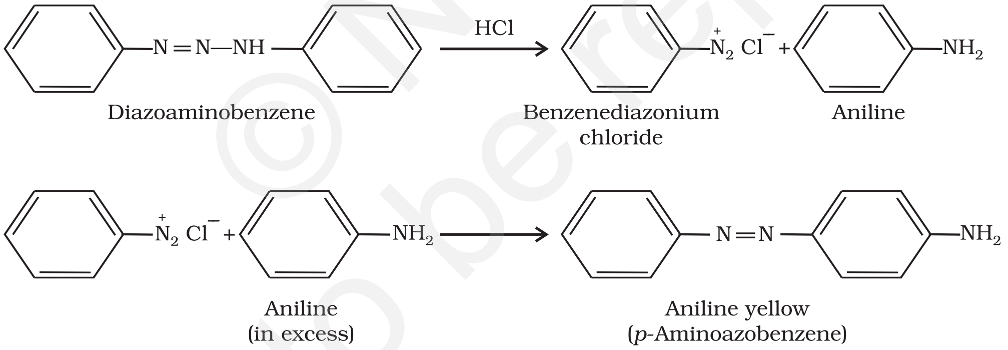
EXPERIMENT 10.5

Aim

To prepare aniline yellow (*p*-amino-azobenzene).

Theory

p-aminoazobenzene can be prepared in a good yield by rearrangement reaction of diazoaminobenzene with a small quantity of aniline hydrochloride in the presence of aniline as solvent. The chemistry of this conversion is as follows:



The above reaction is carried out only in weekly acidic conditions.

Material Required

• Conical Flask (100 mL)	:	One
• Thermometer	:	One
• Funnel	:	One
• Melting point assembly	:	One
• Waterbath	:	One

• Diazoaminobenzene	:	3 g
• Aniline	:	7 mL
• Aniline hydrochloride	:	1.5 g
• Glacial acetic acid	:	9 mL
• Carbon tetrachloride	:	9 mL

Procedure

Aniline

Acetic acid causes severe burns

Carbon tetrachloride

(i) Dissolve 3 g of finely powdered diazoaminobenzene in 7 mL of aniline in a 100 mL conical flask.
(ii) Add 1.5 g of finely powdered aniline hydrochloride to the above mixture.
(iii) Warm the mixture with occasional shaking on a water bath at about 40-45°C, for a period of about one hour.
(iv) Remove the flask from the water bath and allow the reaction mixture to stand at room temperature for about 30 minutes.
(v) Add 9 mL of glacial acetic acid diluted with an equal volume of water and shake the reaction mixture thoroughly to convert excess aniline to its acetate, which is water-soluble.
(vi) Allow the mixture to stand for 15 minutes with occasional stirring.
(vii) Filter *p*-aminoazobenzene, wash with a little cold water and dry between the folds of a filter paper.
(viii) Recrystallise a small portion of crude *p*-aminoazobenzene from carbon tetrachloride.
(ix) Report the yield and melting point of *p*-aminoazobenzene.

Result

Yield of *p*–aminoazobenzene is _____ g and its melting point is ____°C.

Precautions

(a) Maintain the temperature of the reaction mixture at about 40-50°C.
(b) Wash the crude product with a small volume of water repeatedly.
(c) Note the melting point of the perfectly dry sample.

AN ALTERNATIVE PROCEDURE FOR PREPARING ANILINE YELLOW

Theory

Aniline yellow can also be prepared by direct diazotisation and coupling as followed for phenyl-azo-β-naphthol dye. However, coupling of the diazonium salt with aniline or any other aromatic amine is carried out in a weakly acidic medium.

Material Required

- Funnel : One
- Conical flask (100 mL) : One
- Thermometer : One
- Melting point assembly : One

- Aniline : 6 mL
- 1.0 M HCl : 4 mL
- Carbon tetrachloride : As per need

Procedure

Aniline ☠

Carbon tetrachloride ☠

HCl

(i) Prepare a solution of benzene diazonium chloride using 2 mL of aniline according to the method described for the preparation of phenyl-azo–β–naphthol dye (see experiment 10.4).

(ii) Prepare a solution of 4 mL aniline in 4 mL 1.0 M HCl.

(iii) Add the cold solution of aniline hydrochloride slowly into the cold solution of benzene diazonium chloride.

(iv) Filter the yellow compound and dry it between the folds of a filter paper.

(v) Recrystallise the small amount of crude sample from carbon tetrachloride and report the yield and melting point.

Discussion Questions

(i) Why is acetic anhydride preferred over acetyl chloride for acetylation reaction?

(ii) In the preparation of *p*-nitroacetanilide another minor product is formed. What is this compound and how can this be separated from *p*-nitroacetanilide?

(iii) Is it necessary to recrystallise the compound obtained from the reaction? Explain why.

(iv) How is an organic compound recrystallised?

(v) What is the role of acetic acid or pyridine in acetylation?

(vi) How is crude solid compound purified?

(vii) Which of the following compounds on diazotisation followed by coupling with β–naphthol will form an azo dye?

(a) *p*-Toluidine (b) Benzylamine (c) N-Methylaniline.

(viii) Why are diazonium chlorides usually soluble in water?

(ix) How is methyl orange prepared in the laboratory?

(x) How can phenol and aniline be distinguished chemically?

(xi) Why is aniline soluble in hydrochloric acid while it is insoluble in water?

(xii) Why is aniline a weaker base than ammonia?

(xiii) In contrast to aromatic primary amines, aliphatic primary amines do not form stable diazonium salts. Why?