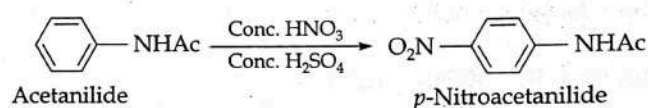




Nitration under cold condition

4.14 Preparation of *p*-nitroacetanilide

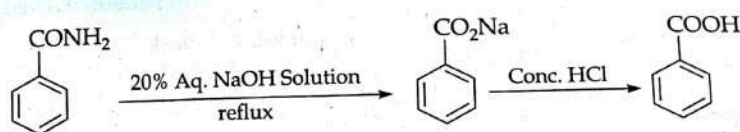


Chemicals required	Apparatus required
1. Acetanilide	1. 100 mL beaker
2. Concentrated nitric acid	2. Thermometer
3. Concentrated sulphuric acid	3. Suction filtering apparatus with Buchner funnel
4. Glacial acetic acid	
5. Ice- salt freezing mixture	
6. Rectified spirit	

- **Procedure** : Take 5 g of acetanilide in a 100 mL beaker and add 5 mL of glacial acetic acid to it. Add 10 mL of concentrated sulphuric acid with stirring. A clear solution results and the mixture becomes warm. Place the beaker in a ice-salt mixture. To this solution, add a mixture of 2.5 mL of concentrated nitric acid and 1.5 mL of concentrated sulphuric acid drop wise maintaining the temperature below 10°C. After the addition is complete, keep the beaker at room temperature for 1 hr. Pour the reaction mixture into 100 g of crushed ice. Stir well and filter the crude product under suction. Wash thoroughly with cold water until free from acid, drain well and dry the solid on a steam bath. Record the yield.
- Crystallise a portion of the crude product (*p*-Nitro acetanilide) from rectified spirit and record the melting point of the recrystallised product.
- Literature melting point of *p*-Nitro acetanilide is 214 °C.

exemplifies the basic nature of benzamide.

4.3.1 Hydrolysis of benzamide



Chemicals required	Apparatus required
1. Benzamide	1. 250 mL R.B. flask
2. Sodium hydroxide	2. 250 mL beaker
3. Concentrated hydrochloric acid.	2. Suction filtering apparatus with Buchner funnel

- **Procedure** : Reflux 5 g of benzamide with 50 mL of 20% sodium hydroxide solution in a 250 mL round bottom flask for 45 minutes. Cool the reaction mixture and acidify it with concentrated hydrochloric acid. Filter the solid under suction, wash it with cold water (3×10 mL), drain well, dry the solid on a steam bath and record the yield.

Crystallise a portion of the crude product from hot water and record the melting point of the recrystallised product.

Literature melting point of benzoic acid is 122°C .

- **Calculation of the percentage of yield** : If 1 mole *i.e.* 121 g of benzamide (molecular weight of benzamide = 121) gives 1 mole *i.e.* 122 g of benzoic acid, (molecular weight of benzoic acid = 122) yield of the reaction is 100%. So for 100% yield $[(122 \times 5)/121]$ g of benzoic acid should be obtained from 5 g of benzamide. If the weight of benzoic acid is w g, yield of the reaction would be $(100 \times w) / [(122 \times 5)/121]\%$.

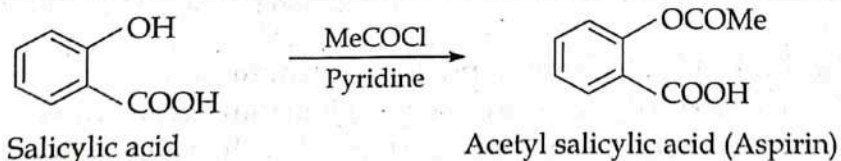
* Allow thorough cooling before filtration as benzoic acid is soluble in hot water.

4.4

Acetylation of Phenols / Aromatic Amines

Replacement of hydrogen of the —OH group of phenols and the —NH— group of amines with an acetyl (MeCO) group is the acetylation of phenols and amines. The reaction occurs through nucleophilic attack of phenolic oxygen or amine nitrogen at the carbonyl carbon of the acetylating agent. Acetyl chloride, acetic anhydride, glacial acetic acid (preferably in presence of zinc dust) are some of the common examples of acetylating agents. The following section depicts acetylation with acetyl chloride and glacial acetic acid. [*Since acetic anhydride is no longer commercially available*]

4.4.1 Acetylation of salicylic acid



Chemicals required	Apparatus required
1. Salicylic acid	1. 100 mL conical flask
2. Acetyl chloride	2. 250 mL beaker
3. Pyridine	3. water bath

- **Procedure** : Dissolve 5 g of salicylic acid in 4-5 mL of pyridine in 100 mL conical flask. Cool the mixture in an ice bath. Add 3.5 mL of acetyl chloride drop wise with continuous stirring to the cooled solution of salicylic acid in pyridine. Heat the reaction mixture on a water bath for 15 minutes with occasional stirring with a glass rod. Cool the reaction mixture and dilute it with 75 mL of water. Filter the separated solid under suction, wash it with ice-cold water (3 × 5 mL), drain well, dry the solid on a steam bath and record the yield.

Crystallise a portion of the crude product from (1:1) ethanol and record the melting point of the recrystallised product. Literature melting point of acetyl salicylic acid is 130-132 °C.

- **Calculation of the percentage of yield** : If 1 mole *i.e.* 138 g of salicylic acid (molecular weight of salicylic acid = 138) gives 1 mole *i.e.* 180 g of acetyl salicylic acid, (molecular weight of acetyl salicylic acid = 180), yield of the reaction is 100%.

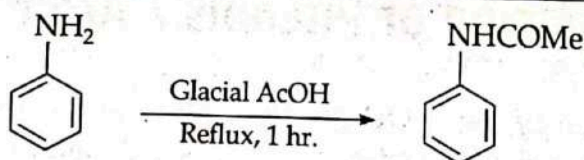
So for 100% yield $[(180 \times 5)/138]$ g of acetyl salicylic acid should be obtained from 5 g of salicylic acid. If the weight of acetyl salicylic acid is w g, yield of the reaction would be $(100 \times w) / [(180 \times 5)/138]\%$.

Starting material	Molecular weight	Weight taken (g)	gram-mole	Molar proportion
1. Salicylic acid	138	5	0.036	1 : 1.36
2. Acetyl chloride	78.5	3.85 ($d = 1.1$ g/mL)	0.049	

Product	Molecular weight	Theoretical yield (g)	Yield obtained (g)
Acetyl salicylic acid	180	6.52	w (say)

Yield of the reaction = $(w/6.52) \times 100 \%$

4.4.2 Acetylation of aniline



Chemicals required	Apparatus required
1. Aniline	1. 100 mL R.B. flask
2. Glacial acetic acid	2. Water bath
	3. 250 mL beaker
	4. Suction filtering apparatus with Buchner funnel

- **Procedure** : Reflux 5 mL of aniline with 15 mL of glacial acetic acid in a 100 mL dry round bottom flask for 1 hour*. Cool the reaction mixture and pour it in thin stream into 150 g ice-water mixture taken in a 250 mL beaker with continuous stirring. Filter the solid under suction, wash it with cold water (3 × 15 mL), drain well, dry the solid on a steam bath and record the yield. Crystallise a portion of the crude product from hot water and record the melting point of the recrystallised product. Literature melting point of acetanilide is 112-114°C.

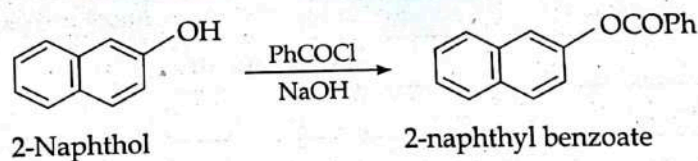
* Addition of ~ 500 mg of Zn dust to the reaction mixture dramatically increases the yield of the reaction. The same method may be used for the acetylation of *p*-toluidine, *p*-chloroaniline etc.

4.5

Benzoylation of Phenols / Aromatic Amines

Replacement of hydrogen of the —OH group of phenols and the —NH— group of amines with a benzoyl (PhCO—) group is the benzoylation of phenols and amines. The reaction occurs through nucleophilic attack of phenolic oxygen or amine nitrogen at the carbonyl carbon of the benzoylating agent. Benzoyl chloride is mostly used as an efficient benzoylating agent. The reaction for phenols requires alkali but for amines the reaction can be conducted with and without using alkali.

4.5.1 Benzoylation of 2-naphthol (Schotten Baumann Method)



Chemicals required	Apparatus required
1. 2-Naphthol	1. 100 mL conical flask with cork
2. Benzoyl chloride	2. Suction filtering apparatus with Buchner funnel
3. Sodium hydroxide	
4. Ethanol	

- **Procedure :** Dissolve 4 g of 2-naphthol in 12-15 mL of 10% NaOH in a 100 mL conical flask. Cool the solution and add slowly 4 mL of benzoyl chloride to it. Cork the flask and shake vigorously

till the disappearance of the odour of benzyl chloride. During shaking cool the flask from time to time by immersing it in ice cold water. Filter the separated solid under suction, wash it with cold water (3×10 mL), drain well, dry the solid air and record the yield.

Crystallise a portion of the crude product from rectified spirit and record the melting point of the recrystallised product. Literature melting point of 2-naphthyl benzoate is 110°C .

- **Calculation of the percentage of yield :** If 1 mole i.e 144 g of 2-naphthol (molecular weight of 2-naphthol = 144) gives 1 mole i.e 247 g of 2-naphthyl benzoate, (molecular weight of 2-naphthyl benzoate = 247), yield of the reaction is 100%.

So for 100% yield $[(247 \times 4)/144]$ g of 2-naphthyl benzoate should be obtained from 4 g of 2-naphthol. If the weight of 2-naphthyl benzoate is w g, yield of the reaction would be $(100 \times w) / [(247 \times 4)/144]\%$.

Starting material	Molecular weight	Weight taken (g)	gram-mole	Molar proportion
1. 2-Naphthol	144	4	0.028	1 : 1.25
2. Benzoyl chloride	140.5	4.84 ($d = 1.21$ g/mL)	0.035	

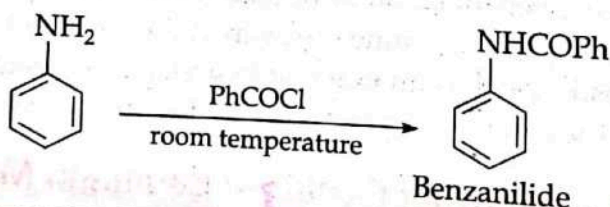
Product	Molecular weight	Theoretical yield (g)	Yield obtained (g)
2-Naphthyl benzoate	247	6.86	w (say)

$$\text{Yield of the reaction} = (w/6.86) \times 100 \%$$

4.5.2 Benzoylation of aniline

[The same Schotten Baumann method as described under the preparation of 2-naphthyl benzoate can be used for the benzoylation of amines]

■ Green Method :



Chemicals required	Apparatus required
1. Aniline	1. 100 mL dry beaker
2. Benzoyl Chloride	

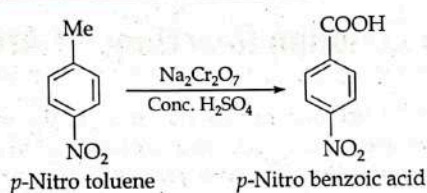
- **Procedure:** Add 3.0 mL of benzoyl chloride to 2 mL of aniline in a dry 100 mL beaker and stir with a glass rod until a thick paste is formed. Keep the reaction mixture at room temperature for 15 minutes and add 10 g of crushed ice to it. Stir well with a glass rod until the ice melts. Filter the solid under suction, wash it with cold water (3×15 mL), drain well, dry the solid on a steam bath and record the yield.

Crystallise a portion of the crude product from rectified spirit and record the melting point of the recrystallised product. Literature melting point of benzanilide is $162-164^{\circ}\text{C}$.

[This method can be applied for the benzoylation of other primary amines. Use the amine and the benzoyl chloride in (1:1) molar ratio. However amino acids like glycine, alanine etc. and sulfanilic acid i.e which mainly exist as zwitterions, can't be benzoylated by this procedure].

Yield of the reaction = $(w/4.77) \times 100\%$

4.63 Side chain oxidation of *p*-nitrotoluene



Chemicals required	Apparatus required
1. <i>p</i> -Nitro toluene	1. 250 mL R.B. flask with reflux condenser
2. Sodium dichromate	2. Water bath
3. Conc. Sulphuric acid	3. 250 mL beaker
4. Sodium hydroxide	4. Suction filtering apparatus with Buchner funnel

■ **Procedure :** Add 30 mL of water to a mixture of 4.5 g of *p*-nitro toluene and 14 g of sodium dichromate taken in a 250 mL R.B. flask. Add 19 mL of conc. sulfuric acid to this mixture during a period of about 20–25 minutes. *p*-Nitro toluene melts as a result of heat of dilution of the acid with commencement of the reaction. After the completion of addition of acid allow the temperature of the reaction mixture to drop. Then reflux the mixture gently for 30–35 minutes. Cool the reaction mixture and pour it into 40–50 mL of water with continuous stirring. Filter the crude *p*-nitro benzoic acid under suction and wash it with water (2×10 mL). Digest the solid with 20 mL of 5% sulfuric acid on a water bath with continuous stirring. Chromium salts will be removed as completely as possible. Allow the mixture to cool and filter. Treat the residue with 5% sodium hydroxide solution until it becomes distinctly alkaline. Add about 0.5 g of decolourising charcoal and warm to about 50°C for 5 minutes with stirring. Filter into 40 mL of 15% sulfuric acid. Filter the solid under suction, wash it thoroughly with cold water and dry it on a steam bath. Record the yield.

Crystallise a portion of the crude product from glacial acetic acid and record the melting point of the recrystallised product.

Literature melting point of *p*-nitro benzoic acid is 237–239°C.

4.7

Diazo Coupling Reactions of Aromatic Amines

Aromatic primary amines react with nitrous acid to form diazonium salt which can couple with phenols and amines or even highly activated aromatic hydrocarbons. Diazonium cations are weakly electrophilic in nature. Coupling with phenols requires weakly alkaline medium for the deprotonation of phenols to form more powerfully nucleophilic phenoxide ions. However for coupling with amines, slightly acidic medium is recommended to ensure dissolution of amines and absence of any competing nucleophile.

4.7.1 Preparation of methyl orange



Chemicals required	Apparatus required
1. Sulfanilic acid	1. 250 mL and 500 mL beaker
2. Anhydrous sodium carbonate	2. Thermometer
3. Sodium nitrite	3. Suction filtering apparatus with Buchner funnel
4. Conc. HCl	
5. N,N-Dimethylaniline	

Chemicals required	Apparatus required
6. Glacial AcOH	
7. Starch-KI paper	
8. Sodium hydroxide	
9. Ethanol	

- **Procedure :** Dissolve 7 g of sulfanilic acid dihydrate and 1.8 g of anhydrous sodium carbonate in 70 mL of water in a 250 mL beaker. Cool the solution to 10-15°C. Dissolve 2.5 g of sodium nitrite in 7 mL of water. Slowly add this aqueous solution of sodium nitrite to the cold solution of sodium sulfanilate. Slowly pour the resulting mixture with stirring into a mixture of 7 mL of conc. Hydrochloric acid and 40 g of crushed ice contained in a 500 mL beaker. Test with starch-potassium iodide paper for the presence of free nitrous acid after 15 minutes. Fine crystals of the sodium salt of diazotised sulfanilic acid separate soon. Add a solution of 4.2 mL of N,N-dimethyl aniline in 2 mL of glacial acetic acid to the diazotised solution of the sodium salt of sulfanilic acid with vigorous stirring. Allow the mixture to stand for 15 minutes. The red coloured acid form of methyl orange gradually separates. Then add slowly with constant stirring 25 mL of 20% sodium hydroxide solution. The reaction mixture becomes orange due to separation of the sodium salt of methyl orange. Heat the solution with stirring almost to boiling when most of the methyl orange goes into the solution. Add 7 g of sodium chloride and warm at 80-90°C until the salt dissolves completely. Cool the mixture in ice-water bath. Filter the precipitated methyl orange under suction, wash with a little cold, saturated solution of sodium chloride, drain well and dry on a steam bath. Record the yield.

Crystallise a portion of the crude product from hot water and record the melting point of the recrystallised product.

Melting point of methyl orange is not sharp and well defined as it is a salt.

- **Calculation of the percentage of yield :** If 1 mole *i.e.* 327 g of sodium salt of methyl orange (molecular weight of sodium salt of methyl orange = 209) is obtained from 1 mole *i.e.* 209 g of sulfanilic acid dihydrate (molecular weight of sulfanilic acid = 209), yield of the reaction is 100%.

So, for 100% yield $[(327 \times 7)/209]$ g of sodium salt of methyl orange should be obtained from 7 g of sulfanilic acid dihydrate. If the weight of sodium salt of methyl orange is w g, yield of the reaction would be $(100 \times w) / [(327 \times 7)/209]\%$.

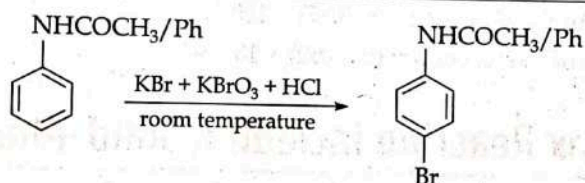
Starting material	Molecular weight	Weight taken (g)	gram-mole	Molar proportion
1. Sulfanilic acid	173	7	0.040	~ 1 : 0.83
2. N,N-Dimethylaniline	121	4.03 ($d = 0.96$ g/mL)	0.033	

Product	Molecular weight	Theoretical yield (g)	Yield obtained (g)
Sodium salt of methyl orange	327	10.95	w (say)

$$\text{Yield of the reaction} = (w/10.95) \times 100 \%$$

using bromate-bromide method.

4.8.1 Bromination of acetanilide / benzanilide

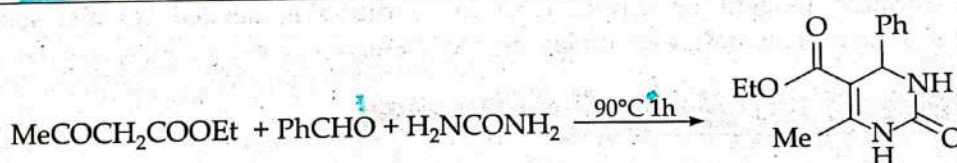


Chemicals required	Apparatus required
1. Acetanilide / Benzanilide	1. 100 mL beaker
2. Potassium bromide	2. 100 mL conical flask
3. Potassium bromate	3. Glass rod
4. Hydrochloric acid	4. Suction filtering apparatus with Buchner funnel
5. Glacial acetic acid	
6. Rectified spirit	

■ **Procedure :** Dissolve 2 g of acetanilide or 2.8 g of benzanilide in 20 mL of glacial acetic acid in a 100 mL beaker by slight warming. Dissolve 1.0 g of potassium bromate and 3.5 g of potassium bromide in 20 mL of water in a separate 100 mL conical flask by slight warming. Slowly add the aqueous solution of potassium bromide and potassium bromate to the solution of acetanilide or benzanilide with continuous stirring. Then add 8 mL of (1 : 1) HCl with stirring to this solution and allow the 100 mL beaker to stand for 20 minutes at room temperature with occasional stirring with a glass rod. Pour the contents of the beaker into 100 mL of cold water with stirring. Filter the solid under suction, wash it with cold water (3 × 10 mL) or until the filtrate becomes colourless, drain well, dry the solid on a steam bath and record the yield.

Yield of the reaction - (w/3.7) ^ 100 %

4.10.2 Synthesis of 5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydro-2-pyrimidone, Biginelli Reaction)



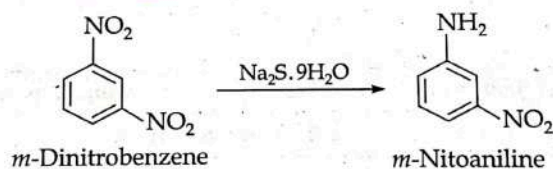
Chemicals required	Apparatus required
1. Ethylacetoacetate	1. 50 mL R.B. flask
2. Benzaldehyde	2. Water bath
3. Urea	3. Suction filtering apparatus with Buchner funnel

- **Procedure** : Heat a mixture of freshly distilled benzaldehyde (1.1 g), ethyl acetoacetate (1.3 g) and urea (0.7 g) on a water bath at 90°C for one hour in a 50 mL round bottom flask. With progress of the reaction, a solid begins to deposit and after one hour the flask becomes filled with the yellow solid. Wash the yellow solid with cold water (1 mL), Dry the solid on a steam bath and record the yield. Crystallise a portion of the crude product from rectified spirit and record the melting point of the recrystallised product. Literature melting point of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydro-2-pyrimidone is 201-202°C.
- **Calculation of the percentage of yield** : If 1 mole *i.e.* 130 g of ethyl acetoacetate (molecular weight of ethyl acetoacetate = 130) produces 1 mole *i.e.* 260 g of 5-ethoxycarbonyl-6-methyl-4-

4.11 Selective Reduction

For a multifunctional organic compound selective transformation at a specified functionality is often required for synthetic purpose. A particular reagent may reduce more than one functional groups. So a suitable reagent or proper reaction condition is needed for the selectivity in transformations. Two representative examples are cited here.

4.11.1 Selective reduction of *m*-dinitrobenzene



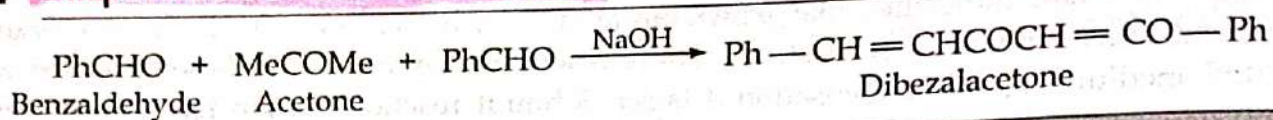
Chemicals required	Apparatus required ¹
1. <i>m</i> -Dinitrobenzene	1. 100 mL conical flask
2. Crystalline sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$)	2. 250 mL beaker (two pieces)
3. Sulphur powder	3. Suction filtering apparatus with Buchner funnel
4. Hydrochloric acid	
5. Ammonia solution	
6. Ice	

- **Procedure** : Prepare a clear solution of sodium polysulphide by warming a mixture of 9 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 2.5 g of finely powdered sulphur in 40 mL water in a 100 mL conical

flask. Grind 5 g of *m*-dinitrobenzene into a powder as far as possible. Add 40 mL of water to the powdered *m*-dinitrobenzene in a 250 mL beaker and boil the mixture gently on a wire gauze. Add the sodium polysulphide solution drop wise to the constantly boiling mixture of *m*-dinitrobenzene in water during 30-35 minutes, swirling frequently. Boil the reaction mixture for a further period of 20 mins with occasional shaking. Allow to cool the reaction mixture. Add a little of crushed ice. Filter the mixture under suction and wash with a little cold water. Transfer the residue into a beaker containing 30-35 mL of water and 10 mL of concentrated hydrochloric acid and boil the mixture for 15 minutes to dissolve *m*-nitro aniline leaving any unreacted sulphur and *m*-dinitrobenzene. Cool the mixture to room temperature, filter under suction and wash the residue with little water. Basify the combined filtrate and wash with liquor ammonia for complete precipitation of the product (*m*-nitro aniline). Filter the precipitate under suction, wash thoroughly with cold water, drain well, dry on a steam bath and record the yield.

Crystallise a portion of the crude product (*m*-nitroaniline) from boiling water and record the melting point of the crystallised product. Literature melting point of *m*-nitroaniline is 114 °C.

4.2.2 Preparation of dibenzalacetone



Chemicals required	Apparatus required
1. Benzaldehyde	1. 250 mL conical flask
2. Acetone	2. Thermometer
3. Sodium hydroxide	3. Suction filtering apparatus with Buchner funnel
4. Ethanol	

- **Procedure** : Prepare a solution of 5 g sodium hydroxide in 50 mL of water in a 250 mL conical flask. Add 40 mL of absolute alcohol to this solution. Cool the conical flask in cold water so as to maintain the temperature between 20-25°C. Mix 1.8 mL of acetone and 5 mL of benzaldehyde in a test tube. Then add about one half of the mixture prepared in the test tube to the ethanolic alkali solution kept in the 250 mL conical flask and stir vigorously for 10 minutes. Then add the remaining portion of the mixture prepared in the test tube into the 250 mL conical flask and continue shaking for an additional 30 minutes. Filter the solid under suction, wash it with cold water (4 × 10 mL), drain well, dry the solid in air and record the yield.

Crystallise a portion of the crude product from rectified spirit and record the melting point of the recrystallised product.

Literature melting point of dibenzalacetone is 112°C.

- **Calculation of the percentage of yield** : If 1 mole *i.e.* 58 g of acetone (molecular weight of acetone = 58) gives 1 mole *i.e.* 234 g of dibenzalacetone, (molecular weight of dibenzalacetone = 234) yield of the reaction is 100%. Now 1.8 mL of acetone = (1.8 × 0.8) g *i.e.* 1.44 g of acetone (density of acetone = 0.8 g/mL)

So for 100% yield [(234 × 1.44)/58] g of dibenzalacetone should be obtained from 1.44 g of acetone. If the weight of dibenzalacetone is *w* g, yield of the reaction would be (100 × *w*) / [(234 × 1.44)/58] %.

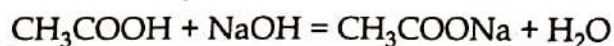
Or, If 2 moles *i.e.* 212 g of benzaldehyde (molecular weight of benzaldehyde = 106) gives 1 234 g of dibenzalacetone, (molecular weight of dibenzalacetone = 234), yield of the reaction is 100%.

Now 5 mL of benzaldehyde = (5 × 1.04) g *i.e.* 5.2 g of benzaldehyde (density of benzaldehyde = 1.04 g/mL)

6.18 Estimation of Acetic Acid in Commercial Vinegar

■ Principle :

Commercial vinegar contains 4-8% (V/V) acetic acid. Acetic acid can be estimated by titration against a strong alkali like sodium hydroxide.



■ Chemicals required :

- ① **Standard (N/20) oxalic acid solution** : Weigh out accurately ~ 0.8 g (w) (exactly 0.7879 g) of A.R oxalic acid, dissolve it in distilled water in a 250 ml volumetric flask and make up the volume with distilled water upto the mark. Mix well to ensure homogeneity of the solution.
- ② **(N/20) NaOH solution** : Dissolve ~1 g of solid NaOH in 500 ml of distilled water.
- ③ **Phenolphthalein indicator** : 0.5% in (1:1) ethanol.
- ④ **Sample commercial vinegar solution** : Mix 75-80 ml of commercial vinegar in distilled water and dilute to one litre with distilled water.

Procedure :

- ① **Standardisation of NaOH against standard oxalic acid solution :** Pipette out 25 ml of standard oxalic acid solution in a 250 ml conical flask. Add 2-3 drops of phenolphthalein indicator. Add NaOH solution from a burette until the appearance of a faint pink colour.
- ② **Estimation of acetic acid :** Dilute the supplied vinegar solution as directed. Pipette out 25 ml of the diluted unknown vinegar solution in a 250 ml conical flask. Add 2-3 drops of phenolphthalein indicator. Add NaOH solution from a burette until the appearance of a faint pink colour.

Results :

① **Standardisation of sodium hydroxide solution against standard oxalic acid solution :**

Volume of oxalic acid (ml)	Volume of NaOH (ml)	Mean volume of NaOH(ml) (V_1)
25	a	$(a+b+c)/3$
25	b	
25	c	

Strength of oxalic acid solution = $(w/0.7879) \times (N/20)$

So the strength of NaOH solution = $S_1 = (25 \times w)/(V_1 \times 0.7879) \times (N/20)$

② **Estimation of acetic acid in vinegar :**

Volume of vinegar (ml)	Volume of NaOH (ml)	Mean volume of NaOH (ml) (V_2)
25	x	$(x+y+z)/3$
25	y	
25	z	

Calculation :

1000 ml of (N) NaOH \equiv 1000 ml of (N) acetic acid \equiv 60 g of acetic acid

So V_2 ml of $S_1(N)$ NaOH $\equiv (60 \times V_2 \times S_1)/1000$ g of acetic acid

25 ml of vinegar solution contains $(60 \times V_2 \times S_1)/1000$ g of acetic acid

So 1000 ml of vinegar solution contains $(40 \times 60 \times V_2 \times S_1)/1000$ g of acetic acid

$= (40 \times 60 \times V_2 \times 25w/V_1 \times 0.7879 \times 20)/1000$ g of acetic acid

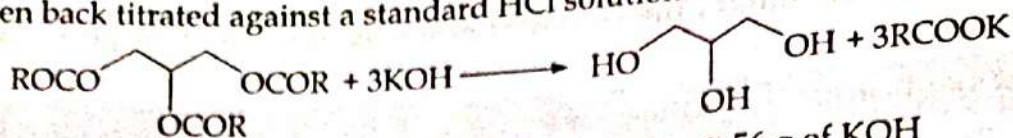
$= 3.8076 \times (wV_2/V_1)$ g of acetic acid.

- [0.0100 (4.2-3) 0.0] / (1/5) 0.000

6.110 Estimation of Saponification Value of Oil

- **Principle** : Saponification value of an oil/fat/ester is the number of milligrams of KOH needed to completely saponify 1 g of oil/fat/ester. A weighed quantity of oil/fat/ester is completely

saponified by boiling with a measured excess of standard alcoholic KOH solution. The excess KOH is then back titrated against a standard HCl solution.



1000 ml of (N) HCl solution \equiv 1000 ml of (N) KOH solution \equiv 56 g of KOH

So 1 ml of (N) HCl solution \equiv 1 ml of (N) KOH solution \equiv 56 mg of KOH

Chemicals required :

- ① **Standard (N/20) oxalic acid solution** : Weigh out accurately ~ 0.8 g (w) (exactly 0.7879 g) of A.R oxalic acid, dissolve it in distilled water in a 250 ml volumetric flask and make up the volume with distilled water upto the mark. Mix well to ensure homogeneity of the solution.
- ② **Coconut oil or mustard oil**
- ③ **(N/2) alcoholic KOH solution** : Dissolve ~ 7.0 g of KOH in minimum volume of distilled water. Dilute to 250 ml with ethanol. Then dilute 10 ml of this solution to 100 ml in a 100 ml volumetric flask to prepare \sim (N/20) KOH solution.
- ④ **(N/2) HCl solution** : Dilute 10-12 ml of Conc. HCl to 250 ml with distilled water. Then dilute 10 ml of this solution to 100 ml in a 100 ml volumetric flask to prepare \sim (N/20) HCl solution.

Procedure :

- ① **Standardisation of KOH against standard oxalic acid solution** : Pipette out 25 ml of standard oxalic acid solution in a 250 ml conical flask. Add 2-3 drops of phenolphthalein indicator. Add KOH solution from a burette until the appearance of a faint pink colour.
- ② **Standardisation of HCl against standard KOH solution** : Pipette out 25 ml of \sim (N/20) HCl solution in a 250 ml conical flask. Add 2-3 drops of phenolphthalein indicator. Add KOH solution from a burette until the appearance of a faint pink colour.
- ③ **Estimation of saponification value** : Weigh out accurately ~ 2.0 g (w_1) of coconut or mustard oil in a 250 ml conical flask fitted with an air condenser. Add 50 ml of standard \sim (N/2) alcoholic KOH solution to it. Reflux the resulting solution on a hot water bath till the complete disappearance of the oily layer. Allow the mixture to cool to room temperature and add 2-3 drops of phenolphthalein indicator to it. The solution turns pink. Titrate the unreacted KOH by the standard (N/2) HCl solution till the disappearance of the pink colour forming a colourless solution.

Perform a blank experiment under the same conditions using the same quantity of (50 ml) of KOH without using the oil. Titrate the solution against standard (N/2) HCl solution using phenolphthalein indicator up to a colourless end point.

Results :

- ① **Standardisation of potassium hydroxide solution against standard oxalic acid solution :**

Volume of oxalic acid (ml)	Volume of KOH (ml)	Mean volume of KOH(ml) (V_1)
25	a	$(a+b+c)/3$
25	b	
25	c	

Strength of oxalic acid solution = $(w/0.7879)(N/20)$

So the strength of KOH solution = $(25 \times w)/(V_1 \times 0.7879)(N/20)$

Hence the exact strength of $(\sim N/2)$ KOH solution = $S_1 = (25 \times w)/(V_1 \times 0.7879)(N/2)$

② Standardisation of HCl solution against standard KOH solution :

Volume of HCl (ml)	Volume of KOH (ml)	Mean volume of KOH (ml) (V_2)
25	x	$(x+y+z)/3$
25	y	
25	z	

So the strength of HCl solution = $[(25 \times w)/(V_1 \times 0.7879)(N/20)] \times V_2/25$

$$= [(V_2 \times w)/(0.7879 \times V_1)](N/20)$$

Hence the exact strength of ($\sim N/2$) HCl solution = $S_2 = [(V_2 \times w)/(0.7879 \times V_1)](N/2)$

③ Estimation of the saponification value :

Weight of Mustard/coconut oil (g)	Volume of (N/2) KOH Solution (ml)	Volume of (N/2) HCl (ml) (V_3)
w_1	50	d

④ Blank experiment :

Volume of (N/2) KOH Solution (ml)	Volume of (N/2) HCl (ml) (V_4)
50	e

■ Calculation :

V_4 ml S_2 (N) HCl is needed for 50 ml of S_1 (N) KOH.

V_3 ml S_2 (N) HCl is needed for back titration of S_1 (N) KOH after consumption by w_1 g of oil/fat/ester.

Hence KOH consumed by w_1 g of oil/fat/ester $\equiv (V_4 - V_3)$ ml of $(V_2 \times w/0.7879 \times V_1)(N/2)$ HCl.

$$\equiv (V_4 - V_3) \text{ ml of } [(V_2 \times w)/(0.7879 \times V_1)](N/2) \text{ KOH.}$$

$$\equiv [(V_4 - V_3) \times V_2 \times w]/(2 \times 0.7879 \times V_1) \text{ ml (N) KOH}$$

$$\equiv [56 \times (V_4 - V_3) \times V_2 \times w]/(2 \times 0.7879 \times V_1) \text{ mg of KOH}$$

[As 1 ml of (N) KOH \equiv 56 mg of KOH].

Thus saponification value of the oil/fat/ester

$$= \text{number of milligrams of KOH consumed by 1.0 g of oil/fat/ester}$$

$$= 56 \times (V_4 - V_3) \times V_2 \times w/2 \times w_1 \times 0.7879 \times V_1$$

■ Alternative procedure :

① Standard (N/2) oxalic acid solution : Prepare a solution of (N/2) oxalic acid by dissolving ~ 8 g (w) (exactly 7.879 g) of oxalic acid in distilled water and making up to the mark in a 250 ml volumetric flask with distilled water.

② Estimation of saponification value : Weigh out accurately ~ 2.0 g (w_1) of coconut or mustard oil in a 250 ml conical flask fitted with an air condenser. Add 50 ml of ($\sim N/2$) alcoholic

KOH solution to it. Reflux the resulting solution on a hot water bath till the complete disappearance of the oily layer. Allow the mixture to cool to room temperature and add 2-3 drops of phenolphthalein indicator to it. The solution turns pink. Titrate the unreacted KOH by the standard oxalic acid solution till the disappearance of the pink colour forming a colourless solution.

Perform a blank experiment under the same conditions using the same quantity (50 ml) of KOH without using the oil. Titrate the solution against standard oxalic solution using phenolphthalein indicator up to a colourless end point.

■ Results :

① Estimation of the saponification value :

Weight of Mustard/coconut oil (g)	Volume of (N/2) KOH Solution (ml)	Volume of oxalic acid (ml) (V_3)
w_1	50	d

② Blank experiment :

Volume of (N/2) KOH Solution (ml)	Volume of oxalic acid(ml) (V_4)
50	e

■ Calculation :

$$\begin{aligned} \text{KOH consumed by } w_1 \text{ g of oil/fat/ester} &\equiv (V_4 - V_3) \text{ ml of } (w/7.879)(N/2) \text{ oxalic acid} \\ &\equiv (V_4 - V_3) \text{ ml of } (w/7.879)(N/2) \text{ KOH.} \\ &\equiv [(V_4 - V_3) \times w / (2 \times 7.879)] (N) \text{ KOH} \\ &\equiv [56 \times (V_4 - V_3) \times w] / (2 \times 7.879) \text{ mg of KOH} \end{aligned}$$

[As 1 ml of (N) KOH \equiv 56 mg of KOH].

Thus saponification value of the oil/fat/ester = number of milligrams of KOH consumed by 1.0 g of oil/fat/ester = $[56 \times (V_4 - V_3) \times w] / (2 \times 7.879) / w_1$

Saponification values of some oils/fats/esters :

Oils/fats/esters	Saponification value
Coconut Oil	250-265
Mustard Oil	172
Neem Oil	197
Olive Oil	184-196
Palm Oil	190-205
Rapeseed Oil	175
Rice Bran Oil	185-195
Soybean Oil	180-200

Oils/fats/esters	Saponification value
Sunflower Oil	188-194
Peanut Oil	190
Mango butter	183-198
Lanolin Oil	90-110
Kokum butter	187-193
Goat tallow	195
Beef tallow	196