

CHAPTER 2  
EXPERIMENTAL

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### 2.1 Material :-

Cardanol was procured from Mercury Engineering company division, Hyderabad and was distilled at reduced pressure.

Chloroacetic acid (sd fine chemicals) was crystallised from benzene m.p. 60°C.

Sodium hydroxide (sd), Conc, sulfuric acid, hexanes, triphenyl phosphite (Merck) and Phase Transfer catalyst such as tetrabutyl ammonium bromide, benzyl trimethyl ammonium bromide or triethyl propyl ammonium bromide were used as received.

Methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol and isoamyl alcohol were obtained from local market and purified using standard procedures to obtain dry alcohols.

N-methyl pyrrolidone was kept over phosphorous pentoxide, refluxed for 6 hours and then vacuum distilled. Distillate was stored on 5-A molecular sieves.

Pyridine was refluxed for 4 hours on potassium hydroxide pellets, distilled and distillate stored over fresh potassium hydroxide pellets. Commercial anhydrous lithium chloride (sd) was dried under vacuum at 150°C for 6 hours.

m-Nitroaniline and p-nitroaniline were recrystallised from distilled water and crystals vacuum dried at 70°C for several hours, m.p. 112-114°C and 149-151°C respectively.

Aniline, m-toluidine were distilled prior to use

p-Bromoaniline,  $\alpha$ -naphthylamine and p-anisidine were recrystallised from absolute alcohol to get pure crystals with

m.p. 63°C, 50°C and 58°C respectively.

#### 2.2 Preparation of 3-Pentadecenyl phenol (Anacardol) :-

Cardanol commercial 400 g was distilled under vacuum. The flask was heated slowly till initial frothing subsided and distillate was collected between 190-220°C/5mm of Hg. This was redistilled to give pale yellow anacardol b.p. =195-205°C/5mm.

#### 2.3 Preparation of 3-Pentadecyl phenol (Tetrahydroanacardol) :-

Anacardol 300 g dissolved in 300 ml ethanol was hydrogenated at 70°C in a AMAR make autoclave under 600 psi pressure of hydrogen in the presence of 3g Raney Nickel catalyst. When no more absorption was noticed, the reaction was stopped, the product filtered and solvent distilled out when residue solidified.

Recrystallisation from petroleum ether (40-60°C) gave pink white waxy solid 3-pentadecyl phenol.

Yield = 270g            m.p. 50-51°C

#### 2.4 Preparation of 3-pentadecyl phenoxy acetic acid (1) :-

In a 250 ml R.B. flask equipped with magnetic stirrer and reflux condenser, 30.4g (0.1 mole) of tetrahydroanacardol (THA), 80 ml methanolic solution of sodium hydroxide (8g NaOH in 80 ml Methanol), 3g phase transfer catalyst (Triethyl propyl ammonium bromide), 25 ml methanolic solution of chloroacetic acid [dissolving 9.45g (0.1 mole) of chloroacetic acid in 25 ml methanol] were placed. Reaction mixture was stirred at room temp. for 30 minutes and then at reflux temp. for 8-12 hours.

Methanol was distilled out and the reaction mass was then

acidified by sulphuric acid (10 ml conc. sulphuric acid in 50 ml water) and refluxed again for 20 minutes. It was then cooled, so that solid separated out, which was filtered and washed with water till free from acid. It was then dried.

To remove unreacted tetrahydroanacardol if any the above dried solid was stirred with hexane. White crystalline product was filtered and freed from THA by washing it with (6 X 100 mls) of hexane.

Product is (3-pentadecyl) phenoxy acetic acid, which gave single spot for TLC.

Yield 28.6g (79%) m.p. 101°C.

#### 2.5 Preparation of (3-pentadecyl)Phenoxy alkylacetates (2a to 2e):-

##### **(3-Pentadecyl)phenoxy methyl acetate (2a) :-**

2g(0.0055 moles) of(3-pentadecyl) phenoxy acetic acid, and 15 ml distilled and dry methanol were placed in 100 ml R.B. flask equipped with water condenser, and 1 ml conc. Sulphuric acid was added as a catalyst. Reaction mixture was refluxed for 10-12 hours. Excess methanol was removed by distillation and finally dried under vacuum.

The product (3-pentadecyl) phenoxy methylacetate was extracted with hexane. Hexane layer was washed with dil. sodium bicarbonate solution (3 X 50ml) and by water ( 3 X 50ml) and was dried over anhydrous magnesium sulphate. Solvent hexane was evaporated to get white solid (3-pentadecyl) phenoxy methyl acetate.

The product was purified by recrystallisation from methanol. Similarly other esters 2(b) to 2(e) were prepared. The physical constants and % yields of products are given below.

Table - IV

**Physical constants and % yields of the (3-pentadecyl)  
Phenoxy alkyl acetates**

Sr. No.	Ester Code	Name	yield (%)	mp/bp (°C)
1	(2a)	(3-pentadecyl)-phenoxy methyl acetate	94	45
2	(2b)	(3-pentadecyl)-Phenoxy ethyl acetate)	90	36
3	(2c)	(3-pentadecyl)-Phenoxy isopropyl acetate	85	42
4	(2d)	(3-pentadecyl)-Phenoxy butyl acetate	68	210-215 /5 mm
5	(2e)	(3-pentadecyl)-Phenoxy Isoamyl acetate	80	240-250 / 5mm

**2.6 Preparation of (3-pentadecyl) Phenoxy N-aryl Acetamides :-**

**(3-pentadecyl) phenoxy (-N-Phenyl) acetamide (3a) :-**

In a 100 ml perfectly dry 3 neck R.B.flask, equipped with water condenser with guard tube, magnetic stirrer, Nitrogen gas inlet and thermowell, 2 ml N-methyl pyrrolidine, 1 ml pyridine, 2 millimoles i.e. 0.724 g of (3-pentadecyl) phenoxy acetic acid, 2 millimoles i.e. 0.186 g of distilled aniline were placed. Triphenyl phosphite 1.3 ml was added as catalyst or acid activator, and reaction mixture was heated with constant stirring at 100 to 110°C for 8-10 hours. It was then cooled and added to methanol, to precipitate the product. It was filtered on buckner funnel, washed with 3 X 50ml methanol, dried under reduced pressure. Recrystallisation was performed from methanol.

Similarly other amides 3(b) to 3(g) were prepared. The physical constants and % yields are given below.

Table-V

**% yield and physical constants of (3-pentadecyl)Phenoxy N-aryl acetamides**

Sr. No.	Ester Code	Name	yield (%)	mp/bp (°C)
1	3a	(3-pentadecyl)-phenoxy (-N-phenyl)acetamide	75	78
2	3b	(3-pentadecyl)-Phenoxy [N-(m-nitrophenyl)] acetamide	70	78
3	3c	(3-pentadecyl)-Phenoxy [(P-nitrophenyl)] acetamide	75	102
4	3d	(3-pentadecyl)-Phenoxy [N-(P-bromophenyl)] acetamide	67	89
5	3e	(3-pentadecyl)-Phenoxy [N-( $\alpha$ -naphthyl)] acetamide	73	98
6	3f	(3-pentadecyl)-Phenoxy [N-(m-methylphenyl)] acetamide	71	74
7	3g	(3-pentadecyl)-Phenoxy [N-(P-methoxyphenyl)] acetamide	63	75

**Measurements :- U V Spectra :-** Ultra violet spectra of compounds were recorded on shimadzu UV- viz double beam record spectrophotometer model-160-A, using chloroform solutions.

**Infrared Spectra :-** The transmission IR spectra of all samples were recorded on a Perkin Elmer model 883, as a nujol mull.

**NMR Spectra :-** Proton NMR spectra were recorded on varian FT-80A (80 MHz) spectrometer at room temperature in  $CDCl_3$  with tetramethylsilane (TMS) as an internal standard.

Proton decoupled and DEPT Carbon-13.

Carbon-13 NMR spectra were recorded on AC-200 (super cond) NMR spectrometer using  $CDCl_3$  solvent. Chemical shifts are

expressed in PPM form TMS.

Mass Spectra :- The mass spectra were run on IIMS 30 double beam mass spectrometer.

All melting, boiling points are uncorrected.