Chapter 1

DYES DERIVED FROM 2-(2', 4'-DIMETHYL BENZOYL) 3-NITRO BENZOIC ACID.

\[
\begin{align*}
&\text{CH}_3 \\
&\text{CO} \\
&\text{O}_2\text{N} \\
&\text{COOH}
\end{align*}
\]

2-(2', 4' dimethyl benzoyl)-3- nitrobenzoic acid

3.1 PREPARATION OF 2-(2', 4'-DIMETHYL BENZOYL) NITRO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between m-xylene (dry AR 100ml.) and 3-nitro phthalic anhydride (20.0g, 0.1mole) with anhydrous aluminium chloride (27.0g, 0.2mole) used as a catalyst. The reaction was carried out in one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap aluminium chloride in installment. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased.

The heavy dark coloured complex was decomposed by adding 30ml of concentrated hydrochloric acid (in 250ml ice cold water). The excess of m-xylene was removed by distillation. The residue was extracted three four times with boiling 10% solution of Na₂CO₃ and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid m.p. 127-129°C, yield 21.0g. It is soluble in ether, acetone and methanol.

Anal. For \[\text{C}_{16}\text{H}_{13}\text{NO}_5\] (mol. wt. = 299)
C.1I PREPARATION OF ACETYL DERIVATIVE OF THE ACID

The acid (1.0g) and fused sodium acetate (3.0g) were refluxed with 20ml of freshly distilled acetic anhydride at 125-135°C for four hours. The hot contents were poured into a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of brown coloured solid mass. The coloured acid derivative was decolourized by treatment with animal charcoal. It was crystallized from acetone in the form of amorphous solid, m.p. 117-118°C. It is soluble in acetone, chloroform and acetic acid, yield 0.75g.

Anal. : C_{18}N_{15}NO_{6} or C_{16}H_{12}NO_{5} \text{ (OC.CH_{3}) (mol. wt. = 341)}
Calc. : C, 63.34; H, 4.37; N, 4.41; acetyl. 12.61;
Found : C, 63.18; H, 4.37; N, 4.10; acetyl. 12.56;

The dyes prepared from the acid may be represented by the following structures.

![Chemical structures](image-url)
C.1.2 (2, 4 dimethyl phenyl) phenol nitro phthal-as-ein
\[ R_1 = R_2 = R_4 = R_5 = H, \ R_3 = OH; \]

C.1.3 (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein
\[ R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OH; \]

C.1.4 (2, 4 dimethyl phenyl) catechol nitro phthal-as-ein
\[ R_3 = R_4 = R_5 = H, \ R_1 = R_2 = OH; \]

C.1.5 (2, 4 dimethyl phenyl) hydroquinone nitro phthal-as-ein
\[ R_2 = R_3 = R_5 = H, \ R_1 = R_4 = OH; \]

C.1.6 (2, 4 dimethyl phenyl) pyrogallol nitro phthal-as-ein
\[ R_4 = R_5 = H, \ R_1 = R_2 = R_3 = OH; \]

C.1.7 (2, 4 dimethyl phenyl) phloroglucinol nitro phthal-as-ein
\[ R_2 = R_4 = H, \ R_1 = R_3 = R_5 = OH; \]

C.1.8 (2, 4 dimethyl phenyl) diacetyl resorcinol nitro phthal-as-ein
\[ R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OCOCH_3 \]

C.1.9 (2, 4 dimethyl phenyl) dibromo resorcinol nitro phthal-as-ein
\[ R_3 = H, \ R_1 = R_3 = OH, \ R_2 = R_4 = Br \]

**C.1.2 PREPARATION OF (2, 4 DIMETHYL PHENYL)-PHENOL NITRO PHTHAL-AS-EIN:**

The acid (1.5g) and phenol (1.0g) were condensed in an oil bath in presence of 4-5 drops of concentrated sulphuric acid at 160-170\(^\circ\)C for about four and half hours till the molten mass of the flask became brittle on cooling. The condensed mass was taken out from the flask and subjected to steam distillation to remove excess of phenol. The buff coloured tube solid mass left in the flask was powdered and extracted with 2% NaOH solution. It was filtered and the dye was precipitated from filtrate by the gradual addition of hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in a vacuum desiccator, yield 1.2g.

The purity of the dye was tested by paper chromatography.

Paper Whatman No 1
Mobile phase  Butanol saturated with ammonia
Developing agent  1% aqueous caustic soda
Reference dye  Phenolphthalein

A 25- x 10-cm strip was taken and a very dilute solution of the dye was spotted on the paper on a base line 4.0 cm from the end) with a micro syringe. Similarly, a dilute aqueous solution of the reference dye was also spotted on the base line about 3.0 cm from the first spot. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed. Chromatogram of each dye gave only one corresponding spot. This confirmed the homogeneity and purity of the dye.

Found : \( R_f \) (phenolphthalein): 0.93

: \( R_f \) [(2, 4 dimethyl phenyl) phenol phthal-as-ein]: 0.95

Reported : \( R_f \) (phenolphthalein): 0.92

The brown coloured micro-crystalline dye m.p. 117-118\(^0\)C gives light yellow colour in ethanol which turns into light violet on adding a drop of an alkali. It is soluble in benzene, acetone and ethanol.

Anal. For : \( C_{22} H_{17} NO_5 \) (mol. wt. 375)
Calc. : C, 70.40; H, 4.53; N, 3.73;
Found : C, 70.19; H, 4.50; N, 3.68;

**C.1.3 PREPARATION OF (2, 4 DIMETHYL PHENYL)-RESORCINOL NITRO PHTHAL-AS-EIN:**

It was prepared by condensing an intimate mixture of the acid (3.0g) and resorcinol (3.0g) in the oil bath in presence of 4-5 drops of concentrated sulphuric acid at 150-160\(^0\)C for about four and half hours till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from reddish brown with green fluorescent filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 80\(^0\)C and then in a vacuum desiccator, yield 3.5g.
The brown microcrystalline dye having m.p. 284-286°C, is soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is brown which alters to brownish red with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown colour is obtained.

Anal. For : C_{22}H_{17}NO_{6} (Mol. Wt. 391)
Calc. : C, 67.52; H, 4.35; N, 3.58;
Found : C, 67.44; H, 4.32; N, 3.56;

**C.1.4 PREPARATION OF (2,4-DIMETHYL-PHENYL)-CATECHOL-NITRO PHTHAL-AS-EIN:**

The dye was prepared by heating a homogeneous mixture of the acid (1.2 g) and catechol (1.5 g) in an oil bath at 120-130°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein. Yield 1.5 g.

The dye is black in colour, m.p. above 360°C. Its ethanolic solution is brown in colour. It gives blackish brown colour on addition of alkali. It is soluble in acetone, ethanol and acetic acid.

Anal. For : C_{22}H_{17}NO_{6} (Mol. Wt. 391)
Calc. : C, 67.52; H, 4.35; N, 3.58;
Found : C, 67.38; H, 4.32; N, 3.55;

**C.1.5 PREPARATION OF (2,4 DIMETHYL PHENYL) HYDROQUINONE NITRO PHTHAL-AS-EIN:**

It was prepared by condensing a homogeneous mixture of the acid (1.5 g) and hydroquinone (1.2 g). The intimate mixture was heated on oil bath at 160-170°C in presence of 4-5 drops of concentrated sulphuric acid for about four hours till the molten mass became hard and brittle on cooling. The isolation and purification of the dye were done as in the case of (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein, yield 1.5 g.

The black coloured dye having m.p. 210°C, is soluble in chloroform, ethanol and methanol. Its alcoholic solution gives light brown colour that turns into dark brown on addition of an alkali.

-167-
$\text{C}_{22}\text{H}_{17}\text{NO}_6$ (Mol. Wt. 391)

Calc.  $: \begin{align*} &\text{C}, 67.52; \text{H}, 4.35; \text{N}, 3.58; \\
\end{align*}$

Found $: \begin{align*} &\text{C}, 67.41; \text{H}, 4.30; \text{N}, 3.56; \\
\end{align*}$

$\text{C.1.6 PREPARATION OF (2,4 DIMETHYL PHENYL) PYRO GALLOL NITRO PHTHAL-AS-EIN:}$

The mixture of acid (1.0g) and pyrogallol (1.0g) was heated in the oil bath in the presence of 4-5 drops of concentrated sulphuric acid at 130-150 $^\circ\text{C}$ for about four hours. The dye was isolated and purified in a manner similar to the other dyes, yield 1.0g.

The black shining crystals having a m.p. above 360$^\circ\text{C}$, is soluble in ethanol, methanol and acetic acid. It dissolves in ethanol yielding light brown colour which turns violet on addition of a drop of an alkali.

$\text{C.1.7 PREPARATION OF (2,4 DIMETHYL PHENYL) PHLOLOGICINOL NITRO PHTHAL-AS-EIN:}$

It was prepared by condensing a homogenous mixture of the acid (1.0g) and phloroglucinol (1.2g). The intimate mixture was heated on oil bath at 190-200$^\circ\text{C}$ for about four hours. The dye was isolated and purified in a manner similar to C.1.3 dye chapter V, yield 1.29.

The brownish red dye decomposed at 340$^\circ\text{C}$ gives brown colour with ethanol, which turns into red on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and acetic acid.

$\text{C}_{22}\text{H}_{17}\text{NO}_7$ (Mol. Wt. 407)

Calc. $: \begin{align*} &\text{C}, 64.86; \text{H}, 4.18; \text{N}, 3.44; \\
\end{align*}$

Found $: \begin{align*} &\text{C}, 64.75; \text{H}, 4.16; \text{N}, 3.39; \\
\end{align*}$
[Acetylation of (2,4 dimethyl phenyl) resorcinol phthal-as-ein]

The dye (2,4 dimethyl phenyl) resorcinol nitro phthal-as-ein (1.0g) and fused sodium acetate (3.0g) with 15.0ml of freshly distilled acetic anhydride were taken in a sodium acetate (3.0g) with 15.0 ml of freshly distilled acetic anhydride were taken in a 50 ml round bottomed flask fitted with an air condenser. The contents refluxed at 130-140°C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 40°C and then over phosphorus pentoxide under reduced pressure, yield 0.70g.

The crystalline acetyl derivative is yellow coloured and has a m.p. of 235-236°C.

It is soluble in benzene, ether, chloroform and acetic acid.

Anal. For : C_{26}H_{21}NO_{8} or C_{22}H_{15}NO_{6} (COCH_{3})_{2} (Mol. Wt. 475)
Calc. : C, 65.68; H, 4.42; Acetyl 18.11; N, 2.95;
Found : C, 65.50; H, 4.40; Acetyl 18.07; N, 2.90;

[2,4 DIMETHYL PHENYL ) DIBROMO RESORCINOL PHTHAL-AS-EIN]

The dye (2,4 dimethyl phenyl)- resorcinol-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with air condenser and the contents were refluxed at 120-130°C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80°C in an oven and then in a vacuum desiccator, yield 1.0g.
The dirty orange crystalline compound decomposed at 212°C, is soluble in benzene, ether, chloroform, acetone, and acetic acid.

Anal. For : C_{22}H_{15}NO_{6} Br_{2} (Mol. Wt. 549)
Calc. : Br, 29.14
Found : Br, 29.05

C.I.I. CAUSTIC POTASH TREATMENT OF (2,4 DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0g) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50 ml of the water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. It was crystallized from aqueous ethanol and dried in a vacuum desiccator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

**Residue I**

It was identified and confirmed to be the unreacted dye from its colour reactions and determination of the mixed melting point with the authentic sample.

**Residue II**

It was acidic in nature and gave positive tests for the presence of carboxylic groups. It was identified as 2-(2,4 dimethyl benzoyl) benzoic acid and confirmed by mixed melting point determination (m.p. 127-129°C) and by superimposition of the IR spectra of the authentic sample.

**Residue III**

The purified sample melted at 109-110°C. It gave positive tests with ferric chloride, Fehling’s solution and ammoniacal silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. Acetylation, bromination and caustic potash treatment of the dye are shown in chart A in chapter II.
Chapter V

DYES DERIVED FROM 2-(3'-CARBOMETHOXY-4'-HYDROXY BENZOYL)-3-NITRO BENZOIC ACID:

\[
\text{OH} \\
\text{4} \\
\text{5'} \text{COOCH}_3 \\
\text{6} \\
\text{1'} \\
\text{2'} \text{COOH} \\
\text{3} \\
\text{C}=\text{O} \\
\text{2} \text{O}_2\text{N}
\]

C.2 PREPARATION OF 2-(3'-CARBOMETHOXY-4'-HYDROXY BENZOYL)-3-NITRO BENZOIC ACID:

The acid was prepared isolated by carrying out Friedel Crafts reaction between methyl salicylate (dry AR 80ml), and nitro phthalic anhydride (20.0g, 0.1mole) in presence of anhydrous aluminium chloride (27.0g, 0.2mole) as the acid C.1 chapter V. The acid was crystallised from hot water in the form of white crystalline solid, m.p. \(153^\circ\text{C}\) acetone, yield 15.0g.

Anal. For.: \(C_{16}H_{11}NO_8\) (mol. wt. = 345)

Calc.: C, 55.65; H, 3.19; N, 4.06;

Found: C, 55.47; H, 3.16; N, 4.04;

C.2.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acetyl derivative of the acid was prepared and isolated by taking (1.0g) acid, (3.5g) of fused sodium acetate and 15ml of acetic anhydride in similar manner as acetyl derivative C.1.1 chapter V. The coloured acetyl derivated was treated with animal charcoal till decolourised and finally recrystallised from acetone. The yield 0.9g m.p. 115\(^\circ\text{C}\) (Decomposed). It is soluble in acetone, chloroform and acetic acid.
The dyes prepared from the acid may be represented by the following general formula:

C.2.2 (3-carbethoxy 4-hydroxy phenyl) phenol nitro phthal-as-ein.
R₁ = R₂ = R₄ = R₅ = H; R₃ = OH

C.2.3 (3-carbethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein.
R₂ = R₄ = R₅ = H; R₁ = R₃ = OH

C.2.4 (3-carbethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein.
R₁ = R₂ = OH; R₃ = R₄ = R₅ = H

C.2.5 (3-carbethoxy 4-hydroxy phenyl) hydroquinone nitro phthal-as-ein.
R₂ = R₃ = R₅ H; R₁ = R₄ = OH
C.2.6 (3-carbomethoxy 4-hydroxy phenyl) pyrogallol nitro phthal-as-ein.
   \[ R_1 = R_2 = R_3 OH; R_4 = R_5 = H \]

C.2.7 (3-carbomethoxy 4-hydroxy phenyl) phloroglucinol nitro phthal-as-ein.
   \[ R_1 = R_3 = R_5 OH; R_2 = R_4 = H \]

C.2.8 (3-carbomethoxy 4-hydroxy phenyl) diacetyl resorcinol nitro phthal-as-ein.
   \[ R_2 = R_4 = R_5 H; R_1 = R_3 = OCOCH_3 \]

C.2.9 (3-carbomethoxy 4-hydroxy phenyl) dibromo resorcinol nitro phthal-as-ein.
   \[ R_5 = H; R_1 = R_3 OH; R_2 = R_4 = Br \]

C.2.2 PREPARATION OF (3-CARBOMETHOXY 4-HYDROXY PHENYL) PHENOL PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (1.5g) and phenol (1.2g) in
presence of few (4-5) drops of concentrated sulphuric acid. The heating was
carried out for four hours at 175-180\(^\circ\) C, till brittle mass was obtained on cooling.
Excess of phenol was removed by steam distillation. The mass left in the flask
was powdered and extracted with 2% sodium hydroxide solution. It was filtered
and the dye was precipitated from coloured filtrate by the gradual addition of
dilute hydrochloric acid with constant stirring. It was purified by repeated
crystallization from rectified spirit and dried in vacuum desiccator, yield 1.3g.
The purity of the dye was tested by paper chromatography as in case of C.1.2
chapter V.

The orange coloured dye has m.p.135-136\(^\circ\) C. Its ethanolic solution is
brownish-red in colour, which turns into pink on adding a drop of alkali.

Analysis:

- C\(_{22}\)H\(_{15}\)NO\(_8\) (Mol.Wt. 421)
- Calculated: C, 62.71; H, 3.56; N, 3.33;
- Found: C, 62.52; H, 3.54; N, 3.30;

C.2.3 PREPARATION OF (3-CARBOMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (2.5g) and resorcinol (2.5g)
in presence of 6-7 drops of concentrated sulphuric acid. Heating was continued
for four and half hours at 130-148\(^\circ\) C, till brittle mass was obtained on cooling.
The isolation and purification were done as in the case of C 1.3 chapter V, yield
4.5g.
The red microcrystalline dye having m.p. 190-192° C is soluble in benzene chloroform ethanol and methanol. Its ethanolic solution is yellowish red with green fluorescence and turns into yellowish orange with green fluorescence on adding a drop of alkali. In strong basic medium it gives reddish brown colour with green fluorescence.

Anal. For. : C_{22}H_{15}NO_{9} (mol. wt. 437)
Calc. : C, 60.41; H, 3.43; N, 3.20;
Found : C, 60.28; H, 3.41; N, 3.18;

**C.2.4 PREPARATION OF (3-CARBOMETHOXY 4-HYDROXY PHENYL) CATECHOL NITRO PHTHALAS-EIN:**

The dye was prepared by condensing the acid (1.5g) and catechol (1.0g) in presence of conc. Sulphuric acid (5-6 drops) at the temp. 140-150° C for four hours, till molten mass becomes hard brittle on cooling. The isolation and purification were done as in the case of C.1.3 chapter V, yield 1.0g.

The dye is black in colour, m.p. above 360° C. Its ethanolic solution is brown in colour which turns into brownish black on adding a drop of alkali.

Anal. For. : C_{22}H_{15}O_{9} (mol. wt. 437)
Calc. : C, 60.41; H, 3.43; N, 3.20;
Found : C, 60.24; H, 3.40; N, 3.18;

**C.2.5 PREPARATION OF (3-CARBOMETHOXY 4-HYDROXY PHENYL) HYDROQUINONE NITRO PHTHALAS-EIN:**

The dye was prepared by heating the homogeneous mixture of the acid (1.5g) and hydroquinone (1.0g) in an bath at the temp. 160-180° C for about four hours in presence of 5-6 drops of concentrated sulphuric acid. The isolation and purification were done similarly as in the case of C.1.3 chapter V, yield 1.5g.

The black coloured dye decomposes above 300° C. Its ethanolic solution is (light brown) in colour. It gives brown colour on addition of alkali. It is soluble in ethanol, methanol and acetic acid.

Anal. For. : C_{22}H_{15}NO_{9} (mol. wt. 437)
It was prepared by carrying out the condensation of homogeneous mixture of the acid (1.5g) and pyrogallol (1.0g) in an oil bath in presence of 5-6 drops of conc. Sulphuric acid at the temperature 140-150° C for about four hours. The isolation and purification were done as in case of C 1.3 chapter V, yield 1.0g.

The shining black crystal decompose above 340° C. It is soluble in ethanol, methanol and acetic acid. Its ethanolic solution is light red in colour, which turns into violet on adding a drop of alkali.

Anal. For. : C_{22}H_{15}NO_{10} (mol. wt. 453)
Calc. : C, 58.28; H, 3.31; N, 3.09;
Found : C, 58.16; H, 3.30; N, 3.06;

An intimate mixture of the acid (1.5g) and phloroglucinol (1.0g) was heated in an oil bath to make it homogeneous and then 6-7 drops of conc. Sulphuric acid were added and heating was continued for about four hours at 180-200° C. The isolation and purification of the dye were done in a similar manner as described in the case of (3-carbomethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein yield 1.2g.

The yellowish orange coloured dye has m.p. above 360° C. Its ethanolic solution is golden yellow in colour, which turns into reddish orange on addition of a drop of alkali. It is soluble in ethanol, methanol, acetone and acetic acid.

Anal. For. : C_{22}H_{15}NO_{10} (mol. wt. 453)
Calc. : C, 58.28; H, 3.31; N, 3.09;
Found : C, 58.12; H, 3.30; N, 3.06;
[(4-acetoxy 3-carbomethoxy phenyl) diacetyl resorcinol nitro phthal-as-ein]

The dye (3-carbomethoxy 4-hydroxy phenyl) resorcinol phthal-as-ein (1.0g) and fused sodium acetate (3.0g) and freshly distilled acetic anhydride (15ml), were taken in a 50ml round bottom flask fitted with an air condenser. The purification and crystallization were done in a similar manner as in case of C. 1.8 chapter V. The acetylated compound was dried in an oven at 80° C and then over phosphorous penta-oxide under reduced pressure, yield 0.7g.

The acetylated product light yellow in colour m.p. 210-212° C, is soluble in ether, methanol, chloroform and acetic acid.

Anal. For. : C_{28}H_{21}NO_{12}  C_{22}H_{12}NO_{9} (OC CH_{3})_{3} (mol. wt. 563)
Calc. : C, 59.68; H, 3.73; acetyl, 22.91;
Found : C, 59.46; H, 3.71; acetyl, 22.86;

C.2.9 BROMINATION OF (3-CARBMETHOXY 4-HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

[(3-bromo 5-carbomethoxy 4-hydroxy phenyl) dibromo resorcinol nitro phthal-as-ein]

The dye (3-carbomethoxy 4-hydroxy phenyl) resorcinol nitro phthal-as-ein (1.0g) was brominated, isolated and purified in a similar manner as in case of C. 1.9 chapter V yield 0.8g.

The pale-orange coloured dye has m.p. 248-250° C. Its ethanolic solution is yellowish orange in colour. In moderate and strong basic medium it gives orange colour with green fluorescence.

Anal. For. : C_{22}H_{12}Br_{3}NO_{9} (mol. wt. 674)
Calc. : Br, 35.61;
Found : Br, 35.48;

C.2.10 CAUSTIC POTAISH TREATMENT OF (3-CARBMETHOXY 4-
HYDROXY PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:
Caustic potash treatment of the resorcinol dye (1.0g) was carried out in identical manner as in the case of C.1.10 chapter V. As a result of fusion three residues were obtained.

Identification of residue – I

It was identified and confirmed as the unreacted residual dye from its colour reactions and mixed melting point determination with the authentic sample of the dye.

Identification of residue – II

It was recrystallised from acetone, m.p. 160.4°. It was acidic in nature and gave positive tests for carboxyl and phenolic groups. It was identified to 2-(3’-carbomethoxy 4’-hydroxy benzoyl) 3 nitro benzoic acid and confirmed by mixed melting point determination and superimposition of the IR spectra with the authentic sample.

Identification of residue – III

The purified sample melted at 109-110° C. It gave positive test with Fehling’s solution, ferric chloride, ammonical silver nitrate. It gave fluorescein test with phthalic anhydride, on the basis of these observations it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are shown in chart C chapter II.
Chapter V

**DYNS DERIVED FROM 2-(5'-CHLORO-2'-CHLOROMETHYL BENZOYL) 3-NITRO BENZOIC ACID:**

![Chemical structure](image)

2-(5'-chloro-2'-chloromethyl benzoyl)-3-nitrobenzoic acid

**C.3 PREPARATION OF 2-(5'-CHLORO-2'-CHLOROMETHYL BENZOYL) NITRO BENZOIC ACID:**

The acid was prepared by carrying out Friedel Crafts reaction between para chlorobenzyl chloride and m-nitro phthalic anhydride and anhydrous AlCl₃. Starting with para chlorobenzyl chloride (AR, dry 100ml), along with m-nitro phthalic anhydride (20.0g, 0.1mole) and anhydrous aluminum chloride (27.0g, about 0.2 moles) used as a catalyst, the acid was prepared following the procedure outlined in C.1 chapter V.

The acid was isolated as shining white crystals, which had melting point of 196-198° C. The crystalline solid was found to be soluble in rectified spirit and methanol, yield 15.0g.

**Anal. For** : C₁₅H₉NCl₂O₅ (mol. wt. = 354)

**Calc.** : C, 51.52; H, 2.78; N, 3.54; Cl, 17.93; acetyl. 10.86;

**Found** : C, 51.40; H, 2.76; N, 3.52; Cl, 17.90; acetyl. 10.80;

**C.3.1 PREPARATION OF ACETYL DERIVATIVE OF THE ACID:**

1.0g of acid 3.0g of fused sodium acetate was refluxed with 15ml of freshly distilled acetic anhydride at 130-140° C in the same way as in case of 2-(5'-chloro-2'-chloromethyl benzoyl) benzoic acid chapter III. It was crystallised
from acetone in the form of a black crystalline solid, m.p. 240°C. It is slightly soluble in methanol but highly soluble in acetone. Yield 0.60g.

Anal. : C_{17}H_{11}NCl_{2}O_{6} or C_{15}H_{8}NCl_{2}O_{5} (OC.CH_{1}) (mol. wt. = 396)

Calc. : C, 51.52; H, 2.78; N, 3.54; Cl, 17.93; acetyl 10.86;

Found : C, 51.50; H, 2.76; N, 3.52; Cl, 17.90; acetyl 10.80;

The dyes prepared from the acid may be represented by the following.

\[
\begin{align*}
\text{Acid (Lactol form)} & \xrightarrow{\text{Conc H}_2\text{SO}_4} \\
\text{Dye molecule}
\end{align*}
\]

DYES:

C.3.2 (5-chloro-2-chloromethyl phenyl) phenol nitro phthal-as-ein:
\[R_1 = R_2 = R_4 = R_5 = H, \ R_3 = OH\]

C.3.3 (5-chloro-2-chloromethyl phenyl) resorcinol nitro phthal-as-ein:
\[R_2 = R_4 = R_5 = H, \ R_1 = R_3 = OH\]
C.3.4 (5-chloro-2-chloromethyl phenyl) catechol nitro phthal-as-ein:
R₃ = R₄ = R₅ = H, R₁ = R₂ = OH

C.3.5 (5-chloro-2-chloromethyl phenyl) hydroquinone nitro phthal-as-ein:
R₂ = R₃ = R₅ = H, R₁ = R₄ = OH

C.3.6 (5-chloro-2-chloromethyl phenyl) pyrogallol nitro phthal-as-ein:
R₄ = R₅ = H, R₁ = R₂ = R₃ = OH

C.3.7 (5-chloro-2-chloromethyl phenyl) phloroglucinol nitro phthal-as-ein:
R₂ = R₄ = H, R₁ = R₃ = R₅ = OH

C.3.8 (5-chloro-2-chloromethyl phenyl) diacetyl resorcinol nitro phthal-as-ein:
R₂ = R₄ = R₅ = H, R₁ = R₃ = 0.CO.CH₃

C.3.9 (5-chloro-2-chloromethyl phenyl) dibromo resorcinol nitro phthal-as-ein:
R₃ = H, R₁ = R₃ = OH, R₂ = R₄ = Br

C.3.2 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PHENOL NITRO PHTHAL-AS-EIN:

An intimate mixture of 2.0g of the acid and 1.5g of phenol was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175⁰ C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallization from rectified spirit and dried in vacuum in a desiccator, yield 1.20g.

The light pink dye has a m.p. 222-224⁰ C. The ethanolic solution of the dye is light brown in colour that turns into violet colour on adding a drop of an alkali.

The purity of the dye was tested as done in the case of other phenol dyes described in earlier pages.

Anal. For. : C₂₁H₁₃NCl₂O₅ (mol. wt. 430)
Calc. : C, 58.60; H, 3.02; N, 3.26; Cl, 16.51;
The dye was prepared by heating mixture of 3.0g of the acid and 2.5g resorcinol in an oil bath at 120-130 °C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of C 1.3 chapter V, yield 0.6g.

The golden yellowish crystalline dye having a m.p. 225-227 °C is soluble in ethanol to yield a brown colour in ethanol that turns to reddish brown with alcoholic caustic soda solution.

**Anal. For.** : C₂₁H₁₃NCl₂O₆ (mol. wt. 446)

**Calc.** : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;

**Found** : C, 56.37; H, 2.90; N, 3.11; Cl, 15.80;

It was prepared by the condensation of 1.0g of the acid and 1.0g of catechol little excess than the molecular proportion on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 115-125 °C for about four and half-hours. It was isolated and purified as described for C 1.3 chapter V, yield 0.8g.

The black crystalline dye having a m.p. 315-317 °C, it dissolves in ethanol giving a brown colour with an alkali and reddish brown colour with 2% soda solution.

**Anal. For.** : C₂₁H₁₃NCl₂O₆ (mol. wt. 446)

**Calc.** : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;

**Found** : C, 56.27; H, 2.90; N, 3.12; Cl, 15.79;
1.5 g of the acid and 1.0 g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath 160-180°C for three hours in presence of a few drop of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for C 1.3 chapter V, yield 1.0 g.

The blackish brown dye, having m.p. above 320-321°C is soluble in ethanol giving a brown colour that turns into reddish brown on the addition of 2% caustic solution.

Anal. For. : C_{21}H_{13}NCl_{2}O_{6} (mol. wt. 446)
Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92;
Found : C, 56.32; H, 2.89; N, 3.11; Cl, 15.84;

C.3.6 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PYROGALLOL NITRO PHTHAL-AS-EIN:

The intimate and homogenized mixture of 1.5 g of the acid and 1.0 g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 190-200°C for about three hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for C 1.3 chapter V yield 0.80 g.

The black coloured dye having m.p. above 340-342°C gives an ethanolic solution reddish brown in colour which on adding a drop of an alkali darkens in shade.

Anal. For. : C_{21}H_{13}NCl_{2}O_{7} (mol. wt. 462)
Calc. : C, 54.55; H, 2.81; N, 3.03; Cl, 15.37;
Found : C, 54.42; H, 2.80; N, 3.00; Cl, 15.25;

C.3.7 PREPARATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.0 g of the acid and 1.0 g of phlorogluconol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 180-200°C for about three hours. The isolation and purification of the dye was performed in the same way as that described for C 1.3 chapter V, yield 0.65 g.
The brown coloured dye m.p. 292-294° C yields a wine red coloured solution in ethanol that turns dark red on adding a drop of an alkali. It gives wine red colour with alcoholic potash solution.

Anal. For. : C_{21}H_{13}NCl_{2}O_{7} (mol. wt. 462)

Calc. : C, 54.55; H, 2.81; N, 3.03; Cl, 15.37;

Found : C, 54.40; H, 2.78; N, 3.00; Cl, 15.28;

C.3.8 ACETYLATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

((5-CHLORO-2-CHLOROMETHYL PHENYL) DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN:

1.0g of the 5-chloro-2-chloromethyl phenyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of resly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser and refluxed for about three hours. The isolation and purification of acetylated product was carried out in exactly the same manner as in the case of C 1.8 chapter V, yield 0.7g.

The buff coloured diacetyl derivative (m.p. 272-274° C) is soluble in acetone, methanol and chloroform.

Anal. For. : C_{25}H_{17}NCl_{2}O_{8} or C_{21}H_{11}NCl_{2}O_{6} (OC.CH_{3})_{2} (mol. wt. 530)

Calc. : C, 56.60; H, 3.21; N, 2.64; Cl, 13.40; acetyl, 16.23;

Found : C, 56.48; H, 3.18; N, 2.58; Cl, 13.32; acetyl, 16.16;

C.3.9 BROMINATION OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

((5-CHLORO-2-CHLOROMETHYL PHENYL) DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN)

The 1.0g of the dye (5-chloro-2-chloromethyl phenyl) resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10 ml of 10% solution of bromine in glacial acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed
at 120-130° C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A blackish rose powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110° C in an oven then in a vacuum desiccator, yield 0.90g.

The yellowish orange coloured crystalline dye having m.p. 178-180° C is soluble in ethanol yielding a yellowish red colour that turns into orange with green fluorescence on adding a drop of an alkali. In strong alkaline medium, it exhibits deep red colour.

Anal. For. : C_{2}H_{11}NBr_{2}Cl_{2}O_{6} (mol. wt. 604)

Calc. : Br, 26.49;

Found : Br, 26.42;

**C.3.10 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-FIN:**

10.0g of potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to carry out the caustic potash treatment exactly in the same way as described in C 1.10 chapter V.

**Identification of residue I:**

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

**Identification of residue II:**

It was recrystallised from acetone. It gives tests for carboxyl group and chloride groups and was identified and confirmed as 2-(5'-chloro-2'-chloromethyl benzoyl) 3-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.
The purified residue melted at 109-110\(^{\circ}\) C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescence test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in chart E chapter II.
The acid was prepared by carrying out Friedel-Crafts reaction between acenaphthene and nitro phthalic anhydride in presence of anhydrous aluminium chloride as catalyst and nitro benzene was used as solvent. The preparation and isolation of acid were carried out as in case of (C.1 chapter V). The acid was crystallized from aqueous ethanol in the form of white needles having m.p. 208-210°C. The acid is soluble in ethanol, ether, chloroform, and sparingly soluble in benzene and insoluble in carbondisul phide.

Anal. for \( \text{C}_{20}\text{H}_{13}\text{NO}_3 \) (molecular weight 347)

Calc. C, 69.16; H, 3.75; N, 4.03;

Found C, 69.12; H, 3.70; N, 4.01;

C.4.1. PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acetyl derivative of the acid (1.0g) was prepared and purified in a similar way as the acetyl derivative C.1.1 chapter V, yield 0.70g, m.p 180-182°C. It is soluble in chloroform, acetone, ethanol and acetic acid.

Anal. for \( \text{C}_{20}\text{H}_{12}\text{NO}_3(\text{COCH}_3) \) (molecular weight 389)

Calc. C, 61.70; H, 3.08; N, 5.60; Acetyl, 11.05;

Found C, 61.48; H, 3.04; N, 5.58; Acetyl, 11.02;
The dye prepared from the acid may be represented by the following general formula:

![Dye molecule diagram](image)

C.4.2 3-Acenaphthyl phenol nitro phthal-as-ein:
\[ R_1 = R_2 = R_4 = R_5 = H; R_3 = OH \]

C.4.3 3-Acenaphthyl resorcinol nitro phthal-as-ein:
\[ R_2 = R_4 = R_5 = H; R_1 = R_3 = OH \]

C.4.4 3-Acenaphthyl catechol nitro phthal-as-ein:
\[ R_3 = R_4 = R_5 = H; R_1 = R_2 = OH \]

C.4.5 3-Acenaphthyl hydroquinone nitro phthal-as-ein:
\[ R_2 = R_3 = R_5 = H; R_1 = R_4 = OH \]
C.4.6 3-Acenaphthyl pyrogallol nitro phthal-as-ein:
   \( R_4 = R_5 = H \); \( R_1 = R_2 = R_3 = \text{OH} \)

C.4.7 3-Acenaphthyl phloroglucinol nitro phthal-as-ein:
   \( R_2 = R_4 = H \); \( R_1 = R_3 = R_5 = \text{OH} \)

C.4.8 3-Acenaphthyl diacetyl resorcinol nitro phthal-as-ein:
   \( R_2 = R_4 = R_5 = H \); \( R_1 = R_3 = R_5 = \text{OCOCH}_3 \)

C.4.9 3-Acenaphthyl dibromo resorcinol phthal-as-ein:
   \( R_5 = \text{H} \); \( R_2 = R_4 = \text{Br} \); \( R_1 = R_3 = \text{OH} \)

C.4.2 PREPARATION OF (3-ACENAPHTHYL) PHENOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (3.0g) and phenol (1.5g) in
presence of 5-6 drops of concentrated sulphuric acid. The heating was carried out for
eight hours at 150-165\(^\circ\)C, till brittle mass on cooling was obtained. Excess of phenol
was removed by steam distillation. The isolation and purification of the dye were done
in the same manner as described in case of other phenol phthal-as-ein, yield 1.6g.

The grey coloured dye m.p 115-117\(^\circ\)C gives light yellow colour in ethanol which
turns into pink on adding a drop of alkali. With strong alkali it gives pinkish red colour.

Anal. for \( \text{C}_{26}\text{H}_{17}\text{NO}_5 \) (molecular weight 423)
Calc. : C, 73.76; H, 4.02; N, 3.31;
Found : C, 73.64; H, 4.00; N, 3.28;

C.4.3 PREPARATION OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing the acid (3.0g) and resorcinol (3.0g) by
using 6-8 drops of concentrated sulphuric acid as condensing agent. Heating was
continued for four hours at 140-150\(^\circ\)C, till brittle mass was obtained on cooling. The
isolation and purification of the dye were done in the same manner as in case of other
resorcinol dyes, yield 2.5g.

Red coloured micro crystalline dye has, m.p. 315-317\(^\circ\)C. Its ethanolic solution is
yellow in colour which turns into yellowish orange with green fluorescence on addition
of a drop of alkali. In strong basic medium it gives yellowish orange colour with
intensified green fluorescence.

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Anal. for : C_{26}H_{17}NO_{6} (molecular weight 439)
Calc. : C, 71.07; H, 3.87; N, 3.19;
Found : C, 70.82; H, 3.84; N, 3.17;

C.4.4 PREPARATION OF (3-ACENAPHTHYL) CATECHOL NITRO PHTHAL.-AS-EIN:

The dye was prepared by taking the acid (1.5g) and catechol 1.0g and 5-6 drops of conc. H_{2}SO_{4} exactly with the same manner as C.1.4 chapter V. The isolation and purification were also done in identical manner, yield 0.8g.

Dark brown coloured dye has m.p >300\(^{0}\)C. Its ethanolic solution is brown in colour which turns into bluish green on addition of alkali.

Anal. for : C_{26}H_{17}NO_{6} (molecular weight 439)
Calc. : C, 71.07; H, 3.87; N, 3.19;
Found : C, 70.82; H, 3.84; N, 3.17;

C.4.5 PREPARATION OF (3-ACENAPHTHYL) HYDROQUINONE NITRO PHTHAL.-AS-EIN:

The dye was prepared, isolated & purified exactly as C.4.3 by taking approximate quantity of acid and hydroquinone, yield 50%.

The dark brown powdery dye has m.p. 202-204\(^{0}\)C. Its ethanolic solution is brownish red in colour which turns into purple on addition of alkali.

Anal. for : C_{26}H_{17}NO_{6} (molecular weight 439)
Calc. : C, 71.07; H, 3.87; N, 3.19;
Found : C, 70.05; H, 3.85; N, 3.16;

C.4.6 PREPARATION OF (3-ACENAPHTHYL) PYROGALLOL NITRO PHTHAL.-AS-EIN:

The dye was prepared isolated and purified by taking pyrogallol (1.5g) and acid (1.0g) in a similar manner as C.4.3, Yield (0.8g)
The shining black dye has m.p 215-217° C. Its ethanolic solution is reddish brown which becomes violet on adding a drop of alkali. In strong basic medium, it shows blue-black colour.

**Anal. for**  \( \text{C}_{26}\text{H}_{17}\text{NO}_7 \)  (molecular weight 455)

**Calc.**  
\( \text{C}, \ 68.57; \ \text{H}, \ 3.74; \ \text{N}, \ 3.08; \)

**Found**  
\( \text{C}, \ 68.42; \ \text{H}, \ 3.72; \ \text{N}, \ 3.04; \)

**C.4.7 PREPARATION OF (3-ACENAPHTHYL) PHLOROGLUCINOL NITRO PHTHHAL-AS-EIN:**

The dye was prepared, isolated and purified by a similar method as C.4.3. Yield 0.9g. The light brown coloured dye has m.p 240° C (decomp.). It gives light brown colour with ethanol, which becomes dark brown on adding a drop of alkali. In strong basic medium it gives dark brown colour.

**Anal. for**  \( \text{C}_{26}\text{H}_{17}\text{NO}_7 \)  (molecular weight 455)

**Calc.**  
\( \text{C}, \ 68.57; \ \text{H}, \ 3.74; \ \text{N}, \ 3.08; \)

**Found**  
\( \text{C}, \ 68.50; \ \text{H}, \ 3.72; \ \text{N}, \ 3.04; \)

**C.4.8 ACETYLATION OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHHAL-AS-EIN:**

[3-Acenaphthyl diacetyl resorcinol nitro phthal-as-ein]

The dye 3-acenaphthyl resorcinol nitro phthal-as-ein was acetylated in a similar manner as C.1.8. The crude yellowish white product was treated with animal charcoal & crystallized from aqueous ethanol in presence of 2, 3 drops of acetic acid, Yield 60%.

The acetylated product is yellowish white, amorphous in nature, m.p 146-148° C. It is soluble in ethanol, acetone and acetic acid.

**Anal. for**  \( \text{C}_{26}\text{H}_{15}\text{NO}_6(\text{COCH}_3)_2 \)  (molecular weight 523)

**Calc.**  
\( \text{C}, \ 59.66; \ \text{H}, \ 2.87; \ \text{N}, 2.68; \ \text{Acetyl}, \ 16.44; \)

**Found**  
\( \text{C}, \ 59.52; \ \text{H}, \ 2.84; \ \text{N}, 2.62; \ \text{Acetyl}, \ 16.40; \)
[3-Acenaphthyl dibromo resorcinol nitro phthal-as-ein]

The dibromo derivative of the dye (3-acenaphthyl resorcinol nitro phthal-as-ein) was prepared, purified and crystallized in a similar manner as described in the case of C.1.9 chapter V, yield 60%.

The brick red microcrystalline dye has m.p 130-132 °C its ethanolic solution is yellow in colour which turns into yellowish orange with green fluorescence on adding a drop of alkali. In strong basic medium it gives deep red colour

Anal. For : C_{26}H_{15}Br_{2}NO_{6} (molecular weight 597)
Calc. : Br, 26.80;
Found : Br, 26.65

C.4.10 CAUSTIC POTASH TREATMENT OF (3-ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was subjected to caustic potash treatment in a similar manner as C.1.10 chapter V. The following three residues were obtained.

Residue I:

It was identified to be the unreacted residual dye from its colour reactions confirmed by mixed melting point determination.

Residue II:

The yellowish white compound, m.p208-210°C, gave the usual test of a carboxyl group and was identified as 2 (3' acenaphthoyl) 3-nitro benzoic acid & was confirmed by mixed melting point determination and superimposition of IR spectra with the authentic sample.

Residue III:

The brownish red residue was purified & was identified to be resorcinol from its colour reactions & confirmed by mixed melting point determination with the authentic sample.

Bromination, acetylation & caustic potash fusion of the dye was shown in chart G chapter II.