

SYNTHESIS AND CHARACTERIZATION OF SOME PHTHAL-AS-EIN DYES

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Abstract

A series of new phthal-as-ein dyes derived from o-(2-amino-4-methyl benzoyl) Benzoic acid. These dyes synthesized from γ -keto acid and characterised on the basis of IR spectra, NMR spectra, paper chromatography. The analytic data are given in percentage.

Keywords- IR spectra, NMR spectra, Elemental analysis

Introduction

Colour plays a remarkable dominant role in our life. Colour chemistry deals with the chemistry associate with coloured chemicals like dyes, pigments, paints etc.

Graebe and libermann¹ in 1868 pointed out that unsaturation was important for producing colour and that reduction of coloured compounds always resulted in the formation of colourless products.

O.N. Witt² (1876) in his "Chromophore-auxo chrome theory" brought forth the importance of unsaturation in the appearance of colour.

An object that selective absorbs red light will not look red. That is the colours that are not absorbed are what in visible.³

Dyes are generally known composed of a group of atom called-

Chromophores which are responsible for intensifying the dye colour and auxochrome which influence its colour⁴.

According to literature these are over 10000 different dyes and pigment available which are used in industry and around 7×10^5 tons of synthetic dyes that are produced globally throughout the year^{5,6}.

In this paper we will synthesized and charaterised Phthal-as-ein dyes which are derived from O-(2-amino 4-methyl benzoyl) Benzolic acid.

Methods –

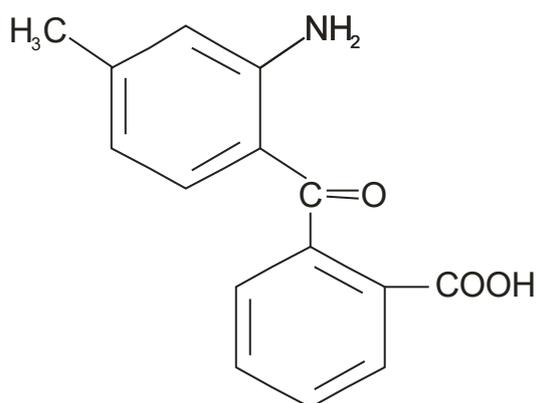
IR spectra were recorded by using Perkin-Flemen Infracard (KBr) and NMR was recorded on varian A-60 T.M.S. as internal reference and solvent CDCl_3 were used and the chemical shift have been given in (Tau) values.

The purity of a dye was checked by TLC or paper chromatography. In case of TLC methanol has been used as solvent and in case of paper Chromatography butanol saturated with ammonia has been used as the mobile phase and 1% KOH solution as deveveloping agent

The analytical data were given in percentage.

Experiment-

(1) Preparation of O-(2-Amino 4-Methyl. Benzoyl) Benzoic Acid:



The acid¹ was prepared by carrying out Friedel-Crafts reaction between m-toluidine (dry AR, 80 ml) and phthalic anhydride (14.8 g, 0.1 mole) in presence of anhydrous aluminium chloride (23.0 g, 0.2 mole) as catalyst. The yield of the acid was 17.8 g.

The reaction was carried out in a 1 litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 20^o by adding anhydrous aluminium chloride in portions. When the vigorous reaction subsided, the mixture was heated on boiling water bath until the evolution of hydrogen chloride ceased.

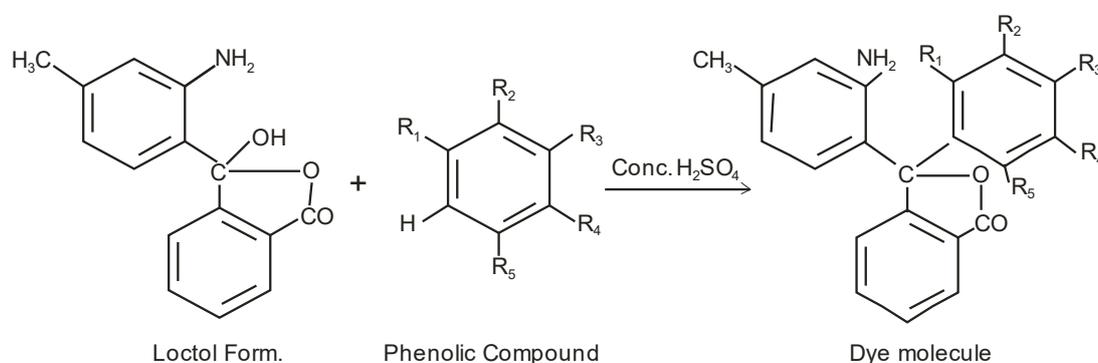
The heavy dark coloured complex was decomposed by adding 30 ml. of concentrated hydrochloric acid (in 250 ml ice cold water). The excess of m-Toluidine was removed by steam distillation. The residue of m-Toluidine was removed by steam distillation. The residue was extracted 3-4 times with hot boiling 10% solution of sodium carbonate 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 benzene/ petroleum

ether, m.p. 139-141^oc. The white crystalline acid is soluble in benzene, chloroform acetone and ethanol.

Preparation of acetyl derivative of the acid :

The acid (1.0 g) and fused sodium acetate (3.0 g) were refluxed with 15 ml of freshly distilled acetic anhydride at 125-135^o for three and half hours. The hot contents were poured in a beaker containing ice cold water with constant stirring. The acetyl derivative settled down in the form of grey coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charceal and filtered while hot. It was finally crystallized from acetone, yield 0.65 g, m.p. 131-135^oC. It is soluble in chloroform, acetone, ethanol and acetic acid.

Synthesis of Dyes :



Dyes :

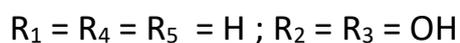
Dye-1 : (2-Amino 4-methyl phenyl) Phenol Phthal-as-ein :

$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

Dye-2 : (2-Amino 4-methyl phenyl) Resorcinol Phthal-as-ein :



Dye-3 : (2-Amino 4-methyl phenyl) catcchol Phthal-as-ein :



Dye-4 : (2-Amino 4-methyl phenyl) hydroquinone Phthal-as-ein :



Dye-1

Preparation of (2-Amino 4-methyl phenyl) phenol phthal-as-ein:

An intimate mixture of the acid (2.5 g) and phenol (2.0 g) (slight excess than the molecular proportion) was taken in a hard boiling tube and heated in an oil bath to make the contents homogeneous. 5-6 drop of concentrated sulphuric acid were then added and heating was continued at 165-175⁰c for six hours till the moltan mass of the tube become brittle on cooling. The condensed mass was taken out from the tube and subjected to steam distillation to remove excess of phenol. The brown solid mass left in the flask was powdered and extracted with 2% sodium hydroxide solution. It was filtered and the dye was precipitated from the buff 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 desiccators, yield 2.5 g, m.p. 230-232⁰c.

Dye-2**(2-Amino 4-methyl phenyl) resorcinol phthal-as-ein :**

A well ground mixture of the acid (5.0 g) and resorcinol (2.5 g) was heated in an oil bath to 120⁰ to make it homogeneous. A few drops (8-10) of concentrated sulphuric acid were added and the contents were stirred well. The heating was continued at 140⁰-160⁰ for about four hours, till the melt become hard and brittle on cooling. The condensed mass was crushed and washed well with water to remove excess of resorcinol. It was extracted with 2% aqueous caustic soda solution and filtered. The dye was precipitated as reddish-brown with green fluorescent from filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 120⁰C and then in a vacuum desiccators, yield 4.5 g.

Dye-3**(2-Amino 4-methyl phenyl) catechol phthal-as-ein :**

An intimate mixture of the acid (2.5 g) and catechol (1.5 g) was heated in an oil bath at 110⁰ to make it homogeneous. 4-5 drops of concentrated sulphuric acid were added and the hard brittle mass was obtained on cooling. The isolation and purification were done as in the case of (2-amino 4-methyl phenyl) resorcinol phthal-as-ein yield 1.8g.

Dye-4**(2-Amino 4-methyl phenyl) hydroquinone phthal-as-ein :**

An intimate mixture of the acid (2.5 g) and hydroquinone (1.5 g) was heated to make it homogeneous. A few drops (4-6)of concentrated

sulphuric acid were added and the mixture was heated for four hours at 165-180°C, yield (2.0 g).

Result and Discussion :

A series of new phthal-as-ein dyes derived from o-(2-amino-4-methyl benzoyl) Benzoic acid. These dyes synthesized from γ -keto acid and characterised on the basis of IR spectra, NMR spectra, paper chromatography. The analytic data are given in percentage.

IR spectral examination of these acid clearly reveals their existence as a mixture of ring and chain tautomers.

The open chain substituted or unsubstituted γ -keto acids possess a characteristic structural requirement due to which they are capable of existing in cyclic tautomeric form also. The formation of ring tautomer (lactol form) takes place due to electrophilic ring-chain tautomerism where the electrophile is proton (hydrogen). Amount of the lactol depends on the extent of this prototropic change. Generally it has been observed that γ -keto acids exist chiefly as lactol or equilibrium mixture of ring and chain tautomers^{7,8}. The lactols give well crystalline acetyl derivatives, still retaining their cyclic structures. Therefore, it is obvious that the cyclic tautomer is comparably more stable form than the chain tautomer⁹⁻¹².

There are notable peaks showing the presence of diaryl ketonic $\text{C}=\text{O}$ (1675-1700 cm^{-1}) and aryl ketonic (1660-1670 cm^{-1}).

IR spectra of the acetyl derivatives of the acids were also studied. It shows notable peaks of $\text{>C}=\text{O}$ in acetate (new peaks 1000-1250 Cm^{-1} and 1735-1760 cm^{-1}) and lactonic $\text{>C}=\text{O}$ (1735-1790 Cm^{-1}). The peaks,

due to diaryl ketonic $>C=O$ ($1675-1700\text{ Cm}^{-1}$), aryl ketonic $>C=O$ (1660 to 1670 Cm^{-1}), Carboxyl $>C=O$ ($1695-1710\text{ Cm}^{-1}$), Carboxyl $-OH$ ($2600-2700\text{ Cm}^{-1}$), which were present originally in acids, were found absent in acetyl derivatives of the acids. (Table-1)

Chemical shifts recorded in NMR spectra of different acids and their derivatives further confirm the present of lactol tautomer in each case ($\tau = 4.2-4.35$) which disappears in the case of their acetyl derivatives and a new chemical shift of $OCOCH_3$ ($\tau = 7.65-7.85$) was observed. Thus it is amply clear that the γ -keto acids exist in keto as well as lactol forms which makes it possible to condense these acids with different phenolic compounds giving unsymmetrical phthaleins. (Table-2).

The melting point, shade colour in different mediums and λ_{max} of dyes o-(2-amino-4-methyl benzoyl) Benzoic acid is in form of table 3 & Elemental analysis is in table 4.

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