Dyes and Pigments **9** (1988) 351–356

Novel Synthesis of Fluorescent Whiteners of the Palanil White R Series*

H. A. Naik & S. Seshadri†

Dyes Research Laboratory, Department of Chemical Technology,
University of Bombay, Matunga, Bombay 400019, India

(Received 9 September 1987; accepted 29 October 1987)

ABSTRACT

A novel route for the synthesis of the commercially important 1,4-bis(styryl)benzene fluorophore is described. The synthesis involves the reaction of 1,4-benzenediacetic acid with phthalic anhydride to yield a 1,4-bis(phthalyl)benzene, reduction and subsequent dehydration of which gives the 1,4-bis(o-carboxystyryl)benzene derivative which can be readily converted into the desired dinitrile.

1 INTRODUCTION

An important development in the fluorescent whitening of polyester was the introduction of the 4-styrylstilbene system by the BASF company in 1961[1] under the tradename Palanil Brilliant White R. The usual synthetic route involves condensation of terephthalaldehyde with *o*-cyanobenzylphosphonic ester under basic conditions.

We report here a new approach (Scheme 1) to the synthesis of the compounds of this type which involves the use of much simpler chemicals and reagents.

2 RESULTS AND DISCUSSION

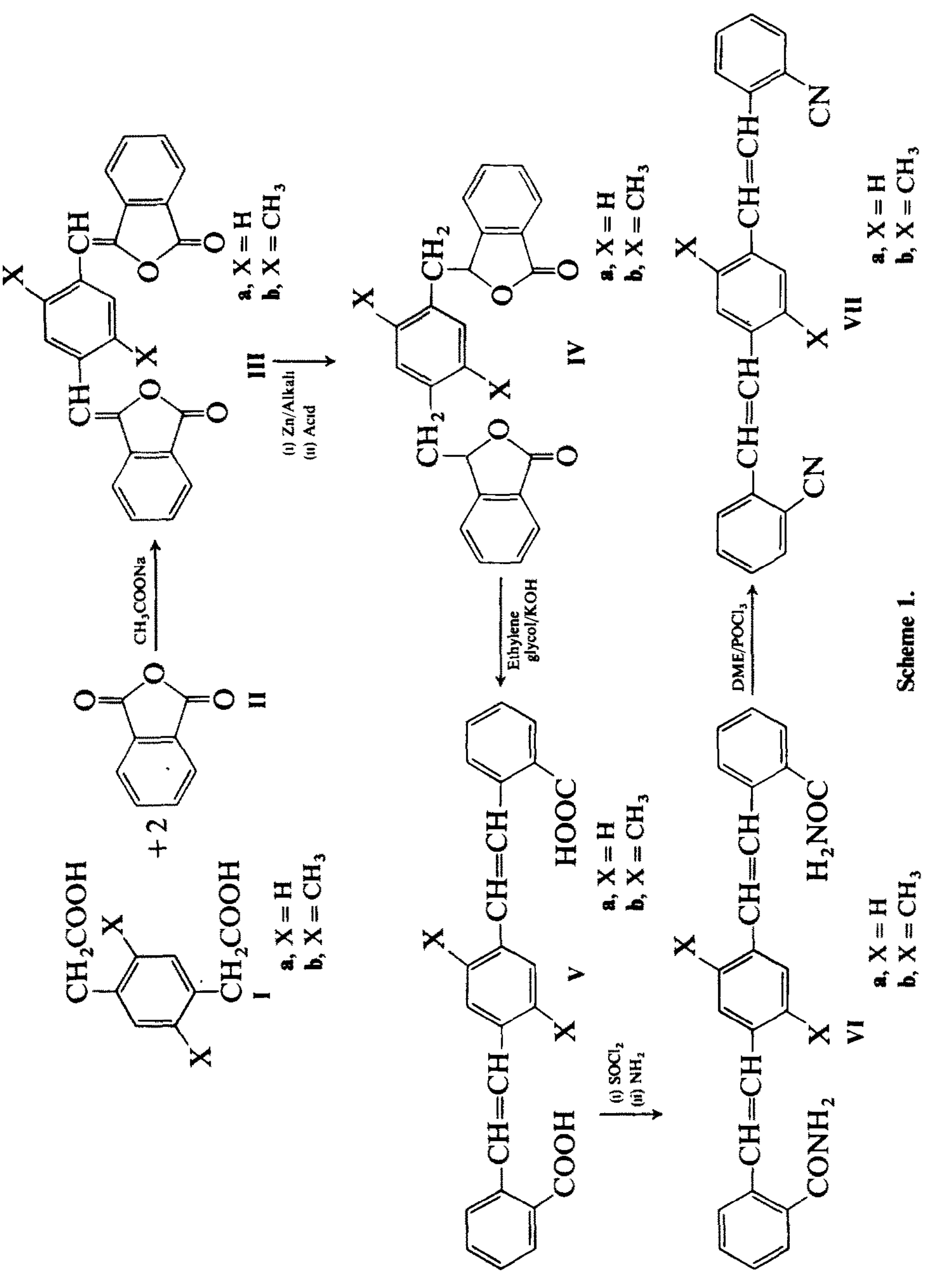
It is known that phenylacetic acid reacts with phthalic anhydride in the presence of sodium acetate at high temperatures to give benzylidene

---

* Abstracted from H. A. Naik, Ph.D. (Tech.) Thesis, Bombay University, 1985.

† To whom all correspondence should be addressed.

Dyes and Pigments 0143-7208/88/$03·50


I
a, X = H
b, X = CH3
+ 2
II
CH3COONa
III
a, X = H
b, X = CH3
(i) Zn/Alkali
(ii) Acid
IV
a, X = H
b, X = CH3
Ethylene glycol/KOH
V
a, X = H
b, X = CH3
(i) SOCl2
(ii) NH3
VI
a, X = H
b, X = CH3
DME/POCl3
VII
a, X = H
b, X = CH3

Scheme 1.

phthalide.[2] Reaction of 1,4-benzenediacetic acid (**Ia**) with phthalic anhydride (**II**) under similar conditions gave rise to the expected benzylidenephthalide derivative (**IIIa**), the structure of which was confirmed by elemental analysis and mass spectrometry. It exhibits a bluish green fluorescence in daylight.

Reduction of the benzylidenephthalide (**IIIa**) with zinc and alkali gave the benzylphthalide (**IVa**) derivative which showed a hypsochromic shift in the absorption spectrum compared with **IIIa**, indicating that reduction had occurred.

Reaction of the benzylidenephthalide (**IVa**) with alkali at elevated temperatures led to ring opening and dehydration to yield the 1,4-bis(2-carboxystyryl)benzene (λ_{max} 351 nm). Conversion of the dicarboxylic acid to the diamide and eventual dehydration to the dinitrile by standard techniques led to the dicyanostyrylstilbene (**VIIa**) which was identical with the commercial sample of Palanil Brilliant White R.

The synthesis is characterised by fairly high yields at each stage. This method was also carried out starting from 2,5-dimethyl-1,4-benzenediacetic acid and similar products were obtained at each stage, leading eventually to 1,4-bis(2-cyanostyryl)-2,5-dimethylbenzene (**VIIb**).

3 EXPERIMENTAL

All temperatures are in degrees Centigrade (°C). Melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 397 spectrophotometer, PMR spectra on a Varian EM 360L spectrophotometer using tetramethylsilane (TMS) as the internal standard and mass spectra were recorded on a Varian Mat 1125 mass spectrophotometer. UV–visible spectra were recorded on a KONTRON spectrophotometer.

Commercially available *p*-xylene dichloride was used. This was converted into 1,4-benzenediacetonitrile by reaction with sodium cyanide in dimethylformamide (DMF)[3] and the product was then hydrolysed to give **Ia**.[4]

1,4-Bis(chloromethyl)-2,5-xylene was prepared[5] by the chloromethylation of xylene and was then converted[6] to 2,5-dimethyl-1,4-benzene diacetonitrile with NaCN in ethanol, followed by hydrolysis[6] to give **Ib**.

3.1 3,3′-(1,4-Phenylenedimethylidene)bis[3-oxo-1*H*(3*H*)-isobenzofuran] derivatives (IIIa and IIIb)

A mixture of the diacetic acid derivative (**Ia**, **Ib**) (0·15 mol), phthalic anhydride (**II**) (0·45 mol) and anhydrous sodium acetate (0·045 mol) was gradually heated to 230°C and the reaction mixture was maintained at this temperature for 4 h, until the distillation of water formed in the reaction ceased. The liquor was cooled, ethanol (20 ml) added and filtered. The product was washed with sodium bicarbonate solution (5%), then with water, and dried.

IIIa: Yield 40%, m.p. 350° (DMF); λ_{max} (log ε) in DMF 390 nm (4·57).
$C_{24}H_{14}O_4$ requires: C, 78·7; H, 3·8%.
Found: C, 78·3; H, 3·9%.

The mass spectrum of the product showed the molecular ion peak M^+ at *m/e* 366 and the compound showed a bluish green fluorescence in daylight.

IIIb: Yield 45%; m.p. 330–332° (DMF); λ_{max}(log ε) in DMF 397 nm (4·65).
$C_{26}H_{18}O_4$ requires: C, 79·2; H, 4·6%.
Found: C, 79·4; H, 4·3%.

The product showed a bluish green fluorescence in daylight.

3.2 3,3′-(1,4-phenylenedimethyl)bis[3-oxo-1*H*(3*H*)-isobenzofuran] (IVa)

A mixture of bisbenzylidenephthalide derivative (**IIIa**) (0·075 mol), potassium hydroxide (0·375 mol), and water (25 ml) was stirred under reflux and zinc dust (0·225 mol) was added slowly. The reaction mixture was refluxed for 6 h and then filtered. The filtrate was acidified with cold dilute hydrochloric acid, and the colourless product which separated was filtered, washed with water and dried. The product (19·0 g; 70%) was recrystallised from DMF as colourless leaflets, m.p. 232–234°; λ_{max} (log ε) in DMF 273 nm (3·83).

$C_{24}H_{18}O_4$ requires: C, 77·8; H, 4·8%.
Found: C, 77·5;H, 4·9%.

The above procedure was used to prepare 3,3′-(1,4-phenylene-2,5-dimethyl)dimethylbis[3-oxo-1*H*(3*H*)-isobenzofuran] (**IVb**) using the bisbenzylidenephthalide derivative (**IIIb**) (0·075 mol). The product (21·0 g; 70%) was recrystallised from DMF as colourless leaflets, m.p. 234–236°; λ_{max} (log ε) in DMF, 281 nm (3·54).

$C_{26}H_{22}O_4$ requires: C, 78·4; H, 5·5%.
Found: C, 78·1; H, 5·3%.

3.3 1,4-Bis(2-carboxystyryl)benzene (Va)

A mixture of potassium hydroxide (14·0 g, 0·25 mol) in ethylene glycol (30 ml) was heated to about 150°C and the solution of the bisbenzylphthalide derivative (**IVa**) (18·5 g, 0·05 mol) in warm ethylene glycol (15 ml) was added at such a rate that slow distillation of water occurred (half an hour). The temperature was then raised gradually to 200–210°C and maintained for 4 h. The reaction mixture was cooled, poured into ice water and acidified with cold dilute hydrochloric acid. The product which separated was filtered, washed free of acid and dried (13·0 g; 70%). Recrystallisation from DMF gave colourless leaflets, m.p. 285–286°C; λ_{max} (log ε) in DMF, 361 nm (4·00).

$C_{24}H_{18}O_4$ requires: C, 77·8; H, 4·9%.
Found: C, 77·9; H,4·9%.

This procedure was also used to prepare 1,4-bis(2-carboxystyryl)-2,5-dimethylbenzene (**Vb**) using the bisbenzylphthalide derivative **IVB** (0·05 mol). The product (13·0 g; 70%) was recrystallised from DMF as colourless leaflets, m.p. 255–257°C; λ_{max} (log ε) in DMF, 342 nm (4·54).

$C_{26}H_{22}O_4$ requires: C, 78·4; H, 5·5%.
Found: C, 78·5; H, 5·4%.

3.4 1,4-Bis(2-carboxamidostyryl)benzene (VIa)

A mixture of the dicarboxylic acid (**Va**) (14·8 g, 0·04 mol), thionyl chloride (0·24 mol) and benzene (120 ml) was refluxed for 6 h. Benzene was removed from the reaction mixture together with excess of thionyl chloride under reduced pressure. Further benzene (30 ml) was then added and then distilled off under reduced pressure. This was repeated three times until most of the thionyl chloride was removed. The reaction mixture was then added to cold ammonia solution (75 ml) with stirring, and the pale yellow product which separated was filtered, washed with 5% sodium bicarbonate solution and then with water and dried: yield, 10·0 g (70%). The product was recrystallised from DMF as pale yellow needles, m.p. 314–315°C. IR: 1650 cm^{-1} (amide C=O); 3200 cm^{-1} and 3400 cm^{-1} (NH of amide).

$C_{24}H_{20}N_2O_2$ requires: C, 78·2; H, 5·4%.
Found: C, 78·4; H, 5·5%.

The procedure was used also to prepare 1,4-bis(2-carboxamidostyryl)-2,5-dimethylbenzene (**VIb**) from the dicarboxylic acid (**Vb**). The product (11·0 g; 70%) was recrystallised from DMF as pale yellow crystals, m.p. 303–304°C. IR: 1650 cm^{-1} (amide C=O); 3200 cm^{-1} and 3400 cm^{-1} (amide NH).

$C_{26}H_{24}N_2O_2$ requires: C, 78·8; H, 6·1; N, 7·1%.
Found: C, 78·7; H, 6·1; N, 7·0%.

3.5 1,4-Bis(2-cyanostyryl)benzene (VIIa)

A mixture of the bisamide (**VIa**) (9·2 g, 0·025 mol), dimethylformamide (20 ml) and phosphorus oxychloride was heated gradually to 90°C and maintained at this temperature for 2 h. The reaction mixture was cooled, poured into ice-cold water and the pale yellow product was filtered, washed free of acid and dried. The product (5·6 g; 68%) was recrystallised from DMF as pale yellow crystals, m.p. 230–232°C (mixed m.p. with authentic sample 231–232°C); λ_{max} ($\log \varepsilon$) in DMF, 360 nm (4·82). The product showed a strong violet fluorescence in daylight; its IR spectrum showed a peak at 2220 cm^{-1} corresponding to the cyano group, its PMR spectrum a multiplet between 7·3 and 7·8 and its mass spectrum the molecular ion peak at *m/e* 332.

The above procedure was used to prepare 1,4-bis(2-cyanostyryl)-2,5-dimethylbenzene (**VIIb**) from the bisamide **VIa** (0·025 mol). The product (6·0 g; 68%) was recrystallised from DMF as pale yellow crystals, m.p. 234–235°C.

$C_{26}H_{20}N_2$ requires: C, 86·7; H, 5·5; N, 7·8%.
Found: C, 86·6; H, 5·4; N, 7·9%.

The IR spectrum of the product showed a peak at 2220 cm^{-1} corresponding to the cyano group.

The PMR spectrum in trifluoroacetic acid showed:

(i) a singlet at 2·5 corresponding to six methyl protons; and
(ii) a multiplet between 7·3 and 7·8 corresponding to the 14 protons assignable to the ten aromatic and four olefinic protons.

The mass spectrum showed the molecular ion peak M^+ at *m/e* 360. The product showed a strong violet fluorescence in daylight, and had λ_{max} ($\log \varepsilon$) in DMF at 352 nm (4·58).

ACKNOWLEDGEMENTS

The authors thank Mr J. R. Patil and Mr A. A. Inamdar of Hico Products Ltd, Bombay for the mass spectra, Mr S. V. Chiplunkar and his associates of the Microanalytical section, UDCT, for microanalysis and Professor T. S. Varadarajan for the infrared spectra. We are also indebted to Colour Chem Ltd for financial support.

REFERENCES

1. BASF, FRG Patent 1108219 (1961).
2. S. Gabriel, *Ber.*, **18**, 3470 (1885).
3. Exxon Research and Engineering Co., US Patent 3917665 (1975).
4. K. Sakamoto and M. Oki, *Bull. Chem. Soc. Jpn*, **46**, 270 (1973).
5. J. H. Wood, C. C. Tung, M. A. Perry and R. E. Gibson, *J. Amer. Chem. Soc.*, **72**, 2992 (1950).
6. R. B. Akin and M. T. Bogert, *J. Amer. Chem. Soc.*, **59**, 1564 (1937).