ELSEVIER

Dyes and Pigments 45 (2000) 185–188

DYES and PIGMENTS

Synthesis of 1-amino-2-(4′-methoxycarbonyl ethyl-2′-methyl)-phenoxy-4-hydroxy anthraquinone

H.B. Li [a], Y.Y. Hu [a], L. Sun [b], Y.J. Shen [b,*]

[a] *School of Environmental and Architectural Engineering, Shanghai University, Shanghai 200072, PR China*
[b] *Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China*

Received 16 September 1999; received in revised form 3 November 1999; accepted 8 February 2000

Abstract

4-(β-Cyanoethyl)-2-methylphenol was synthesized via the Friedel–Crafts reaction between *o*-cresol and acrylonitrile and was then condensed with 1-amino-2-bromo-4-hydroxy anthraquinone. The resulting product was hydrolyzed in alkaline medium and esterified with methanol to afford the title compound. Mass spectra, ^{1}H NMR and visible spectra of the title compound and the intermediates were measured.

Keywords: 1-Amino-2-(4′-methoxylcarbonyl ethyl-2′-methyl)phenoxy-4-hydroxy anthraquinone; 4-(β-Cyanoethyl)-2-methylphenol; Friedel–Crafts reaction; Hydrolysis of nitrile

1. Introduction

While 9,10-anthraquinone is pale yellow in colour, its tri-substituted, 1-, 2- and 4-derivatives are bright red in colour when each of the substituents is a powerful electron-donor group such as amino, hydroxyl or alkoxyl groups. Thus, such compounds are used as dyes, as exemplified by C.I. Disperse Red 60. This dye displays good build-up and level dyeing performance on polyester fibres but does not exhibit high fastness to heat or light on the substrate. Approaches to overcoming this problem have included novel methods of modification the phenoxy substitution in the 2-position of anthraquinone [1].

One example of such a class of compound is 1-amino-2-(4′-methoxycarbonyl ethyl-2′-methyl)-phenoxy-4-hydroxy anthraquinone. As a disperse dye, it is bluish red in colour, displays high chemical and heat stability and good level dyeing behaviour; the dye can also be used as a solvent dye.

Literature on the synthesis of 1-amino-2-(4′-methoxycarbonyl ethyl-2′-methyl)-phenoxy-4-hydroxy anthraquinone is rare. A known procedure [2] is shown in Scheme 1 in which compound **1**, which is available commercially, and compound **2**, which is not commercially available, are both used as starting materials. However, the synthesis of compound **2** has not been reported thus far.

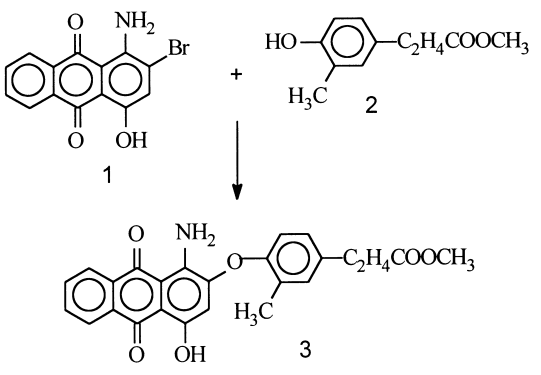
In this study, compound **3** was prepared according to the procedure shown in Scheme 2.

2. Experimetal

Melting points (mp) were measured using an X4 microscope melting point apparatus (Beijing Analytic Instrument Factory) and were uncorrected.

* Corresponding author.

0143-7208/00/$ - see front matter
PII: S0143-7208(00)00020-6



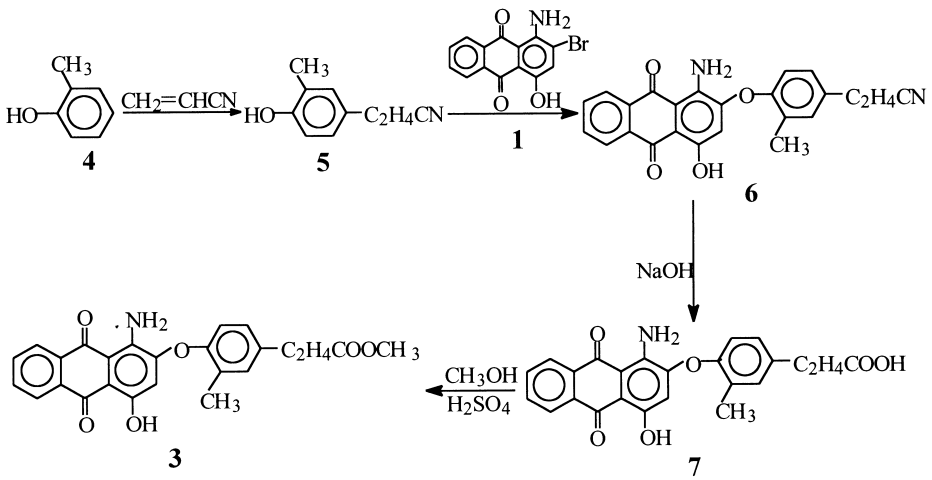
Scheme 1.

^{1}H NMR spectra were recorded at 500 MHz using a Brucker Avance-500 spectrometer. Mass spectra were obtained using a Hitachi M-80 and visible spectra were recorded on a 756MC UV–VIS spectro-photometer (Shanghai No.1 Analytic Instrument Factory).

Thin layer chromatograms were developed on GF_{254} silica (QinDao Ocean Chemical Engineering Group Company). Compound **1** (purity 95.32% tested by HPLC, mp 190°C) was provided by JiangSu YaBang Company (China). All other chemicals were obtained from Shanghai Chemical Reagents Company and were used without further purification.

2.1. 4-(β-Cyanoethyl)-2-methyl phenol **5**

Modifications to the synthetic procedure previously reported [3] were made. A 250 cm^3 four-necked flask was charged with *o*-cresol (43 g, 0.40 mol) and acrylonitrile (30.8 g, 0.57 mol). The stirred mixture was cooled below 10°C while anhydrous (26.68 g, 0.20 mol) aluminum chloride was added slowly. Dry hydrogen chloride was bubbled into the stirred mixture for 0.5 h before the aluminum chloride dissolved in the reaction mixture completely. The reaction mixture was heated to 80°C for 1.5 h. A reaction temperature of 105°C was maintained for another 2 h until the spot of *o*-cresol disappeared on TLC. The reaction product was then poured into water and stirred until all the catalyst was decomposed. The organic layer was dissolved in chloroform and washed with saturated sodium chloride solution. The chloroform layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was then fractionated in vacuo to give compound **5** as a colourless solid (160–180°C/3 mm Hg, 38.6 g, yield 60.0%), mp 52–54°C.



Scheme 2.

^{1}H NMR ($CDCl_3$) ppm: 2.2 (3H, s), 2.57 (2H, t), 2.85 (2H, t), 5.18 (1H, s), 6.7–6.9 (3H, m). MS *m/e* (%): 161 (M^+, 95.2), 135 (161-CN, 3.2), 121 (135-CH_2, 17.5), 107 (135-C_2H_4, 9.0), 92 (107-CH_3, 100), 54 (161-OH-Ph-CH_3, 6.6).

2.2. 1-Amino-2-(4′-(β-cyanoethyl)-2′-methyl) phenoxy-4-hydroxy anthraquinone **6**

A mixture of compound **1** (15.9 g, 0.05 mol), compound **5** (19.4 g, 0.12 mol) and potassium hydroxide (11.2 g, 0.2 mol) was stirred in chlorobenzene (60 cm^3) and heated under reflux for 7 h until the spot of compound **1** disappeared on TLC. The reaction mixture was cooled to room temperature and precipitated with methanol. The solid was collected by filtration and washed with methanol until free of chlorobenzene and then was subsequently washed with water and dried at 70°C; 18.2 g of a bluish red solid was obtained (91.5% yield). The solid (500 mg) was then fractionated on silica gel. Evaporation of appropriate fractions, which were eluted with cyclohexane:acetone (4:1 v/v), gave 459 mg compound **6** as a bluish red solid, mp 230–231°C.

^{1}H NMR ($CDCl_3$) ppm: 2.18 (3H, s), 2.67 (2H, t), 2.95 (2H, t), 6.21–8.39 (8H, m). MS *m/e* (%): 398 (M^+, 29.2), 358 (M^+-CH_2 CN, 25.9), 344 (358-CH_2, 2.5), 254 (344-CH_3-C_6H_3, 2.3), 238 (254-O, 2.3).

2.3. 1-Amino-2-(4′-carboxyl ethyl-2′-methyl) phenoxy-4-hydroxy anthraquinone **7**

A mixture of compound **6** (30 g, 76 mmol) and aqueous sodium hydroxide solution (10%, 100 cm^3) was stirred in a 250 cm^3 three-necked round bottom flask and heated under reflux for 5 h until the spot of compound **6** disappeared on TLC. The reaction mixture was cooled to room temperature and, after acidication, the red solid was filtered off and washed with methanol and cold water, before drying at 70°C; 30.7 g of a bluish red solid was obtained (96.9% yield). The material (500 mg) was then purified by column chromatography on silica gel, evaporation of appropriate fractions, eluted with cyclohexane:acetone (4:1 v/v) gave 456 mg compound **7** as a bluish red solid, mp 198–200°C.

^{1}H NMR ($CDCl_3$) ppm: 2.2 (3H, s), 2.6 (2H, t), 2.9 (2H, t), 6.2–8.4 (8H, m). MS *m/e* (%): 417 (M^+, 30.5), 358 (M^+-CH_2 COOH, 21.4), 254 (358-CH_2-CH_3-C_6H_3, 3.6), 238 (254-O, 5.5).

2.4. 1-Amino-2-(4′-methoxycarbonyl ethyl-2′-methyl)-phenoxy-4-hydroxy anthraquinone **3**

A mixture of compound **7** (30.5 g, 73 mmol) was stirred in anhydrous methanol (100 cm^3) in a 250 cm^3 three-necked round bottom flask while concentrated sulfuric acid (2 cm^3) was added dropwise. The mixture was heated under reflux for 3 h until the spot of compound **7** disappeared on TLC. The reaction mixture was cooled to room temperature and precipitated with cold water. The red solid was filtered off and washed with cold water and dried at 70°C; 20.7 g of a bluish red solid was obtained (65.7% yield). The solid (500 mg) was then purified by column chromatography on silica gel. Evaporation of the appropriate fractions, which were eluted with cyclohexane:acetone (4:1 v/v), gave 425 mg of compound **3** as a bluish red solid, mp 150–151°C.

^{1}H NMR ($CDCl_3$) ppm: 2.18 (3H, s), 2.6 (2H, t), 2.85 (2H, t), 3.7 (3H, s), 6.25–8.45 (8H, m), 14.1 (1H, s). MS *m/e* (%): 431 (M^+, 100), 401 (M^+-$2CH_3$, 5.6), 372 (M^+-$COOCH_3$, 2.5), 358 (372-CH_2, 2.2), 357 (372-CH_3, 4.5), 344 (358-CH_2, 3.5), 343 (357-CH_2, 4.9), 342 (358-NH_2, 4.4), 340 (357-OH, 4.3), 238 (254-O, 3.1). λ_{max} (Methanol) 516.5 nm, lg $\varepsilon_{max} = 4.14$.

3. Results and discussion

3.1. The synthetic routes of 1-amino-2-(4′-methoxycarbonyl ethyl-2′-methyl) phenoxy-4-hydroxy anthraquinone **3**

According to Scheme 1, compound **2** is a key intermediate. For the synthesis of compound **2**, we first reacted methyl acrylate with *o*-cresol, but the yield was too low (< 10%). Consequently, we chose 4-(β-cyanoethyl)-2-methyl phenol **5** for the preparation of compound **2**, because the cyano group could be transformed into the corresponding ester by an alcoholysis reaction; however, the

result was dissapointing. As it was too difficult to obtain compound **3** in reasonable yield, according to Scheme 1, the target compound was synthesized using Scheme 2.

3.2. The Friedel–Crafts reaction

The preparation of compound **5** from compound **4** involves a variation of the Friedel–Crafts reaction. Due to the existence of hydroxyl on the benzene ring that can easily form a complex with the aluminum chloride catalyst, the electron density of the benzene ring is reduced and it is therefore not prone to alkylation. The stronger the electrophile is, the more easily it can react with phenol. This is the reason why acrylonitrile can react with *o*-cresol much more readily than methyl acrylate.

As a Friedel–Crafts catalyst, anhydrous aluminum chloride is insoluble in hydrocarbon solvent and, therefore, is not active towards C–C bond formation with the alkylene, unless a small amount of water or hydrogen chloride is present. Hydrogen chloride and aluminum chloride can form an electrophilic particle (alkyl cation) [3]. In addition, phenol can easily react with aluminum chloride to give $C_6H_5OAlCl_2$, which is insoluble in the reaction mixture and therefore leads to increased viscosity of the system. All of these factors are obviously not favorable for the reaction. The presence of hydrogen chloride considerably reduces the viscosity, presumably by minimizing the formation of the insoluble salt, $C_6H_5OAlCl_2$ [4].

Sun et al. [5,6] used a large amount of hydrogen chloride in their experiments and finally achieved 52% yield. A modification of this approach was made in the present study in that the volume of dry hydrogen chloride was reduced to one third as a result of which, a yield of 60% was achieved. It can be proposed that the addition of hydrogen chloride lowers the pH which makes nitrile liable to react with phenol to form β-phenoxy nitrile [7]. Moreover, due to the existence of the Friedel–Crafts catalyst, the cyano group is protonated and possesses a positive charge, which facilitates C–C bond formation between the cyano group and the benzene ring. Hence, control of the quantity of hydrogen chloride used is necessary.

References

[1] Zhou QK. Shanghai Ranliao 1993;105(3):5(Ch).
[2] Mitsubishi Chemical Industries Co. Ltd. JP 69 15316.
[3] Zhang ZY, Qi GZ, Zhuang P. Jingxi Youji Hecheng Danyuan Fanying, Shanghai, Press of the East China University of Science and Technology, 1995. p. 270 (Ch).
[4] Johnson HW, Gross FJ. J Org Chem 1975;22:1264.
[5] Sun SD, Chen ZJ, Li CJ, Li AF. Youji Huaxue 1992;12(1):96(Ch).
[6] Richter RH, Tucker BW, Ulrich H. US 4051166 (1977).
[7] Lai DY. Gongye Hecheng Ranliao Huaxue, Taiwan, Fuhan Press, 1981. p. 82 (Ch).