

D. W. Rangnekar\*, V. R. Kanetkar, G. S. Shankarling and J. V. Malanker

Dyes Research Laboratory, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India.

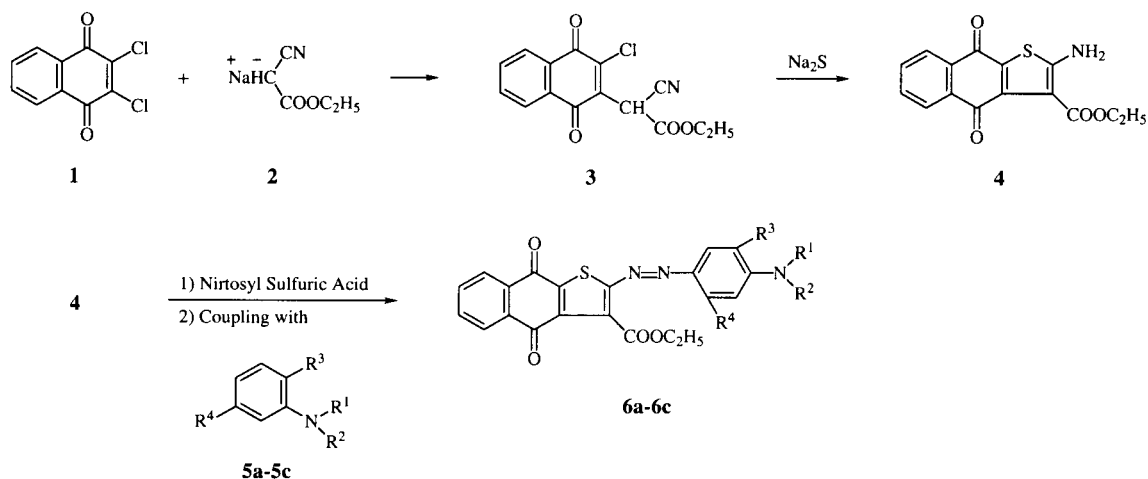
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Synthesis of ethyl 2-arylazo-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate was achieved by diazotization of ethyl 2-amino-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate and coupling with selected *N,N*-dialkylanilines. The key intermediate ethyl 2-amino-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate was synthesized by the condensation of sodium salt of ethyl cyanoacetate with 2,3-dichloro-1,4-naphthoquinone. Ethyl 2-arylazo-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate were applied on polyester fibers as disperse dyes and their dyeing properties were studied.

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Many novel deep coloured monoazo dyes derived from monoazo thiophenes have been reported in the recent past [1-3]. The dyes obtained from 2-amino-5-aryl(or aroyl)-3-nitrothiophene are greenish blue, while those from 2-amino-5-acetylthiophene are violet. Introduction of highly polar substituents bring about bathochromic shift to a greater extent than that caused by moderately polar substituents. Some disperse dye structures dyed on polyester-cellulose blend respond to the treatment with hot alkali by superficial removal of disperse dyes on the surface of polyester and also disperse dye cross stained on cellulose [4]. Thus disperse dye structures having carboxylic acid ester groups as well as those possessing 2-arylazothiophenes/thiazoles respond to such treatment. This phenomenon is termed as dischargeability and is commercially important.

In this communication, we wish to report the synthesis of a few unknown ethyl 2-arylazo-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylates **6a-6c** and a study of their use as disperse dyes on polyester fibers. To achieve the object of the present study, it was planned to use 2,3-dichloro-1,4-naphthoquinone **1** as starting material. This starting material was condensed with sodium salt of ethyl cyanoacetate **2** to yield 2-chloro-3-( $\alpha$ -cyano- $\alpha$ -carboxymethyl)-1,4-naphthoquinone **3**. Compound **3** was cyclized by using sodium sulfide to yield ethyl 2-amino-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate **4**. Aminothiophene **4** thus prepared was diazotized with nitrosyl sulfuric acid and coupled with a variety of substituted *N,N*-dialkylanilines **5a-5c** to yield the title novel azo dyes **6a-6c**.



DYE	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<b>6a</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	H
<b>6b</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	NHCOCH <sub>3</sub>
<b>6c</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	NHCOCH <sub>3</sub>

## EXPERIMENTAL

All melting points are uncorrected and are in °C. The ir spectra were recorded in potassium bromide pellets on a Perkin-Elmer model 397 spectrophotometer. The <sup>1</sup>H nmr spectra were recorded on 60 MHz instrument Hitachi R-1200 RS-NMR and the chemical shifts are given in δ (ppm) scale. The absorption spectra in methanol solution were recorded on a Beckman Model 25 spectrophotometer.

Ethyl 2-Amino-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate (**4**).

A mixture of 1.35 g (0.01 mole) of the sodium salt of ethyl cyanoacetate and 2.55 g (0.01 mole) of 2,3-dichloro-1,4-naphthoquinone **1** in ethanol (50 ml) were refluxed for two hours. The reaction mixture was then cooled to room temperature, when the product separated. It was collected on a Buchner Funnel and dried to yield 2-chloro-3-(α-cyano-α-carbomethoxy)methyl-1,4-naphthoquinone **3**.

A previously cooled solution of 2.58 g (0.01 mole) of sodium sulfide in water (200 ml) was mixed with a solution of (0.01 mole) of 2-chloro-3-(α-cyano-α-carbomethoxy)methyl-1,4-naphthoquinone **3** in acetone (15 ml). The temperature of the mixture should not rise above 20-25° during the addition. The precipitate thus formed was then filtered, washed with water and recrystallized from aqueous *N,N*-dimethylformamide to yield 2.27 g (75%) of **4**, mp 179-182°; ir (potassium bromide): 3300, 3466 and 1691 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulfoxide): δ 1.5 (t, 3H, CH<sub>3</sub>), 3.5 (q, 2H, CH<sub>2</sub>), 7.6-7.9 (m, 4H, aromatic), 8.1-8.3 (m, 2H, NH<sub>2</sub>).

*Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>NO<sub>4</sub>S: C, 59.80; H, 3.65; N, 4.65; S, 10.63. Found: C, 59.72; H, 3.57; N, 4.72; S, 11.12.

Ethyl 2-(4-*N,N*-Diethylaminophenyl)azo-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate (**6a**).

To a solution of 3.66 g (0.01 mole) of ethyl 2-amino-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate **4** in acetic acid (20 ml) at 10°, nitrosyl sulfuric acid (4.6 ml) equivalent to sodium nitrite (0.01 mole) was slowly added at 5° with constant stirring for one hour. The excess nitrous acid was destroyed using urea.

The solution of 1.22 g (0.01 mole) of *N,N*-diethylaniline in acetic acid (10 ml) was cooled to 10° with crushed ice (10 g). The clear diazo solution was slowly run into the above solution at 10-15° with vigorous stirring over a period of half an hour. The pH of the reaction was maintained at 4.5 to 5.5 by the addition of solid sodium acetate in portions, throughout the coupling period. The reaction mixture was poured into ice water (200 g)

followed by the addition of sodium carbonate solution until neutral. The dye which separated was filtered, washed with water and dried to yield 2.62 g (60%) of **6a**, mp 210°; ir (potassium bromide): 1610 and 1721 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulfoxide): δ 1.3-1.8 (m, 9H, 3CH<sub>3</sub>), 3.5 (q, 4H, 2CH<sub>2</sub>), 4.4 (q, 2H, CH<sub>2</sub>), 6.6-6.9 (m, 2H, aromatic), 7.7-7.9 (m, 4H, aromatic), 8.2 (m, 2H, aromatic); λ<sub>max</sub> absorption 530 nm, log ε, 4.26; dyeing on polyester [5]: colour gray, pick-up 3, light fastness 3, sublimation fastness 4-5.

*Anal.* Calcd. C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>S: C, 65.07; H, 4.98; N, 9.11; S, 6.94. Found: C, 64.81; H, 4.58; N, 9.32; S, 7.30.

Ethyl 2-(2-Acetamido-4-*N,N*-diethylaminophenylazo)-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate (**6b**).

The same procedure as described for **6a** was applied except 3-acetamido-*N,N*-diethylaniline was used in place of *N,N*-diethylaniline yielding **6b**, recrystallized from *N,N*-dimethylformamide to yield 3.26 g (63%) of **6b**, mp 190°; ir (potassium bromide): 1610, 1720 and 3380 cm<sup>-1</sup>; λ<sub>max</sub> absorption 576 nm, log ε 4.46; dyeing on polyester: colour gray, pick-up 4, light fastness 4, sublimation fastness 4-5.

*Anal.* Calcd. for C<sub>27</sub>H<sub>26</sub>N<sub>4</sub>O<sub>5</sub>S: C, 62.54; H, 5.02; N, 10.81; S, 6.18. Found: C, 62.67; H, 4.94; N, 10.73; S, 6.72.

Ethyl 2-(2-Acetamido-5-methoxy-4-*N,N*-diethylaminophenylazo)-4,9-dioxonaphtho[2,3-*b*]thiophene-3-carboxylate (**6c**).

The same procedure as described for **6a** was applied except 2-methoxy-5-acetamido-*N,N*-diethylaniline was used in place of *N,N*-diethylaniline yielding **6c**, recrystallized from *N,N*-dimethylformamide to yield 2.96 g (54%) of **6c**, mp 174°; ir (potassium bromide): 1624, 1705 and 3372 cm<sup>-1</sup>; λ<sub>max</sub> absorption 573 nm, log ε 4.20; dyeing on polyester: colour greenish blue, pick-up 4, light fastness 3, sublimation fastness 4.

*Anal.* Calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>S: C, 61.31; H, 5.11; N, 10.22; S, 5.84. Found: C, 61.22; H, 5.24; N, 10.13; S, 5.74.

## REFERENCES AND NOTES

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