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Received April 15, 1998

A novel efficient synthesis of 2-arylazo-5-[styryl-4-(β-cyano/carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazoles was achieved by the condensation of 2-arylazo-5-methyl-1,3,4-thiadiazoles with 4-(β-cyano-β-carb-ethoxyethenyl)benzaldehyde or 4-(β,β-biscyanoethenyl)benzaldehyde in the presence of acetic anhydride.

*J. Heterocyclic Chem.*, **36**, 95 (1999).

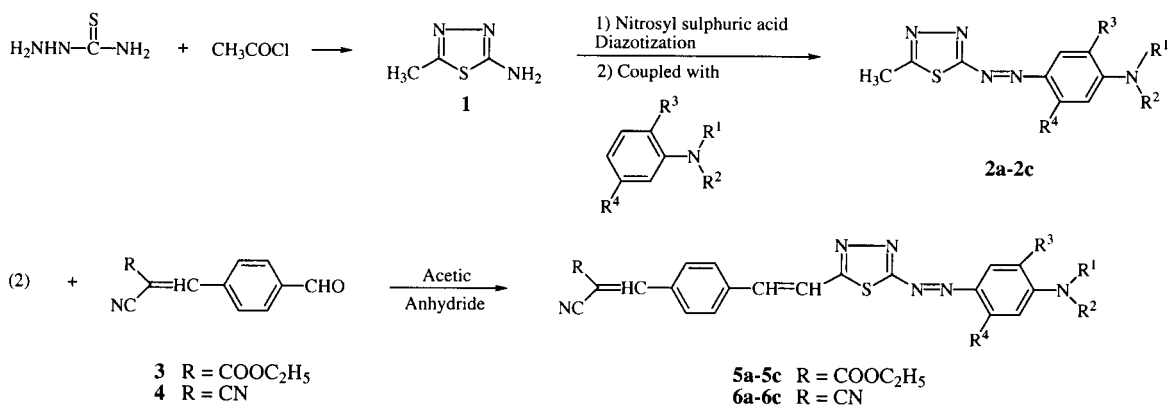
Thiadiazole classes of diazo components were extensively studied over the past thirty-five years, because of their brightness and good light fastness on polyester and polyamide fibers [1]. In 1963, azo dyes derived from 2-amino-5-alkyl(aryl)-1,3,4-thiadiazoles were shown to produce very bright red shades on polyester fibers. Azo disperse dyes from 2-amino-5-alkoxy-1,3,4-thiadiazoles were also bright and showed good light fastness. Earlier patented literature [2-5] proved the versatility of azo dyes derived from 2,5-disubstituted-1,3,4-thiadiazoles. However this heterocycle has not been fully exploited.

In this communication, we wish to report the synthesis of 2-arylazo-5-[styryl-4-(β-cyano/carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazole derivatives **5** and **6**. To achieve the synthesis of the above compound, thiosemicarbazide was acetylated with acetyl chloride and cyclized to get 2-amino-5-methyl-1,3,4-thiadiazole **1** [6]. 2-Amino-5-methyl-1,3,4-thiadiazole **1** was diazotized with nitrosyl sulfuric acid and coupled with various *N,N*-dialkylanilines

at pH 4.5 to 5.5 to give azo dyes **2a-2c**. These azo dyes **2a-2c** were later condensed with 4-(β-cyano-β-carb-ethoxyethenyl)benzaldehyde **3** and 4-(β,β-biscyanoethenyl)benzaldehyde **4** in acetic anhydride at reflux to give 2-(4-aryl)azo-5-[styryl-4-(β-carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazole **5** and 2-(4-aryl)azo-5-[styryl-4-(β,β-biscyanoethenyl)]-1,3,4-thiadiazole **6**, respectively in good yield.

Earlier we had studied the 2-arylazo-5-phenyl substituted-1,3,4-thiadiazole disperse dyes [7]. The encouraging results prompted us to extend our study on 1,3,4-thiadiazole moiety. Thus, dyestuff structures were designed by incorporating styryl groups in 5-position of 2-arylazo-1,3,4-thiadiazole. This change in conjugation pattern by replacing phenyl group by the styryl group was expected to bring about enhancement of bathochromic effect and improvement in fastness properties, of the newly designed dyes on polyester fibers.

The fastness properties of these dyes were studied after applying them to polyester fibers and also the absorption



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

maxima and the values of logarithms of the extinction coefficient of dyes in *N,N*-dimethylformamide solutions were recorded. The application on polyester fibers resulted in bright orange to blue shades.

## EXPERIMENTAL

All the melting points are uncorrected and are in °C. The infrared spectra were recorded on Perkin-Elmer model 397 spectrophotometer in potassium bromide pellet. The <sup>1</sup>H nmr spectra were recorded on Varian 60 MHz instrument EM-360-L and the chemical shifts are given in δ (ppm) scale. Absorption spectra in *N,N*-dimethylformamide solution were recorded on Beckman Model-25 spectrophotometer.

2-(4-*N,N*-Diethylaminophenyl)azo-5-[styryl-4-(β-carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazole (**5a**).

A mixture of 2.97 g (0.01 mole) of 2-(4-*N,N*-diethylaminophenyl)azo-5-methyl-1,3,4-thiadiazole **2a** and 2.17 g (0.01 mole) of 4-(β-cyano-β-carbethoxyethenyl)benzaldehyde **3** in acetic anhydride was stirred and heated to reflux for four hours. The reaction mixture was cooled and neutralized by dilute sodium carbonate solution when the product precipitated. The product was filtered, washed with water, dried and recrystallized from benzene to yield 2.92 g (60%) of **5a**, mp 167°; ir (potassium bromide): 1610 and 1720 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.3-1.5 (m, 9H, 3CH<sub>3</sub>), 3.5-3.6 (m, 2H, OCH<sub>2</sub>), 4.1 (q, 4H, 2CH<sub>2</sub>), 7.8-8.0 (m, 9H, aromatic and CH), 8.3 (s, 2H, 2CH); λ max. absorption 530 nm, log ε 4.13; dyeing on polyester [8]: color reddish orange, pick-up 3, light fastness 3, sublimation fastness 4.

*Anal.* Calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>6</sub>SO<sub>2</sub>: C, 64.19; H, 5.35; N, 17.28; S, 6.58. Found: C, 64.02; H, 5.29; N, 17.34; S, 6.44.

2-(2-Acetamido-4-*N,N*-diethylaminophenyl)azo-5-[styryl-4-(β-carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazole (**5b**).

The same procedure as described for **5a** was applied except 2-(3-acetamido-*N,N*-diethylaminophenyl)azo-5-methyl-1,3,4-thiadiazole **2b** was used in place of **2a** yielding **5b**, recrystallized from benzene to yield 3.40 g (61%) of **5b**, mp 172° to 174°; ir (potassium bromide): 1610, 1720 and 3380 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.3-1.5 (m, 9H, 3CH<sub>3</sub>), 2.2 (s, 3H, CH<sub>3</sub>), 3.4-3.5 (m, 2H, CH<sub>2</sub>), 4.1 (q, 4H, 2CH<sub>2</sub>), 7.1 (s, 1H, NH), 7.7-7.9 (m, 9H, aromatic and CH), 8.5 (s, 2H, 2CH); λ max. absorption 548 nm, log ε 4.06; dyeing on polyester: color reddish violet, pick-up 4, light fastness 4, sublimation fastness 4-5.

*Anal.* Calcd. for C<sub>29</sub>H<sub>31</sub>N<sub>7</sub>SO<sub>3</sub>: C, 62.48; H, 5.56; N, 17.59; S, 5.74. Found: C, 62.52; H, 5.51; N, 17.42; S, 5.81.

2-(2-Acetamido-5-methoxy-4-*N,N*-diethylaminophenyl)azo-5-[styryl-4-(β-carbethoxy-β-cyanoethenyl)]-1,3,4-thiadiazole (**5c**).

The same procedure as described for **5a** was applied except 2-(2-acetamido-5-methoxy-4-*N,N*-diethylaminophenyl)azo-5-methyl-1,3,4-thiadiazole **2c** was used in place of **2a** yielding **5c**, recrystallized from benzene to yield 3.32 g (57%) of **5c**, mp 201°; ir (potassium bromide): 1615, 1718 and 3375 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.2-1.5 (m, 9H, 3CH<sub>3</sub>), 2.4 (s, 3H, CH<sub>3</sub>), 3.7-3.8 (m, 5H, CH<sub>2</sub> & OCH<sub>3</sub>), 4.2 (q, 4H, 2CH<sub>2</sub>), 7.6-7.8 (m, 9H, aromatic and CH), 8.4 (s, 2H, 2CH); λ max. absorption spectra 571 nm, log ε 4.12; dyeing on polyester: color blue, pick-up 3, light fastness 3, sublimation fastness 4-5.

*Anal.* Calcd. C<sub>29</sub>H<sub>28</sub>N<sub>8</sub>SO<sub>4</sub>: C, 59.59; H, 4.79; N, 19.18; S, 5.48. Found: C, 59.70; H, 4.69; N, 19.09; S, 5.55.

2-(4-*N,N*-Diethylaminophenyl)azo-5-[styryl-4-(β,β-biscyanoethenyl)]-1,3,4-thiadiazole (**6a**).

The same procedure as described for **5a** was applied except 4-(β,β-biscyanoethenyl)benzaldehyde **4** was used in place of **3** yielding **6a**, recrystallized from benzene to yield 2.68 g (61%) of **6a**, mp 212°; ir (potassium bromide): 1610 and 2220 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.3-1.5 (m, 6H, 2CH<sub>3</sub>), 4.1 (q, 4H, 2 CH<sub>2</sub>), 7.7-7.9 (m, 9H, aromatic and CH), 8.3 (s, 2H, 2CH); λ max. absorption 513 nm, log ε 4.10; dyeing on polyester: color orange, pick-up 3, light fastness 3-4, sublimation fastness 4.

*Anal.* Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>7</sub>S: C, 65.60; H, 4.78; N, 22.3; S, 7.29. Found: C, 65.56; H, 4.82; N, 22.12; S, 7.13.

2-(2-Acetamido-4-*N,N*-diethylaminophenyl)azo-5-[styryl-4-(β,β-biscyanoethenyl)]-1,3,4-thiadiazole (**6b**).

The same procedure as described for **6a** was applied except 2-(2-acetamido-4-*N,N*-diethylaminophenyl)azo-5-methyl-1,3,4-thiadiazole **2b** was used in place of **2a** yielding **6b**, recrystallized from benzene to yield 2.83 g (57%) of **6b**, mp 210°; ir (potassium bromide): 1610, 2220 and 3385 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.2-1.6 (m, 6H, 2CH<sub>3</sub>), 2.3 (s, 3H, CH<sub>3</sub>), 3.8 (q, 4H, 2CH<sub>2</sub>), 6.9 (s, 1H, NH); 7.8-8.1 (m, 9H, aromatic and CH), 8.4 (s, 2H, 2CH); λ max. absorption 542 nm, log ε 4.13; dyeing on polyester: color red, pick-up 4, light fastness 3, sublimation fastness 4-5.

*Anal.* Calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>8</sub>SO: C, 62.90; H, 4.83; N, 21.58; S, 6.45. Found: C, 63.02; H, 4.87; N, 22.32; S, 6.17.

2-(2-Acetamido-5-methoxy-4-*N,N*-diethylaminophenyl)azo-5-[styryl-4-(β,β-biscyanoethenyl)]-1,3,4-thiadiazole (**6c**).

The same procedure as described for **6a** was applied except 2-(5-methoxy-2-acetamido-4-*N,N*-diethylaminophenyl)azo-5-methyl-1,3,4-thiadiazole **2c** was used in place of **2a** yielding **6c**, recrystallized from benzene to yield 2.96 g (58%) of **6c**, mp 215°; ir (potassium bromide): 1615, 2200 and 3375 cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl-d<sub>6</sub> sulphoxide): δ 1.3-1.6 (m, 6H, 2CH<sub>3</sub>), 2.3 (s, 3H, CH<sub>3</sub>), 3.8 (s, 3H, OCH<sub>3</sub>), 4.1 (q, 4H, 2CH<sub>2</sub>), 7.6-7.9 (m, 9H, aromatic and CH), 8.3 (s, 2H, 2CH); λ max. absorption spectra 556 nm, log ε 4.08; dyeing on polyester: color violet, pick-up 3, light fastness 4, sublimation fastness 5.

*Anal.* Calcd. for C<sub>27</sub>H<sub>26</sub>N<sub>8</sub>SO: C, 63.53; H, 5.10; N, 21.96; S, 6.27. Found: C, 63.58; H, 5.08; N, 21.72; S, 6.13.

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