Synthesis and Application of Ethyl 3-(4-Dialkylaminophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoates and Related Products

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Ethyl quinoxalin-3(4*H*)-on-2-ylacetate was prepared by the condensation of 1,2-diaminobenzene and diethyl oxalacetate (sodium salt). The key quinoxaline intermediate was condensed with a variety of 4-dialkylaminobenzaldehydes/substituted benzaldehydes to yield novel brilliant quinoxalin-2-yl styryl dyes which were applied on polyester fibers as disperse dyes and their dyeing properties were studied.

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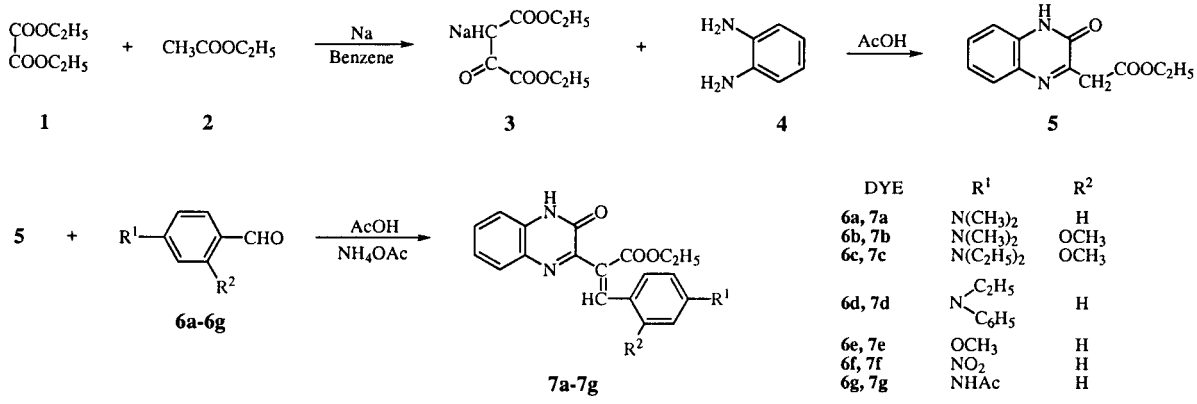
In designing the structures of organic colorants a large number of heterocyclic systems have been incorporated in the recent years, since they offer several advantages over their carbocyclic counterparts. Dye molecules containing a styryl chromophoric unit in conjugation with a heterocyclic ring impart deep colors. This has evoked interest to design dyestuff molecules involving newer structures which provide a variety of shades of disperse dyes applicable to polyester. A variety of novel heterocyclic styryl disperse dyes have been prepared and their usefulness in application to polyester has been studied in our laboratory [1-7].

In this communication, we wish to report the synthesis of ethyl 3-(4-dialkylaminophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoates and their substituted derivatives **7a-7g**. To achieve the synthesis of the above compounds, diethyl oxalate **1** was condensed with ethyl acetate **2** in benzene in the presence of sodium to form the sodium salt of diethyl oxalacetate **3** [8], which was further condensed with 1,2-diaminobenzene **4** in acetic acid [9] to obtain ethyl quinoxalin-3(4*H*)-on-2-ylacetate **5**.

A variety of 4-dialkylaminobenzaldehydes [10-11] **6a-6g** were condensed with the key intermediate **5** to yield styryl disperse dyes **7a-7g**, in good yield.

The fastness properties of these dyes were studied after applying to polyester fibers. Furthermore the absorption maxima and the values of the logarithms of the extinction coefficients of dyes in dimethylformamide solutions were recorded. The application on polyester fibers resulted in bright yellow to pink shades.



DYE	R^1	R^2
6a, 7a	$N(CH_3)_2$	H
6b, 7b	$N(CH_3)_2$	OCH_3
6c, 7c	$N(C_2H_5)_2$	OCH_3
6d, 7d	$N(C_2H_5)(C_6H_5)$	H
6e, 7e	OCH_3	H
6f, 7f	NO_2	H
6g, 7g	NHAc	H

EXPERIMENTAL

All the melting points are uncorrected and are in °C. The infrared spectra were recorded on a Perkin-Elmer model 397 spectrophotometer in potassium bromide pellets. The ^1H nmr spectra were recorded on a Varian 60 MHz instrument EM-360-L and the chemical shifts are given in δ (ppm) scale. Absorption spectra in dimethylformamide solutions were recorded on a Beckman Model-25 spectrophotometer.

Ethyl Quinoxalin-3(4*H*)-on-2-ylacetate (**5**).

A mixture of 10.8 g (0.1 mole) of 1,2-diaminobenzene **4** and 21.0 g (0.1 mole) of the sodium salt of diethyl oxalacetate **3** in 50 ml of acetic acid was stirred and heated to reflux for two hours.

The reaction mixture was cooled, poured into ice water and neutralized with dilute sodium carbonate solution when the product precipitated. The product was filtered, washed with ice water, dried and recrystallized from ethanol to yield 18.5 g (80%) of **5**, mp 205°; ir (potassium bromide): 1670, 1720 and 3259 cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.1-1.3 (t, 3H, CH_3); 1.7 (s, 2H, CH_2), 4.1 (q, 2H, CH_2), 7.1-7.3 (m, 2H, aromatic), 7.5 (t, 1H, aromatic), 7.7 (d, 1H, aromatic); 11.1 (s, 1H, NH, deuterium oxide exchangeable).

Anal. Calcd. for $C_{12}H_{12}N_2O_3$: C, 62.07; H, 5.17; N, 12.07. Found: C, 61.86; H, 5.61; N, 11.91.

Ethyl 3-(4-Dimethylaminophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoate (**7a**).

A mixture of 2.32 g (0.01 mole) of ethyl quinoxalin-3(4*H*)-on-2-ylacetate **5**, 1.49 g (0.01 mole) of 4-dimethylaminobenzaldehyde **6a** and 0.92 g (0.012 mole) of anhydrous ammonium acetate in 20 ml of glacial acetic acid was stirred and heated to reflux for 2 hours. The reaction mixture was cooled, poured into ice water when the styryl dye precipitated. The product was filtered, washed with water, dried and recrystallized from ethanol to yield 2.7 g (75%) of **7a**, mp 105°; ir (potassium bromide): 1686 and 3429 cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.1-1.3 (t, 9H, CH_3 and $N(CH_3)_2$), 4.0-4.2 (q, 2H, CH_2), 7.2-7.8 (m, 9H, aromatic and CH), 11.0 (s, 1H, NH, deuterium oxide exchangeable); uv: λmax absorption 468 nm, log ε 4.17; dyeing on polyester [12]: color orange, pick up 4, light fastness 3-4, sublimation fastness 4-5.

Anal. Calcd. for $C_{21}H_{21}N_3O_3$: C, 69.42; H, 5.78; N, 11.57. Found: C, 69.24; H, 5.63; N, 11.71.

Ethyl 3-(4-Dimethylamino-2-methoxyphenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoate (**7b**).

The same procedure as described for **7a** was applied except 4-dimethylamino-2-methoxybenzaldehyde **6b** was used in place of 4-dimethylaminobenzaldehyde yielding **7b**. The product was recrystallized from ethanol to yield 2.8 g (70%) of **7b**, mp 132°; uv: λmax absorption 531 nm, log ε 4.38; dyeing on polyester: color pink, pick up 3-4, light fastness 3-4, sublimation fastness 5.

Anal. Calcd. for $C_{22}H_{23}N_3O_4$: C, 67.17; H, 5.85; N, 10.68. Found: C, 67.01; H, 5.91; N, 10.65.

Ethyl 3-(4-Diethylamino-2-methoxyphenyl)-2-quinoxalin-3(4*H*)-on-2-yl)propenoate (**7c**).

The same procedure as described for **7a** was applied except 4-diethylamino-2-methoxybenzaldehyde **6c** was used in place of 4-dimethylaminobenzaldehyde yielding **7c,** which was recrystallized from ethanol to yield 2.9 g (72%) of **7c**, mp 126°; uv: λmax absorption 529 nm, log ε 4.48; dyeing on polyester: color pink, pick up 3-4, light fastness 3-4, sublimation fastness 4-5.

Anal. Calcd. for $C_{24}H_{27}N_3O_4$: C, 68.40; H, 6.41; N, 9.97. Found: C, 68.27; H, 6.65; N, 10.05.

Ethyl 3-(4-*N*-Benzylamino-*N*-ethylaminophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoate (**7d**).

The same procedure as described for **7a** was applied except 4-*N*-benzylamino-*N*-ethylaminobenzaldehyde **6d** was used in place of 4-dimethylaminobenzaldehyde yielding **7d,** recrystallized from ethanol to yield 3.6 g (80%) of **7d**, mp 165°; λmax absorption 475 nm, log ε4.56; dyeing on polyester: color orange, pick up 4, light fastness 2-3, sublimation fastness 4.

Anal. Calcd. for $C_{27}H_{25}N_3O_3$: C, 73.80; H, 5.69; N, 9.56. Found: C, 73.56; H, 5.80; N, 9.29.

Ethyl 3-(4-Methoxyphenyl)-2-(quinoxalin-3(4*H*)-on-yl)-propenoate (**7e**).

The same procedure as described for **7a** was applied except 4-methoxybenzaldehyde **6e** was used in place of 4-dimethylaminobenzaldehyde yielding **7e**, which was recrystallized from ethanol to yield 2.8 g (80%) of **7e**, mp 200°; uv: λmax absorption 445 nm, log ε 4.3; dyeing on polyester: color greenish yellow, pick up 3-4, light fastness 2-3, sublimation fastness 4.

Anal. Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.57; H, 5.14; N, 8.00. Found: C. 68.65; H, 5.30; N, 7.90.

Ethyl 3-(4-Nitrophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)-propenoate (**7f**).

The same procedure as described for **7a** was applied except 4-nitrobenzaldehyde **6f** was used in place of 4-dimethylaminobenzaldehyde yielding **7f**, which was recrystallized from ethanol to yield 2.7 g (75%) of **7f**, mp 153°; uv: λmax absorption 448 nm, log ε 4.51; dyeing on polyester: color yellow, pick up 3-4, light fastness 2-3, sublimation fastness 5.

Anal. Calcd. for $C_{19}H_{15}N_3O_5$: C, 62.46; H, 4.10; N, 11.50. Found: C, 62.61; H, 3.93; N, 11.73.

Ethyl 3-(4-Acetamidophenyl)-2-(quinoxalin-3(4*H*)-on-2-yl)propenoate (**7g**).

The same procedure as described for **7a** was applied except 4-acetamidobenzaldehyde **6g** which was used in place of 4-dimethylaminobenzaldehyde yielding **7g**. This compound was recrystallized from ethanol to yield 2.8 g (73%) of **7g**, mp 160°; λmax absorption 461 nm, log ε 4.26; dyeing on polyester: color yellow, pick up 3, light fastness 3, sublimation fastness 5.

Anal. Calcd. for$C_{21}H_{19}N_3O_4$: C, 66.84; H, 5.03; N, 11.14. Found: C, 66.73; H, 5.10; N, 11.11.

REFERENCES AND NOTES

[1] D. W. Rangnekar and S. B. Lokhande, *Indian J. Chem.*, **25B**, 485 (1986).

[2] D. W. Rangnekar and D. D. Rajadyaksha, *Indian J. Technol.*, **28**, 75 (1990).

[3] D. W. Rangnekar and R. W. Sabnish, *J. Chem. Tech. Biotech.*, **56**, 401 (1993).

[4] D. W. Rangnekar and S. V. Mavlankar, *Dyes Pigm.*, **19**, 259 (1992).

[5] D. W. Rangnekar, N. D. Sonawane and R. W. Sabnis, *J. Heterocyclic Chem.*, **35**, 1353 (1998).

[6] S. S. Puro, Heterocyclic Studies, Ph.D. Thesis, University of Bombay (1993).

[7] P. D. Desai, Heterocyclic Studies, Ph.D. Thesis, University of Bombay (1994).

[8] G. Lumm (BASF A.-G.), German Offen., 2,025,427; *Chem. Abstr.*, **76**, 72519 (1972).

[9] P. B. Russell, R. Purmann, W. Schmidt and G. H. Hitchings, *J. Am. Chem. Soc.*, **71**, 3412 (1949).

[10] E. Campigne and W. L. Archer, *Org. Synth.*, Coll. Vol. **IV**, John Wiley and Sons, NY, 1963, p 331.

[11] J. Ernst, (CIBA Ltd) German Offen 1,060,375 (1959); *Chem. Abstr.*, **55**, 13459 (1961).

[12] R. W. Sabnis and D. W. Rangnekar, *Sulfur Letters*, **15**, 263 (1993).