Dyes and Pigments **14** (1990) 1–7

Heterocyclic Monoazo Dyes Derived from 4-Oxoquinazoline

D. N. Naik & K. R. Desai

Department of Chemistry, South Gujarat University,
Surat-395 007, India

(Received 17 July 1989; accepted 11 September 1989)

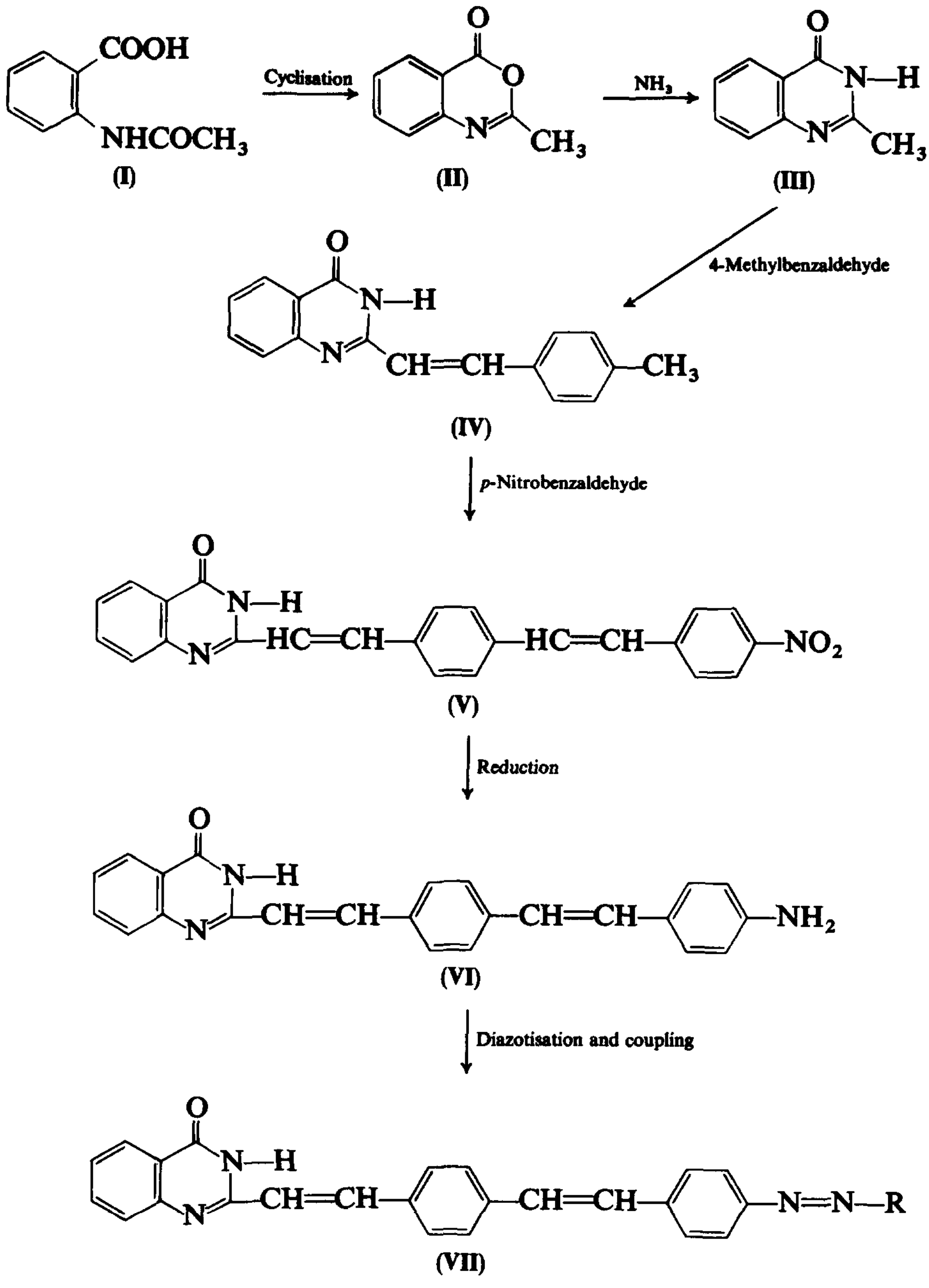
ABSTRACT

From a sequence of reactions starting from N*-acetylanthranilic acid, 2-(1′,4′-bis-styryl-4″-nitro)-4-oxoquinazoline was obtained. This gave on reduction 2-(1′,4′-bis-styryl-4″-amino)-4-oxoquinazoline. Diazotisation and coupling with various coupling components gave a series of monoazo dyes. The dyes were suitable, depending on the coupling component used, for application to viscose, silk and polyester. Dyeing and fastness properties of the dyes were evaluated.*

1 INTRODUCTION

Many dyes based on heterocyclic ring systems are known to possess high tintorial power and excellent fastness properties. A number of azo dyes have been prepared from amino heterocycles[1,2] and azo dyes prepared by using selected quinoline and quinazoline derivatives as coupling components have been described.[3] Dyes based on the quinazoline ring system have also been reported as being useful on natural and synthetic fibres[4] and 4-oxoquinazolines have been used in the synthesis of azo dyes and reactive dyes.[5,6]

We report here the synthesis of some azo dyes based on 4-oxoquinazoline and having the general formula **VII** (Scheme 1).


COOH
NHCOCH3
(I)
Cyclisation
O
O
N
CH3
(II)
NH3
O
N—H
N
CH3
(III)
4-Methylbenzaldehyde
O
N—H
N
CH—CH
CH3
(IV)
p-Nitrobenzaldehyde
O
N—H
N
HC═CH
HC═CH
NO2
(V)
Reduction
O
N—H
N
CH═CH
CH═CH
NH2
(VI)
Diazotisation and coupling
O
N—H
N
CH═CH
CH═CH
N═N—R
(VII)

Scheme 1

2 EXPERIMENTAL

2.1 2-Methyl-4-oxo-3,1-benzoxazine (II)

A mixture of *N*-acetyl-anthranilic acid (17·9 g, 0·1 mol) and acetic anhydride (36 ml) was refluxed for 40 min and the solid which separated on cooling was filtered and washed thoroughly with dry petroleum ether. Yield 85%, m.p. 78–80°C.

$C_9H_7O_2N$ requires:	C, 67·1; H, 4·35; N, 8·1.
Found:	C, 67·1; H, 4·4; N, 8·1%.

2.2 3*H*-2-Methyl-4-oxoquinazoline (III)[7,8]

2-Methyl-4-oxo-3,1-benzoxazine (16·1 g, 0·1 mol) was suspended in ammonia (10·0 ml) and the mixture heated to 100°C, when a clear solution resulted. The reaction was maintained at 100°C for 2 h. The white needles which separated were filtered, dried and recrystallised from ethanol. Yield 90%, m.p. 235–236°C.

$C_9H_8ON_2$ requires:	C, 67·5; H, 5·0; N, 17·5.
Found:	C, 67·4; H, 4·95; N, 17·4%.

2.3 3*H*-2-(4′-Methylstyryl)-4-oxoquinazoline (IV)

3*H*-2-Methyl-4-oxoquinazoline (6·24 g, 0·039 mol) was suspended in acetic anhydride (80 ml) and the mixture gradually heated to 130°C, affording a clear solution. 4-Methylbenzaldehyde (4·68 g, 0·039 mol) was added and the mixture was refluxed for 2 h. The liquor was cooled, filtered, and the residue washed with acetic acid, then with hot water and recrystallised from glacial acetic acid. Yield 81%, m.p. 205°C.

$C_{17}H_{14}ON_2$ requires:	C, 77·9; H, 5·3; N, 10·7.
Found:	C, 77·8; H, 5·3; N, 10·6%.

2.4 3*H*-2-(1′,4′-Bis-styryl-4″-nitro)-4-oxoquinazoline (V)

3*H*-2-(4′-Methylstyryl)-4-oxoquinazoline (10·34 g, 0·39 mol) was suspended in acetic anhydride (80 ml) and the mixture heated to 130°C, affording a clear solution. 4-Nitrobenzaldehyde (5·93 g, 0·039 mol) was added and the mixture refluxed for 2 h. The liquor was cooled, filtered, and the residue washed with acetic acid and then with hot water and recrystallised from glacial acetic acid. Yield 82%, m.p. 260°C.

$C_{24}H_{17}O_3N_3$ requires: C, 72·9; H, 4·3; N, 10·6.
Found: C, 72·9; H, 4·25; N, 10·6%.

2.5 3*H*-2-(1′,4′-Bis-styryl-4″-amino)-4-oxoquinazoline (VI)

3*H*-2-(1′,4′-Bis-styryl-4″-nitro)-4-oxoquinazoline (7·98 g, 0·02 mol) was suspended in a solution of sodium sulphide (14·4 g, 0·06 mol) in water (75 ml) and the mixture refluxed for 2 h, yielding a deep reddish-brown solution. After cooling, diluting with water (75 ml) and acidifying with hydrochloric acid, the solution was boiled for 20 min and filtered. Addition of sodium carbonate precipitated the free amine as a pale yellow compound, which was recrystallised from ethanol. Yield 88%, m.p. 281°C.

$C_{24}H_{19}ON_3$ requires: C, 78·9; H, 5·2; N, 11·5.
Found: C, 78·8; H, 5·15; N, 11·45%.

2.6 Preparation of Azodyes (VII)

3*H*-2-(1′,4′-Bis-styryl-4″-amino)-4-oxoquinazoline (3·19 g, 0·008 mol) was diazotised by standard procedures and the resulting diazo liquor reacted with various coupling components. The following general procedure is typical.

H-Acid (2·67 g, 0·008 mol) was suspended in water (20 ml) and the liquor adjusted to neutral with sodium carbonate solution (10%, w/v) to obtain a clear solution. The solution was cooled to below 5°C and to this solution, the diazo liquor was added dropwise with stirring, maintaining pH 8 by simultaneous addition of sodium carbonate solution (10%, w/v). Stirring was continued for 3 h at 0–5°C. The reaction mixture was then heated to 60°C and sodium chloride added to precipitate the product. After stirring for 1 h, the liquor was filtered and the product washed with a small amount of sodium chloride solution (5%, w/v). The solid was dried and extracted with DMF. The dye was precipitated by diluting the DMF extract with excess chloroform; filtering and washing with chloroform. Yield 83%. In a similar manner were prepared dyes **D1–D23** shown in Table 1.

3 RESULTS

The general route for the synthesis of the dyes **VII** is outlined in Scheme 1. Ring closure of *N*-acetylanthranilic acid afforded 2-methyl-4-oxo-3,1-benzoxazine (**II**), which was converted to 3*H*-2-methyl-4-oxoquinazoline (**III**) by reaction with ammonia, using previously reported procedures.[7,8]

TABLE 1
Characterisation Data for Dyes **VIII**

Dye	*Coupling component* (*R*)	*Colour*	*Yield* (%)	*Nitrogen* (%)		
				Found	*Required*	λ_{max}[a]
D-1	H-acid	Violet	82	9·4	9·5	535
D-2	J-acid	Red	83	10·9	11·0	485
D-3	Gamma-acid	Violet–red	83	10·9	11·0	520
D-4	G-acid	Orange	80	7·7	7·7	515
D-5	R-salt	Pink	82	7·7	7·7	510
D-6	*N*-Methyl-J-acid	Red	80	10·7	10·75	485
D-7	*N*-Phenyl-J-acid	Red–pink	85	9·8	9·8	495
D-8	Schaffer's acid	Maroon	87	8·95	9·0	530
D-9	Peri acid	Maroon	80	11·3	11·3	540
D-10	2-Naphthylamine-3,6,8-trisulphonic acid	Red	79	8·4	8·5	495
D-11	1-4′-Sulphophenyl-5-pyrazolone	Yellow	84	13·2	13·2	400
D-12	1-Phenyl-3-methyl-5-pyrazolone	Yellow	79	15·2	15·3	390
D-13	1-(4′-Sulphophenyl)-3-methyl-5-pyrazolone	Yellow–orange	75	12·8	12·9	420
D-14	1-(4′-Sulphophenyl)-3-carboxy-5-pyrazolone	Yellow–orange	80	12·25	12·3	440
D-15	1-(2′,5′-Dichloro-4′-sulphophenyl)-3-methyl-5-pyrazolone	Orange	82	11·7	11·65	435
D-16	Naphthol AS	Brown–red	79	11·9	11·95	490
D-17	Naphthol AS-D	Red	80	10·7	10·7	485
D-18	Naphthol AS-E	Yellow	79	10·3	10·4	450
D-19	Naphthol AS-G	Brown	76	11·15	11·1	440
D-20	Naphthol AS-BO	Yellow	78	10·1	10·2	500
D-21	Naphthol AS-SW	Red	76	10·2	10·2	495
D-22	Naphthol AS-SD	Yellow	76	12·2	12·3	450
D-23	Naphthol AS-OL	Brown–yellow	80	10·4	10·5	460

[a] λ_{max} of **D1–D15** in water; **D16–D23** in DMF.

The methyl group in **III** behaves as a reactive methylene group and condensation with 4-methylbenzaldehyde gave the styryl derivative **IV**, and thence, by further condensation with 4-nitrobenzaldehyde, the bis-styryl compound **V**. Reduction of **V** with sodium sulphide gave the amino derivative **VI** and this was used as the diazo component in the synthesis of the dyes **VII**.

The dyes varied in hue from yellow to violet depending on the nature of the coupling component used, and their absorption maxima are shown in

TABLE 2
Fastness Properties of Dyes **VII**

Dye	*Viscose*		*Silk*		*Polyester*	
	Washing at 95°C	*Light*	*Washing at 95°C*	*Light*	*Washing at 95°C*	*Light*
D-1	2	3	4	5	—	—
D-2	2	4	3	4	—	—
D-3	3	2–3	5	4	—	—
D-4	3	3	4	5	—	—
D-5	4	4	3	3–4	—	—
D-6	3	3	4	4–5	—	—
D-7	3	3	3	4–5	—	—
D-8	2	3	4	5	—	—
D-9	2–3	4	3	4–5	—	—
D-10	2	5	6	4	—	—
D-11	2	3	2	4	—	—
D-12	3	3	5	5	—	—
D-13	4	4	4	5	—	—
D-14	3	3	4	4	—	—
D-15	2	2	4	4	—	—
D-16	—	—	—	—	3	4–5
D-17	—	—	—	—	4	5
D-18	—	—	—	—	2	4–5
D-19	—	—	—	—	4	5
D-20	—	—	—	—	2	5
D-21	—	—	—	—	3	4
D-22	—	—	—	—	4	3
D-23	—	—	—	—	3	3

Table 1. The dyes were applied to silk, viscose or polyester as acid, direct or disperse dyes. General dyebath exhaustion was assessed by spectrophotometric evaluation of the exhaust liquors. The percentage exhaustion of 2% dyeings was in the region of 58–62% for viscose (dyes **D1**–**D15**), 65–76% for silk (dyes **D1**–**D15**) and 51–65% on polyester (dyes **D16**–**D23**). Relevant fastness data for the dyes are given in Table 2.

The dyes gave generally satisfactory dyeings on all fibres. Fastness to washing on viscose and silk varied from moderate to good and the lightfastness was generally better on the latter fibre, and also on polyester.

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