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Heterocyclic Monoazo Dyes Derived from 4-Oxoquinazoline: Part II

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ABSTRACT

Diazotised 2-(4′-chloro styryl)-6-amino-4-oxoquinazoline was coupled with various coupling components to give 4-oxo quinazoline based dyes. Dyes on diazotisation and treatment with sodium azide gave an azido dye, whilst on reaction with thionyl chloride and sodium azide gave a sulphonazido dye. 2-(4′-Chloro styryl)-6-amino-4-oxoquinazoline was prepared from a sequence of reactions starting from 3H-2-methyl-4-oxoquinazoline. The dyes were suitable, depending on the coupling component used, for application to silk, polyamide and polyester. Dyeing and fastness properties of the dyes were evaluated.

1 INTRODUCTION

The synthesis of 4-oxoquinazoline dyes has previously been described.[1] In continuation of that work, this paper reports on the synthesis of 4-oxoquinazoline dyes containing an azido or sulphonazido group having the general formula (VII) and (X), respectively (Scheme 1). Dyes containing an azido or sulphonazido groups, giving yellow, orange, red, violet and brown shades have been previously reported.[2–11] These dyes have generally good fastness properties. It is visualised that dyes having an azido and sulphonazido group, when applied to synthetic fibres under thermal conditions, generate a singlet nitrene-reactive intermediate, which inserts into the C—H bond of the fibre, thus forming a covalent link with the fibre.

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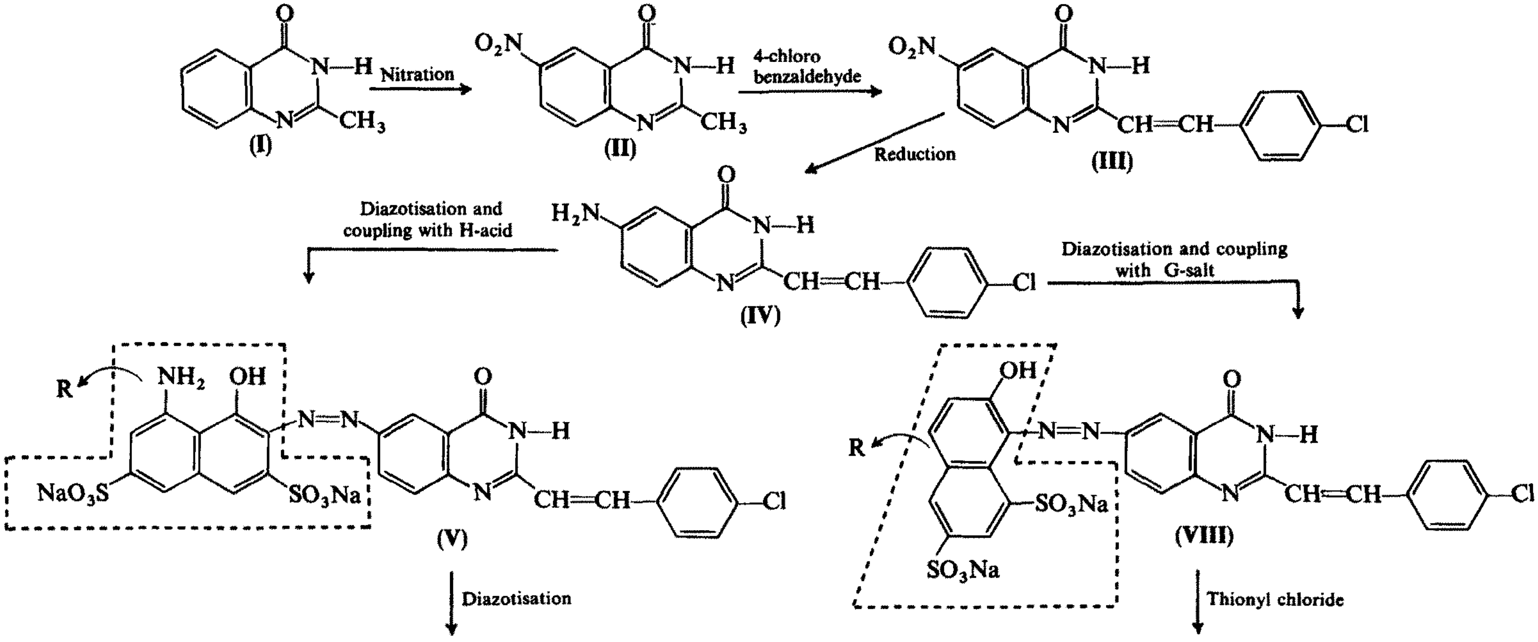
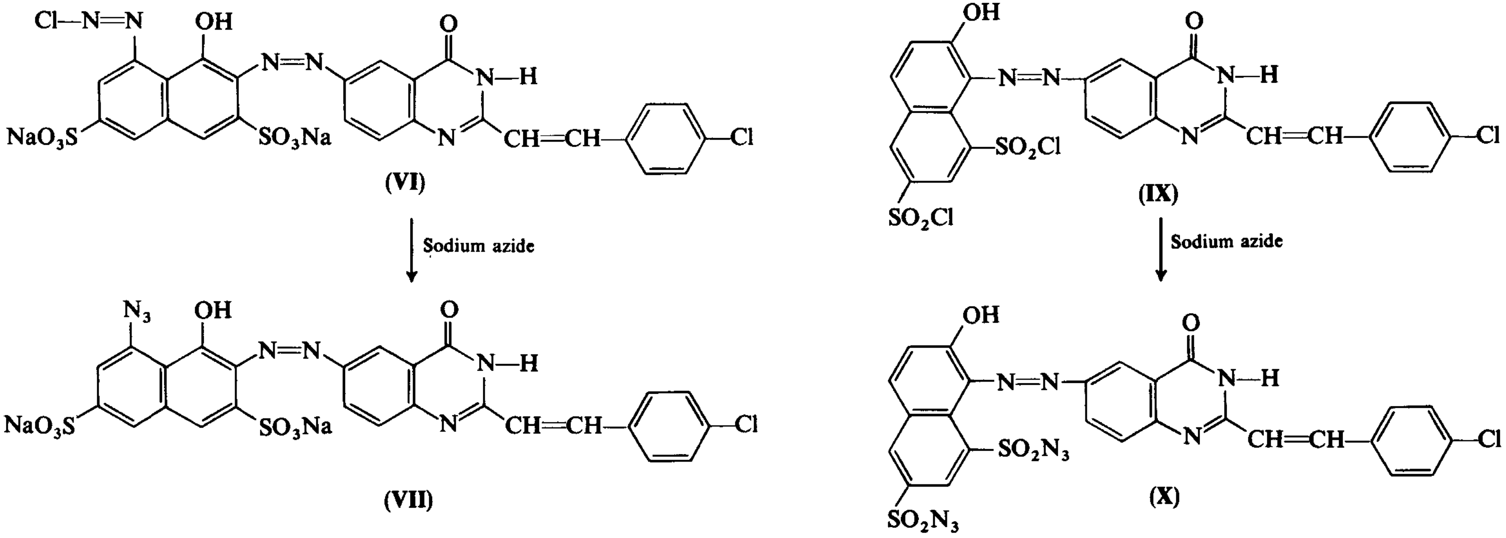

(I)
Nitration
(II)
4-chloro benzaldehyde
(III)
Reduction
(IV)
Diazotisation and coupling with H-acid
Diazotisation and coupling with G-salt
(V)
(VIII)
Diazotisation
Thionyl chloride
R
R



Scheme 1

2 EXPERIMENTAL

2.1 3*H*-2-Methyl-6-nitro-4-oxoquinazoline (II)[12]

3*H*-2-Methyl-4-oxoquinazoline (6·0 g, 0·0375 mol) was dissolved in sulphuric acid (98%, 20 ml). Fuming nitric acid (10 ml, specific gravity 1·5) was then added, keeping the temperature below 75°C. The reaction mixture was poured on to ice (200 g), filtered and the product washed with water, dried and recrystallised from glacial acetic acid. The yield was 95%; the m.p. 299–300°C.

$C_9H_7O_3N_3$ calculated: C, 52·68, H, 3·41, N, 20·48%
found: C, 52·64; H, 3·43; N, 20·50%

2.2 3*H*-2-(4′-Chlorostyryl)-6-nitro-4-oxoquinazoline (III)

3*H*-2-Methyl-6-nitro-4-oxoquinazoline (8·0 g, 0·0390 mol) was suspended in acetic anhydride (80 ml) and the mixture gradually heated to 130°C, affording a clear solution. 4-Chlorobenzaldehyde (5·47 g, 0·0390 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. The yield was 78%; the m.p. 310°C.

$C_{16}H_{10}O_3N_3Cl$ calculated: C, 58·62; H, 3·05; N, 12·82%
found: C, 58·6; H, 3·03; N, 12·84%

2.3 3*H*-2-(4′-Chlorostyryl)-6-amino-4-oxoquinazoline (IV)

3*H*-2-(4′-Chloro styryl)-6-nitro-4-oxoquinazoline (6·55 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 strongly acidifying with hydrochloric acid, the solution was boiled for 20 min and filtered. Addition of sodium carbonate precipitated the free amine as a violet compound, which was recrystallised from ethanol. The yield was 63%; the m.p. 253°C.

$C_{16}H_{12}ON_3Cl$ calculated: C, 64·53; H, 4·03; N, 14·12%
found: C, 64·55; H, 4·0; N, 14·10%

2.4 Preparation of azo dyes (V) and (VIII)

3*H*-2-(4′-Chlorostyryl)-6-amino-4-oxoquinazoline (2·38 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 the 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 dimethylformamide (DMF). The dye was precipitating by diluting the DMF extract with excess chloroform; filtering and washing with chloroform. It was used for subsequent reaction. The other dyes (V) and (VIII) were prepared in a similar manner.

2.5 Preparation of azo dyes having azido group (VII)

Dye (V) (5·37 g, 0·008 mol) was diazotised by standard procedures. The pH of the diazo liquor was increased from 2 to 6 by adding sodium carbonate solution (10%, w/v), and the mixture was stirred at 10–15°. To this, a freshly prepared solution of sodium azide (0·624 g, 0·0096 mol) in a minimum amount of water (3 ml) and acetone (5 ml) was added, maintaining a temperature of 10–15°C. The temperature was gradually raised to 30°C and the liquor stirred for 4 h. The reaction mixture was then heated to 50°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–chloroform. The yield was 81%. Dyes D_1–D_8 were prepared in a similar manner (Table 1).

2.6 Preparation of azo dyes having sulphonazido group (X)

Thionyl chloride (2·86 g, 0·024 mol) was added with stirring to a mixture of dye (VIII) (5·25 g, 0·008 mol) and chlorobenzene (20 ml) in 30 min keeping the temperature below 30°C. DMF (0·584 g, 0·056 mol) was then added dropwise to the well-stirred solution at 60°C in 2 h and finally the temperature was raised to 95°C and the mixture stirred for 2 h. The brownish-yellow sulphonyl chloride (IX) which separated on cooling, was dissolved in acetone (9 ml). To this, a solution of sodium azide (0·124 g, 0·001 92 mol in a minimum amount of water (3 ml) and acetone (5 ml) was added with stirring, maintaining the temperature at 10–15°C. The temperature was gradually raised to 50°C and stirred for 1 h. The reaction mixture was then diluted with

TABLE 1
Characterisation Data for Dyes VII and X

Dye	*Coupling component (R)*	*Colour*	*Yield (%)*	λ_{max}[a] *(nm)*	*Nitrogen (%)*	
					Found	*Required*
D_1	H-acid	Violet	81	495	14·00	14·05
D_2	J-acid	Red–brown	87	490	16·41	16·45
D_3	γ-acid	Brown	73	510	16·37	16·45
D_4	Chicago acid	Violet	71	552	13·97	14·05
D_5	*m*-Amino phenol	Brown	68	450	22·01	22·09
D_6	*o*-Amino phenol	Brown	64	442	22·03	22·09
D_7	1,2,4-acid	Brown–yellow	80	496	16·35	16·45
D_8	Peri acid	Brown	77	492	16·87	16·91
D_9	G-salt	Brown	72	496	21·09	21·13
D_{10}	R-salt	Red–brown	73	501	21·07	21·13
D_{11}	*N*-Methyl J-acid	Red–brown	71	512	19·02	19·09
D_{12}	*N*-Phenyl J-acid	Dark red	69	490	17·21	17·27
D_{13}	1-(4′-Sulphophenyl) -3-methyl-5-pyrazolone	Yellow	72	405	21·39	21·44
D_{14}	1-(4′-Sulphophenyl)-3-carboxy-5-pyrazolone	Orange	83	416	20·85	20·94
D_{15}	1-(4′-Sulphophenyl)-5-pyrazolone	Yellow	83	400	21·93	21·97
D_{16}	1-(2′,5′-dichloro-4′-Sulphophenyl)- 3-methyl-5-pyrazolone	Yellow	80	428	19·60	19·67

[a] λ_{max} of D_1–D_8 in water; D_9–D_{16} in DMF.

water. The solid was filtered, washed with water, dried and recrystallised from DMF. The yield was 72%. Dyes D_9–D_{16} (Table 1) were prepared in a similar manner.

3 RESULTS

The general route for the synthesis of the dyes (**VII**) and (**X**) is outlined in Scheme 1. 3*H*-2-Methyl-6-nitro-4-oxoquinazoline (**II**) was prepared by nitration of 3*H*-2-methyl-4-oxoquinazoline (**I**), using the reported procedure.[12] The methyl group in (**II**) behaves as a reactive methylene group and condensation with 4-chlorobenzaldehyde gave the styryl derivative (**III**). Reduction of (**III**) with sodium sulphide gave the amino compound (**IV**) and this was used as a diazo component in the synthesis of the dyes (**V**) and (**VIII**). The dyes (**V**) were further diazotised and treated with sodium azide to afford

TABLE 2
Fastness Properties of Dyes **VII** and **X**

Dye	*Silk*		*Polyamide*		*Polyester*	
	Washing at 95°C	*Light*	*Washing at 95°C*	*Light*	*Washing at 95°C*	*Light*
D_1	3	4	4–5	3	—	—
D_2	5	4	5	4	—	—
D_3	3	5	4	4	—	—
D_4	4	4–5	4	5	—	—
D_5	3–4	4	5	3–4	—	—
D_6	4	4	4	4–5	—	—
D_7	4	5	5	5	—	—
D_8	3–4	3	4	4	—	—
D_9	—	—	4	3–4	4	5
D_{10}	—	—	4–5	4	4	3–4
D_{11}	—	—	3–4	3	4–5	4
D_{12}	—	—	5	4	5	4
D_{13}	—	—	4	5	4	4–5
D_{14}	—	—	4	3–4	3–4	3
D_{15}	—	—	5	5	4	3–4
D_{16}	—	—	3–4	4–5	4	5

the azido dyes (**VII**). Dyes (**VIII**) on treatment with thionyl chloride and sodium azide afforded sulphonazido dyes (**X**).

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 1. The dyes were applied to silk, polyamide and polyester as reactive, reactive disperse and disperse dyes. General dye bath exhaustion was assessed by spectrophotometric evaluation of the exhaust liquors. The percentage exhaustion of 2% dyeings was in the regions of 66–69% for silk (dyes D_1–D_8), 58–65% for polyamide (dyes D_1–D_{16}) and 71–75% on polyester (D_9–D_{16}). Relevant fastness data for the dyes are given in Table 2.

The dyes generally gave satisfactory dyeings on all fibres. Fastness to washing varied from fair to good on silk and polyamide and good to excellent on polyester. The light fastness was generally moderate to good on all fibres.

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