

Heterocyclic Dye Synthesis : Synthesis and Dyeing Performance of 4-Oxoquinazoline Dyes. Part-I

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In the present study, we report the synthesis of heterocyclic dyes based on 4-oxoquinazoline nucleus and their dyeing performance on viscose and silk fabrics as direct and acid dyes respectively.

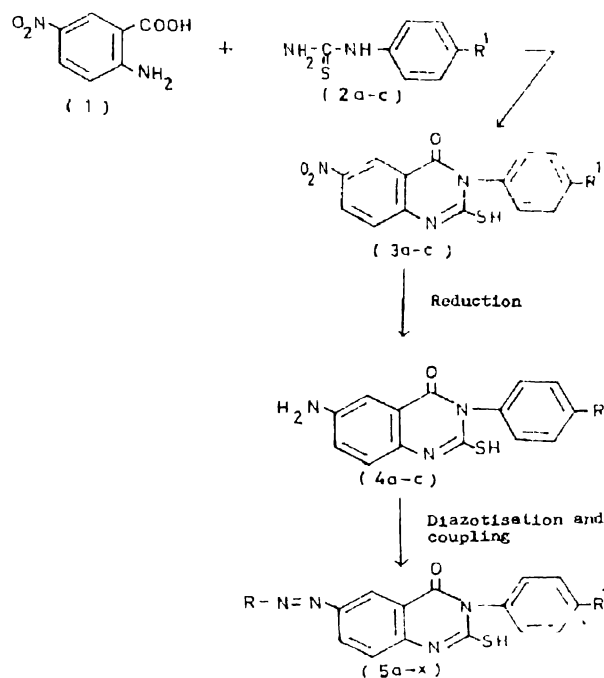
2-Mercapto-3-(4'-substituted-phenyl)-6-nitro-4-oxoquinazolines (**3a-c**) were synthesised by cyclisation of 5-nitroanthranilic acid (**1**) with 4-substituted-phenylthioureas (**2a-c**) which in turn were prepared by the reported procedures^{1,2}. Compounds **3a-c** were reduced by sodium sulphide to afford the 2-mercapto-3-(4'-substituted-phenyl)-6-amino-4-oxoquinazolines (**4a-c**) which were used as diazo components in the synthesis of the dyes (**5a-x**) (Scheme 1).

3H-2-Methyl-6-nitro-4-oxoquinazoline (**7**) was synthesised³ by nitration of 3H-2-methyl-4-oxoquinazoline (**6**). The methyl group in **7** behaves as a reactive methylene group due to its vicinity to both tertiary nitrogen atoms, and on condensation with 4-methyl-benzaldehyde gave the styryl derivatives (**8**) and on further condensation with 4-(un)substituted-benzaldehyde, yielded the bis-styryl compounds (**9a-c**). Reduction of **9a-c** with sodium sulphide gave the amino derivatives (**10a-c**) which were used as the diazo components in the synthesis of the dyes (**11a-x**) (Scheme 2) (Table 1).

These dyes were applied to viscose and silk fabrics in 2% shade as direct and acid dyes respectively, and gave pink to red-violet hue. The pick-up values of these dyes varied from 2 to 3 on viscose and 2 to 4 on silk and the light fastness varied from 2 to 5 on both the fabrics whereas the sublimation fastness was in the range of 1-4 on both fabrics.

Experimental

M.ps. were determined in open capillaries and are uncorrected. The ir spectra (KBr) were recorded on a JICS-9



2a, 3a, 4a, 5a-h: R' = Br
 2b, 3b, 4b, 5i-p: R' = Cl
 2c, 3c, 4c, 5q-x: R' = OCH₃

Scheme 1

Perkin-Elmer 377 spectrophotometer, nmr spectra (DMSO-d₆) on a EM 360 Varian L spectrometer (60 MHz) and electronic spectra on a Hitachi U-3200 spectrophotometer.

2-Mercapto-3-(4'-substituted-phenyl)-6-nitro-4-oxoquinazoline (**3a-c**) were prepared by known procedure¹.

3H-2-(4'-Methylstyryl)-6-nitro-4-oxoquinazoline (**8**) : Compound **7** (9.0 g, 0.039 mol) suspended in

TABLE I—CHARACTERISATION DATA OF DYES 5 AND 11*

| Compd. no. | Coupling component (R) | M.p. ^{**} °C |
|---------------|------------------------------|--------------------------|
| 5a (11a) | H-Acid | 338 (320) |
| 5b (11b) | J-Acid | 312 (283) |
| 5c (11c) | Gamma acid | 291 (270) |
| 5d (11d) | N-Methy-J-acid | 314 (318) |
| 5e (11e) | N-Phenyl-J-acid | 328 (323) |
| 5f (11f) | Chicago acid | 298 (298) |
| 5g (11g) | R-Salt | 296 (331) |
| 5h (11h) | G-Salt | 322 (329) |
| 5i (11i) | H-Acid | 319 (316) |
| 5j (11j) | J-Acid | 317 (287) |
| 5k (11k) | Gamma acid | 297 (297) |
| 5l (11l) | N-Methyl-J-acid | 318 (325) |
| 5m (11m) | N-Phenyl-J-acid | 314 (302) |
| 5n (11n) | Chicago acid | 296 (293) |
| 5o (11o) | R-Salt | 294 (267) |
| 5p (11p) | G-Salt | 316 (309) |
| 5q (11q) | H-Acid | 339 (332) |
| 5r (11r) | J-Acid | 312 (299) |
| 5s (11s) | Gamma acid | 291 (293) |
| 5t (11t) | N-Methyl-J-acid | 328 (329) |
| 5u (11u) | N-Phenyl-J-acid | 318 (310) |
| 5v (11v) | Chicago acid | 296 (293) |
| 5w (11w) | R-Salt | 312 (299) |
| 5x (11x) | G-Salt | 318 (328) |

All compounds gave satisfactory C, H and N analyses.

*M.p. of 11a-x in parenthesis.

acetic anhydride (80 ml) was gradually heated to 130° affording a clear solution. 4-Methylbenzaldehyde (4.68 g, 0.039 mol) was then added to it and the mixture was refluxed for 2 h. It was then cooled and the resulting solid was washed with acetic acid and hot water and crystallised from glacial acetic acid, (80%), m.p. 280° (Found : N, 15.20. Required : N, 15.20%).

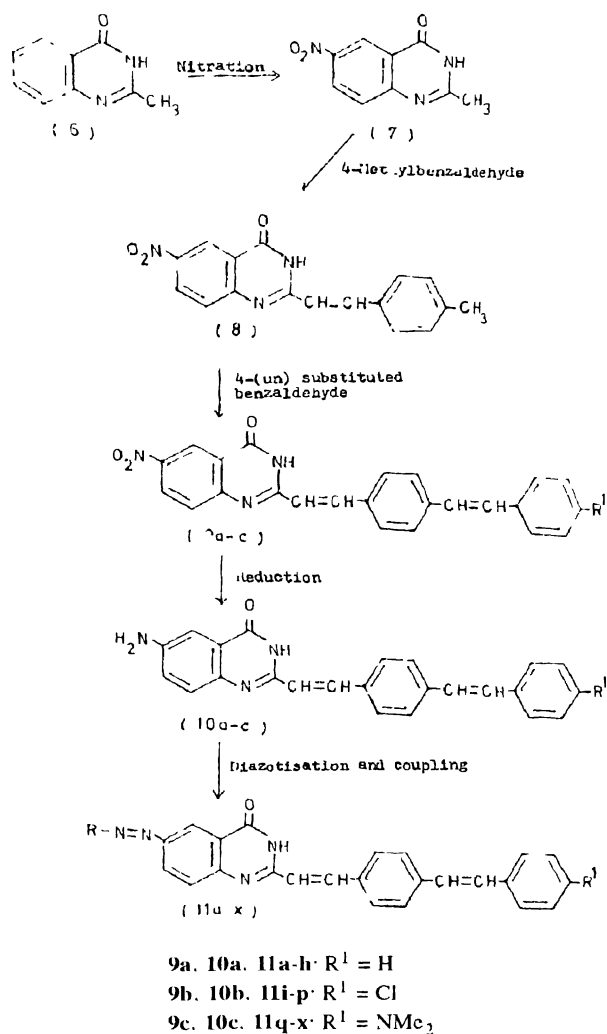
3H-2-(4''-(Un)substituted-1',4'-bis-styryl)-6-nitro-4-oxoquinazoline (9a-c) : Compound 8 (12.0 g, 0.039 mol) suspended in acetic anhydride (90 ml) was gradually heated to 130° affording a clear solution. 4-(Un)substituted-benzaldehyde (0.039 mol) was then added to it and the mixture was refluxed for 2 h. It was then cooled, and the resulting solid washed with

acetic acid and hot water and crystallised from glacial acetic acid : 9a (83%), m.p. 292°; b (78%), 297°; c (69%), 224°.

2-Mercapto-3-(4'-substituted-phenyl)-6-amino-4-oxoquinazoline (4a-c) and 3H-2-(4''-(un)substituted-1',4'-bis-styryl)-6-amino-4-oxoquinazoline (10a-c). General method : Compound 3 or 9 (0.02 mol) suspended in a solution of sodium sulphide (14.4 g, 0.06 mol) in water (75 ml), was refluxed for 2 h yielding a deep reddish brown solution. After cooling, diluting with water (75 ml) and strongly acidifying with HCl, the solution was boiled for 20 min and filtered. Addition of sodium carbonate precipitated free amine as pale yellow compound which was crystallised from ethanol to give 4 or 10 respectively : 4a (52%), m.p. 232°; b (69%), 255°; c (54%), 246°; 10a (87%), 278°; b (63%), 260°; c (89%), 291°.

2-Mercapto-3-(4'-substituted-phenyl)-6-arylazo-4-oxoquinazoline (5a-x) and 3H-2-(4''-(un)substituted-1',4'-bis-styryl)-6-arylazo-4-oxoquinazoline (11a-x). General method : Compound 4 or 10 (0.01 mol) was diazotised in the usual manner. The resulting diazo solution was used for the subsequent coupling reaction.

The coupling component (0.01 mol) was suspended in water (24 ml) and the solution adjusted neutral with sodium carbonate solution (10%, w/v) to obtain a clear solution. The solution was cooled to 0–5° and to it the diazo solution was added dropwise with stirring, maintaining pH 8 by simultaneous addition of sodium carbonate (10%, w/v). Stirring was continued for 3 h at 0–5°. The reaction mixture was then heated to 60° and NaCl added to precipitate the product. After stirring for 1 h, the solution was filtered and the product washed with a small amount of NaCl solution (5%, w/v). The resulting solid was dried and extracted with DMF. The dye was precipitated by diluting the DMF extracted with excess chloroform and then filtered and washed with chloroform to give 5 or 11 respectively : 5a-x, ν_{\max} (KBr) 610 (C–Br), 690–715 (C–Cl), 1190–1205 (S=O), 1580–1590 (N=N), 1600–1640 (cyclic CO), 2490–2510 cm^{-1} (S–H); δ (DMSO- d_6) 2.19 (3H, s, CH_3), 3.80 (2H, s, NH_2), 3.95 (3H, s, OCH_3), 5.95 (1H, bs, OH), 6.16 (1H, s, SH), 6.92–7.60 (m, ArH), 8.16–8.31 (3H, m, ArH of quinazoline); 11a-x, ν_{\max} (KBr) 690–695 (C–Cl), 1010–1015 (CH=CH).



Scheme 2

1 190–1 200 (S=O), 1 580–1 590 (N=H), 1 610–1 620 (cyclic CO), 3 390–3 450 cm^{-1} (NH and OH of free and bonded CO); δ (DMSO- d_6) 2.19–2.22 (3H, s, CH_3), 3.70 (2H, s, NH_2), 5.90 (1H, bs, OH), 6.73 (1H, bs, CH=), 7.17 (1H, s, =CH), 7.3 (1H, bs, NH, exchangeable), 6.60–7.40 (m, ArH), 8.19–8.82 (3H, m,

ArH of quinazoline).

Compounds 5 and 11 were separated on tlc using benzyl alcohol + DMF + water (3 : 2 : 2) solvent system using silica gel G as adsorbent.

Application : All the dyes were applied to viscose rayon and silk fabrics in 2% shade according to the usual procedure in the dye-bath containing the materials listed in Table 2.

TABLE 2—DYE BATH

| Material/condition | For viscose | For silk |
|-------------------------------|-------------|----------|
| Fabric (g) | 2.0 | 2.0 |
| Amount of dye (mg) | 40.0 | 40.0 |
| Glauber salt (20%, w/v; ml) | 1.0 | 1.0 |
| Formic acid (10%, v/v; ml) | — | 1.0 |
| Soda ash (10%, w/v; ml) | 5.0 | — |
| pH | 7.5–8.0 | 4.5–5.0 |
| MLR | 1 : 40 | 1 : 40 |
| Dyeing time (min) | 90 | 90 |
| Dyeing temp. ($^{\circ}C$) | 100 | 100 |
| Total volume of dye bath (ml) | 80 | 800 |

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References

1. N. M. NAIK and K. R. DESAI *J. Indian Chem. Soc.*, 1989, **66**, 35
2. C. F. H. ALLEN and J. V. ALLIN, *Org. Synth.*, 1942, **22**, 16.
3. M. T. BOGERT and H. S. SHINIS *J. Am. Chem. Soc.*, 1905, **27**, 649.

