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Short Communication

Synthesis of 1,4-Dioxino[2,3-*b*]quinoxaline Derivatives and a Study of their Fluorescent Properties

ABSTRACT

*1,4-Dioxino[2,3-*b*]quinoxaline and 6-nitro-1,4-dioxino[2,3-*b*]quinoxaline were synthesised by condensaton of 2,3-dichloroquinoxaline and 6-nitro-2,3-dichloroquinoxaline with 1,2-ethanediol and also by condensation of 2,3-dihydroxyquinoxaline and 6-nitro-2,3-dihydroxyquinoxaline with 1,2-dibromoethane. Reduction of the nitro derivative with zinc and hydrochloric acid gave 6-amino-1,4-dioxino[2,3-*b*]quinoxaline, which was diazotised and coupled to Tobias acid and the resultant* ortho-*aminoazo dye cyclised to give 6-(naphthotriazol-2-yl)-1,4-dioxino[2,3-*b*]quinoxaline. The fluorescent properties of the above compounds were studied.*

1 INTRODUCTION

We have previously reported[1] the synthesis of 2-alkyl- and 2-aryl-thiazolo[4,5-*b*]quinoxaline derivatives by condensation of 2,3-dichloroquinoxalines (**2**) with thioamides[1] (**3**) in refluxing *N,N*-dimethylformamide. We report here an investigation into the applicability of this reaction to the synthesis of oxazolo[4,5-*b*]quinoxaline derivatives (**6**) using carboxamides (**5**) in place of thioamides (see Scheme 1 for pathways).

2 RESULTS AND DISCUSSION

Condensation of 2,3-dichloroquinoxaline (**2**) with carboxamides (**5**) failed to give the corresponding 2-alkyl- or 2-aryl-oxazolo[4,5-*b*]quinoxalines (**6**).

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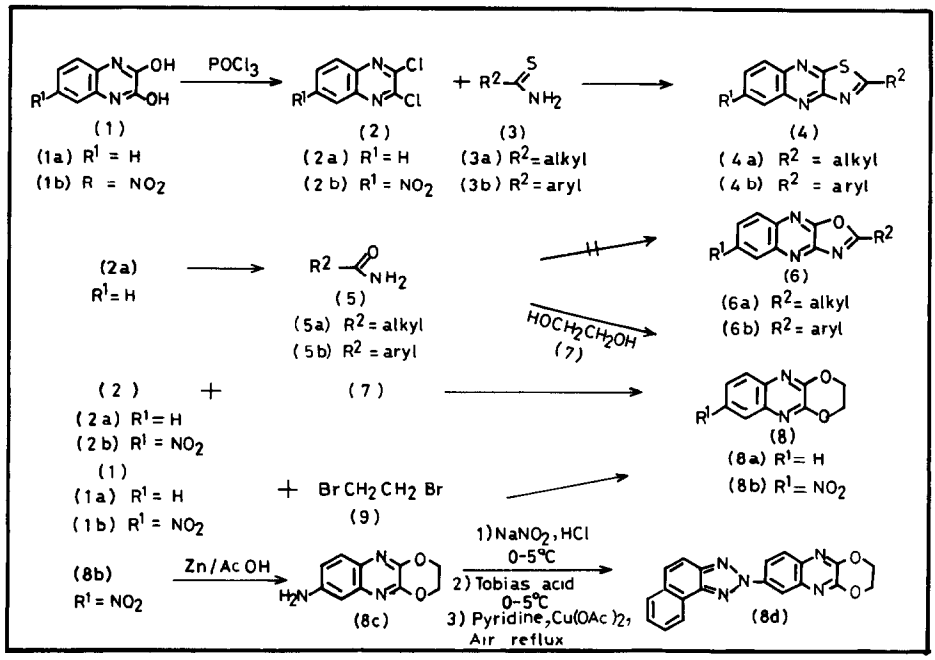

Scheme 1.

While investigating the influence of various solvents in the reaction, it was noted that when 1,2-ethanediol (**7**) was used as solvent the formation occurred of a compound showing weak fluorescence in daylight in common organic solvents. Analytical data for this compound showed it to be 1,4-dioxino[2,3-*b*]quinoxaline (**8a**), and not the anticipated compound **6a**. Thus elemental analysis was in agreement with the molecular formula for 1,4-dioxino[2,3-*b*]quinoxaline (**8a**) and the mass spectrum of the product showed a molecular ion peak (m^+/e) at 188, which corresponds to the molecular weight of **8a**. The ^{1}H NMR spectrum recorded in trifluoroacetic acid showed no methyl group, and the presence of a broad singlet corresponding to two peaks centered at 3·7 could be attributed to 4H aliphatic protons at C-2 and at C-3 of compound **8a**.

Reaction of 2,3-dichloroquinoxaline (**2a**) was effected with 1,2-ethanediol (**7**) without addition of a carboxamide and this yielded 1,4-dioxino[2,3-*b*]-quinoxaline (**8a**) identical to the product obtained as above. The reaction product obtained by condensation of 2,3-dihydroxyquinoxaline (**1a**) with 1,2-dibromoethane (**9**) was also 1,4-dioxino[2,3-*b*]quinoxaline.

Compound **8a** showed a weak blue fluorescence in daylight in common organic solvents and hence some substituted 1,4-dioxino[2,3-*b*]quinoxalines

were synthesised in order to evaluate more fully the fluorescent properties of the 1,4-dioxino[2,3-*b*]quinoxalines.

Thus, 6-nitro-1,4-dioxino[2,3-*b*]quinoxaline (**8b**), obtained by condensation of 6-nitro-2,3-dihydroxyquinoxaline (**1b**) and 1,2-dibromoethane (**9**), was reduced with zinc and refluxing acetic acid to give 6-amino-1,4-dioxino[2,3-*b*]quinoxaline (**8c**). This was diazotised and coupled to 2-aminonaphthalene-1-sulphonic acid (Tobias acid) to yield the corresponding *ortho*-aminoazo dye, which was then oxidatively cyclised to give 6-naphtho(*b*)-1,2,3-triazol-2-yl-1,4-dioxino[2,3-*b*]-quinoxaline (**8d**).

The elemental analyses of 6-nitro-1,4-dioxino[2,3-*b*]quinoxaline (**8b**) was also in agreement with its molecular formula and its ^{1}H NMR spectrum in trifluoroacetic acid showed a broad singlet corresponding to two peaks centered at 3·75, attributed to 4H aliphatic protons at C-2 and C-3, a doublet at 7·3 ($J_{9-8} = 10$ Hz) attributed to ^{1}H at C-9, and a finely split doublet centered at 8·0 ($J_{8-9} = 10$ Hz, $J_{8-6} = 2$ Hz and $J_{6-8} = 2$ Hz) attributed to 2H at C-6 and C-8.

6-Amino-1,4-dioxino[2,3-*b*]quinoxaline (**8c**) gave satisfactory elemental analysis and its IR spectrum showed two peaks characteristic of an amino group at 3260 cm^{-1} and 3320 cm^{-1}. The mass spectrum showed the molecular ion peak (m^+/e) at 203. The structure of 6-naphtho(*b*)-1,2,3-triazol-2-yl-1,4-dioxino[2,3-*b*]quinoxaline (**8d**) was confirmed by elemental analysis.

Compounds **8a** and **8c** showed weak blue fluorescence in daylight, whereas compound **8d** showed an intense violet fluorescence in daylight in solution in *N*,*N*-dimethylformamide. The nitro group in compound **8b** resulted in quenching of the fluorescence and this compound showed a very weak greenish blue fluorescence in daylight. The absorption and fluorescence emission maxima of compounds **8a–8d** are listed in Table 1, the absorption maxima varying from 308 to 357 nm and the fluorescence emission maxima from 430 to 471 nm.

Compounds **8a**, **8c** and **8d** were applied to polyester fibres and gave moderate to good whitening effects.

TABLE 1

Absorption and Fluorescence Emission Spectra (in DMF) of 1,4-Dioxino[2,3-*b*]quinoxalines

Compound	*Absorption maximum (nm)*	*Absorbance*	*Fluorescence emission maximum (nm)*	*log ε*
8a	308	0·586	431	4·13
8b	357	0·437	471	4·03
8c	342	0·608	439	4·04
8d	356	1·138	430	4·61

3 EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a Perkin–Elmer 397 spectrophotometer in Nujol mull. The absorption and fluorescence emission spectra were recorded on a Beckman Model 25 spectrophotometer and Aminco–Bowman spectrophotofluorimeter, respectively. The ^1H NMR spectra were recorded on a Varian 60-MHz instrument.

3.1 Preparation of starting material

2,3-Dihydroxyquinoxaline (**1a**),[2] 2,3-dichloroquinoxaline (**2a**)[3] and 6-nitro-2,3-dihydroxyquinoxaline (**1b**)[4] were synthesised by known methods.

3.2 Attempted synthesis of 2-methyloxazolo[4,5-*b*]quinoxaline (6a)

A mixture of 2,3-dichloroquinoxaline (**2a**) (1·99 g, 0·01 mol), acetamide (0·59 g, 0·01 mol) and 1,2-ethanediol (**7**) (10 ml) was stirred under reflux until reaction was complete (5h, monitored by TLC). The reaction mixture was cooled to room temperature and slowly added to ice–water (about 150 g) with vigorous stirring, when a pale yellow solid separated. This was filtered, dried and recrystallised from acetic acid as colourless needles, 1·32 g, m.p. > 340°C. Calculated for $C_{10}H_7N_3O_2$ corresponding to molecular formula of compound **6a**: C, 59·7; H, 3·5; N, 20·9. Calculated for $C_{10}H_8N_2O_2$ corresponding to molecular formula of compound **8a**: C, 63·8; H, 4·25; N, 14·9. Found: C, 63·75; H, 4·3; N, 14·9%.

3.3 1,4-Dioxino[2,3-*b*]quinoxaline (8a): Method A

A mixture of 2,3-dichloroquinoxaline (**2a**) (1·99 g, 0·01 mol), 1,2-ethanediol (**7**) (10 ml) and sodium carbonate (0·2 g) was gently refluxed until the reaction was complete (6 h, monitored by TLC). The reaction mixture was cooled to room temperature and slowly added to ice–water (about 150 g) with vigorous stirring. The pale yellow solid was filtered, dried and recrystallised from acetic acid in colourless needles, 1·54 g (82·5%), m.p. > 340°C. Calculated for $C_{10}H_8N_2O_2$: C, 63·8; H, 4·25; N, 14·9. Found: C, 63·7; H, 4·35; N, 14·8%.

3.4 1,4-Dioxino[2,3-*b*]quinoxaline (8a): Method B

A mixture of 2,3-dihydroxyquinoxaline (**1a**) (1·62 g, 0·01 mol), 1,2-dibromoethane (**9**) (10 ml) and sodium carbonate (0·2 g) was gently refluxed until the reaction was complete (5 h, monitored by TLC). The product was

isolated as described in Method A. Crystallisation from acetic acid yielded colourless needles, 1·50 g (80%), m.p. > 340°C. Found: C, 63·9; H, 4·2; N, 14·9%.

3.5 6-Nitro-1,4-dioxino[2,3-*b*]quinoxaline (8b)

The procedure described in Section 3.4 was used. Recrystallisation of the product from acetic acid gave pale yellow crystals (78·5%), m.p. > 340°C. Calculated for $C_{10}H_7N_3O_4$: C, 51·5; H, 3·0; N, 18·0. Found: C, 51·4; H, 2·9; N, 18·2%.

3.6 6-Amino-1,4-dioxino[2,3-*b*]quinoxaline (8c)

Conc. hydrochloric acid (5 ml) was added to a mixture of the nitro compound (**8b**) (11·65 g, 0·05 mol) and acetic acid (100 ml) and the mixture was heated to 80°C with stirring. Zinc dust (9·75 g, 0·06 atom) was added in portions over a period of 1 h. After addition was complete, the reaction mixture was refluxed until the reaction was complete (4 h, monitored by TLC). The reaction mixture was filtered hot, then the filtrate was cooled to room temperature and added to ice–water (about 200 g). The product was filtered, washed with water, dried and recrystallised from acetic acid as buff-coloured crystals, 6·19 g (61%), m.p. 225–226°C. Calculated for $C_{10}H_9N_3O_2$: C, 59·1; H, 4·4; N, 20·7. Found: C, 59·0; H, 4·4; N, 20·75%.

3.7 6-Naphtho(*b*)-1,2,3-triazol-2-yl-1,4-dioxino[2,3-*b*]quinoxaline (8d)

The amino compound (**8c**) (1·015 g, 0·005 mol) was dissolved in hydrochloric acid (10%, 20 ml) with external cooling to 0–5°C and a solution of sodium nitrite (0·38 g, 0·0055 mol) in water (5 ml) was slowly added below 5°C over 1 h. The mixture was stirred for a further 1 h and excess nitrous acid removed with urea (0·5 g). The diazonium solution was then slowly added to a solution of 2-aminonaphthalene-1-sulphonic acid (Tobias acid) (1·62 g, 0·005 mol) in sodium carbonate (6 g) and water (15 ml) at 0–5°C. Sodium acetate was gradually added during coupling to maintain the pH at 5–6. The mixture was stirred for 4 h, when the *ortho*-aminoazo dye separated. This was filtered and used as a wet presscake for the triazolisation.

The above *ortho*-aminoazo dye (wet presscake) was dissolved in pyridine (25 ml) and cupric acetate (2 g, 6·01 mol) added. The mixture was refluxed in a current of air until the colour of the dye appreciably disappeared (4 h, monitored by TLC). The reaction mixture was cooled to room temperature and slowly added to ice-cold dilute hydrochloric acid (5%, 100 ml) with vigorous stirring, when a solid product separated. The crude product was

filtered, washed with water and dried. It was stirred into acetic acid (10 ml), zinc dust (0·5 g) added and the mixture refluxed for 1 h to destroy last traces of the dye. The hot mixture was filtered and the filtrate cooled to room temperature and added to ice–water (about 100 g), when a yellow solid separated. This was filtered, washed with water and dried. Recrystallisation from DMF gave pale yellow crystals, 1·12 g (63%), m.p. > 340°C. Calculated for $C_{20}H_{13}N_5O_2$: C, 67·6; H, 3·7; N, 19·7. Found: C, 67·8; H, 3·6; N, 19·6%.

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