Dyes and Pigments 4 (1983) 35–39

Synthesis of Isomeric Azo Disperse Dyes of Pyridobenzimidazole

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(Received: 24 November, 1981)

SUMMARY

*Condensation of 4-(4-methoxyphenyl)-5*H*-pyran-2,6-dione* (**1**) *and 1,2-diaminobenzene* (**2**) *gave 3-(4-methoxyphenyl)-1-oxo-1*H*,5*H*-pyrido-[1,2-*a*]benzimidazole* (**3**). *When* **3** *was coupled with an aryldiazonium salt two isomeric dyes were obtained in equal proportions. These dyes were characterised as 3-(4-methoxyphenyl)-4-(arylhydrazono)-1-oxo-1*H*-pyrido-[1,2-*a*]benzimidazole* (**4**) *and 2-(arylhydrazono)-3-(4-methoxyphenyl)-1-oxo-1*H*-pyrido[1,2-*a*]benzimidazole* (**5**) *on the basis of spectral data. Their structures were confirmed also by an alternative synthetic route.*

1. INTRODUCTION

The benzimidazole ring system is endowed with fluorescent property[1,2] and, when incorporated in a molecule, it generally imparts fluorescence to the compound. The hydroxypyridone system possesses conjugated π electrons and a labile hydrogen atom which give rise to tautomerism. In a coupling component tautomerism has a profound effect on the shade of the dye compound derived from it. Keeping this in mind, a fused ring heterocyclic coupling component possessing a pyridobenzimidazole moiety was prepared and coupled with substituted aryl diazonium salts in order to obtain brighter shades and better fastness properties.

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Dyes and Pigments 0143-7208/83/0004-0035/$03·00

2. RESULTS AND DISCUSSION

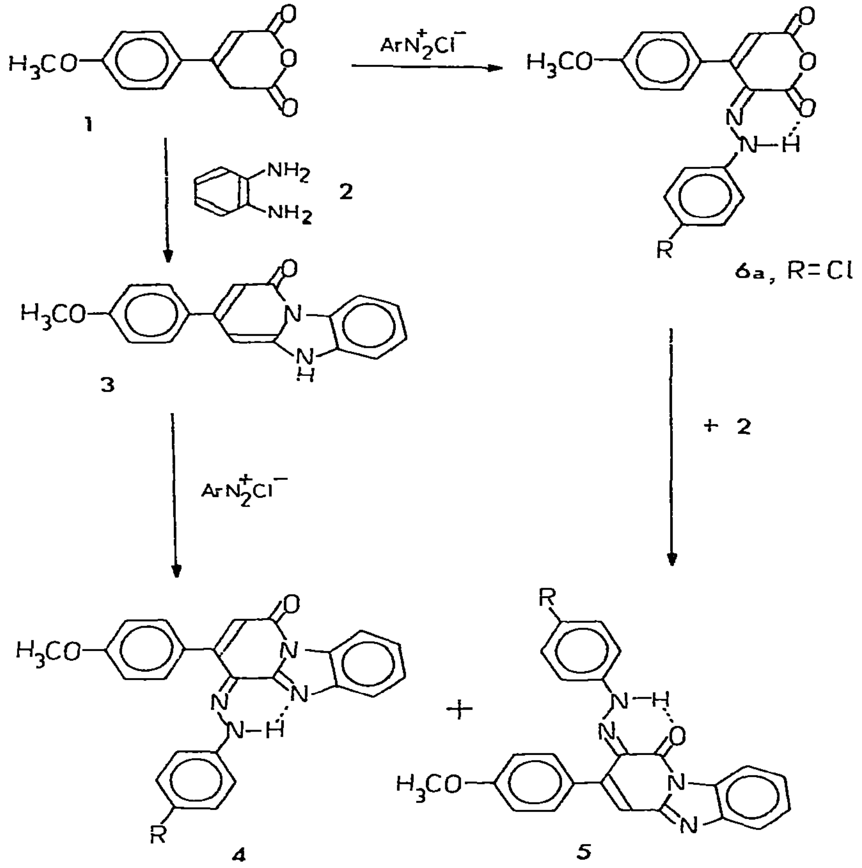
4-(4-Methoxyphenyl)-5*H*-pyran-2,6-dione (**1**) was condensed with 1,2-diaminobenzene (**2**) to obtain 3-(4-methoxyphenyl)-1-oxo-1*H*,5*H*-pyrido-[1,2-*a*]benzimidazole (**3**). Due to its poor solubility the PMR spectrum of **3** could not be run. The structure was determined by inspecting the PMR spectrum of an analogous compound, 3-(4-ethoxy-3-isopropyl-6-methylphenyl)-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole (DMSO-d_6). It showed the following important peaks: 6·06 and 6·2 (two allylic coupled multiplets each integrating for one proton, $J = 2$cps); 7·36(3H,*m*, C_7H, C_8H, C_9H); 12·1 (1H,*s*,NH); and 8·9 (1H,*d*,$C_{10}H$). Compound **3** had two potentially nucleophilic centres, i.e. positions 2 and 4, and was expected to undergo an azocoupling reaction at either or both of these positions depending upon their relative nucleophilicities.

Compound **3**, when coupled with aryl diazonium salt in acetone, gave a mixture of two dyes **4** and **5**. When coupled with 4-chlorobenzenediazonium chloride it yielded again a mixture of two dyes. The mixture was separated by column chromatography (silica gel, 60–120 mesh) using benzene as an eluent to get a bright yellow (**4a**) and a red (**5a**) dye. Dye **4a** was identified as 3-(4-methoxyphenyl)-4-(4-chlorophenylhydrazono)-1-oxo-1*H*-pyrido[1,2-*a*]benzimidazole on the basis of spectral data; MS, *m/e* 429 (M^+); IR (KBr), 2800–3200 (broad hydrazone NH), 1670 (CO); PMR ($CDCl_3$), 3·9 (3H,*s*, OCH_3), 6·5 (1H,*s*, olefinic proton), 7–7·65 (12H,*m*,ArH) and D_2O exchangeable NH.

Similarly **5a** was identified as 2-(4-chlorophenylhydrazono)-3-(4-methoxyphenyl)-1-oxo-1*H*-pyrido[1,2-*a*]benzimidazole; MS, *m/e* 429 (M^+); IR (KBr), 2800–3200 (broad hydrazone NH), 1640 (CO); PMR ($CDCl_3$), 3·9 (3H,*s*, OCH_3), 7–7·65 (13H,*m*, ArH and C_4H) and a D_2O exchangeable NH.

The structures **4a** and **5a** were further confirmed by coupling **1** with *p*-chlorobenzenediazonium chloride in acetone to give a single yellow dye, 4-(4-methoxyphenyl)-5-(4-chlorophenylhydrazono)-2*H*,5*H*,6*H*-pyran-2,6-dione (**6a**). Compound **6a** was then subjected to the condensation with **2** to yield **4a** and **5a** respectively.

Thus, it appeared that the nucleophilicities of the two reactive sites (positions 2 and 4) in **3** are comparable and the attack of aryldiazonium salt is indiscriminate at these centres. In spite of changing the molar ratio of the coupling component to the aryldiazonium salt there was no effect on the composition of the dye mixture. Even with the large excess of the



aryldiazonium salt, bis coupled product was not formed and the same dye mixture was obtained. This observation led to the conclusion that once the coupling component had been attacked by one molecule of the diazonium cation, the second site became no longer nucleophilic enough for the next attack. In **4a** and **5a** there is wide scope for tautomerism and, in fact, **4a** and **5a** are the favourable tautomers of the two positional isomers formed in the reaction. Furthermore, whenever an H atom is available at the coupling site, there exists a tendency to undergo an azo to hydrazo change by 1,3-prototropic shift. Therefore, the azocoupling reaction on an active methylene group invariably results in the hydrazone product. Thus, it can be concluded reasonably that the dyes obtained above were in the hydrazone form.

3. EXPERIMENTAL

Melting points were recorded on a Metler FP 15 model. Ultraviolet spectra were recorded on a Beckmann DK-2 spectrometer employing $CHCl_3$ as a solvent. Infrared spectra, in KBr, were run on a Beckmann Acculab-10 infrared spectrophotometer, PMR spectra on a Varian T-60 spectrometer and mass spectra on a Varian Mat 112S (70 eV) instrument.

3.1. 3-(4-Methoxyphenyl)-1-oxo-1H,5H-pyrido[1,2-a]benzimidazole (3)

A mixture of **1** (2·18 g, 0·01 mol) and **2** (1·08 g, 0·01 mol) was refluxed for 0·5 h in acetic acid. The solution was cooled and filtered to remove the product. The residue was washed with water and then boiled with benzene to remove unreacted **1** and **2**. The compound **3** was thus obtained in sufficiently pure form (TLC); m.p. 310 °C (decomp.), yield 2·32 g (80 %).

3.2. Azocoupling reaction on 3

Compound **3** (2·90 g, 0·01 mol) was dissolved in acetone and the suspension was cooled to 5–10 °C. A cooled solution of 4-chlorobenzenediazonium chloride [prepared by diazotising 4-chloroaniline (1·28 g, 0·01 mol) dissolved in 6 ml of 1 : 1 HCl with $NaNO_2$ (0·69 g, 0·01 mol) in 5 ml water] was added with constant stirring using a magnetic stirrer at 5–10 °C. The coloured product was filtered, washed with water and dried.

The above mixture was chromatographed using a column of activated silica gel (60–120 mesh). On elution with benzene a bright yellow compound **4a**, m.p. 283 °C, was obtained. After the total removal of **4a** from the column the column was dried and **5a** (m.p. 261 °C) was separated by extracting the silica gel with boiling alcohol.

Compounds **4b**–**4d** and **5b**–**5d** were prepared using other aryl amines by a similar procedure. Characteristic data are summarised in Table 1.

3.3. Azocoupling reaction on 1

Following the same procedure as above, **1** (2·18 g, 0·01 mol) was coupled with 4-chlorobenzenediazonium chloride to get a yellow dye **6a**, m.p. 227 °C (Calc. C, 60·67; H, 3·65; N, 7·87; Found C, 60·61; H, 3·67; N, 7·83 %).

TABLE 1
Characterisation Data of Dyes **4** and **5**

Dye	*R*	*Molecular formula*	*Yield* (%)	*Melting point* (°C)	*N* (%)		λ_{max}	
					Calc.	*Found*	*UV*	*Visible*
4a	Cl	$C_{24}H_{17}ClN_4O_2$	39	283	13·08	13·11	288	—
4b	NO_2	$C_{24}H_{17}N_5O_4$	40	297(d)	15·95	16·00	350	466
4c	CH_3	$C_{25}H_{20}N_4O_2$	41	225	13·73	13·70	261	460
4d	OCH_3	$C_{25}H_{20}N_4O_3$	41	244	13·21	13·22	350	470
5a	Cl	$C_{24}H_{17}ClN_4O_2$	38	261	13·08	13·04	272	—
5b	NO_2	$C_{24}H_{17}N_5O_4$	39	298	15·95	15·99	310	470
5c	CH_3	$C_{25}H_{20}N_4O_2$	41	246	13·73	13·80	312	470
5d	OCH_3	$C_{25}H_{20}N_4O_3$	40	233	13·21	13·16	279	488

3.4. Condensation of 6a and 2

A mixture of **6a** (3·58 g, 0·01 mol) and **2** (1·08 g, 0·01 mol) was refluxed for 6 h in acetic acid. The mixture was cooled, filtered and the residue was washed with water. The product was a mixture of two compounds and was separated by column chromatography to obtain **4a** and **5a**.

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