Dyes and Pigments **10** (1988) 79–83

Short Communication

Synthesis of Pyridino[1,2-*b*]pyrazol-2-ones and Study of their Fluorescent Properties

ABSTRACT

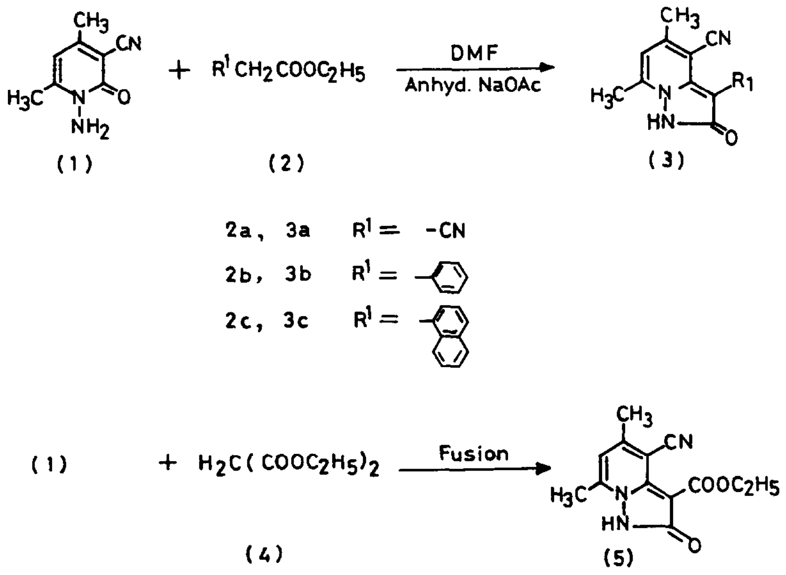
*3-Substituted pyridino[*1,2-b*]purazol-2-ones have been synthesised in a single stage from* N*-amino-3-cyano-4,6-dimethylpyririd-2-one by condensation with substituted ethyl acetates in refluxing DMF or by fusion in the presence of sodium acetate. The fluorescent properties of the resulting compounds have been studied.*

1 INTRODUCTION

Novel structures of fluorescent compounds involve fused heterocycles, which have the dual advantage of compactness and the conjugation necessary for possessing appreciable fluorescent properties. Among various fused heterocyclic derivatives reported in this connection, 1,2-pyridine fused heterocycles are of interest. We have previously described the synthesis and study of the fluorescent properties of 1,2-pyridine fused heterocycles such as pyrido[1,2-*a*]benzimidazoles,[1–3] 1,2,4-triazolo[1,5-*a*]pyridines[4] and pyrazolo[1,5-*a*]pyridines.[5]

In the present study, we report the synthesis and fluorescent properties of some representative derivatives of the pyridino[1,2-*b*]pyrazol-2-one heterocyclic fused system. This small fused heterocyclic system was synthesised in a simple single step. Thus, the condensation of *N*-amino-3-cyano-4,6-dimethylpyridin-2-one (**1**) with α-substituted ethyl acetates (**2a**–**2c** and **4**) yielded various 3-substituted-4-cyano-5,7-dimethylpyridino[1,5-*a*]pyrazol-2-ones (**3a**–**3c** and **5**).

Dyes and Pigments 0143-7208/88/$03·50



2 RESULTS AND DISCUSSION

In the synthesis of 3-substituted-4-cyano-5,7-dimethylpyridino[1,5-*a*]-pyrazol-2-ones (**3a**–**3c** and **5**), obtained by the condensation of *N*-amino-3-cyano-4,6-dimethylpyridin-2-one (**1**) and various substituted ethyl acetates (**2** or **4**), we examined the suitability of a variety of condensing agents and reaction conditions. Thus, the reaction was carried out using anhydrous zinc chloride in solvents, anhydrous sodium acetate in solvents, anhydrous sodium acetate by fusion and using polyphosphoric acid. The use of different solvents such as ethanol, benzene, xylene and *N*,*N*-dimethylformamide and different temperatures of reaction were also studied.

It was observed that for the condensation of **1** with ethyl cyanoacetate (**2a**), ethyl phenylacetic ester (**2b**) and ethyl naphthylacetic ester (**2c**) the use of sodium acetate as condensing agent in refluxing *N*,*N*-dimethylformamide gave the best results, whereas for the condensation of **1** with diethyl malonate (**4**) the careful fusion of the reactants in the presence of sodium acetate at 160°C gave the best results. The products of the reactions yielded compounds **3a**–**3c** and **5**, respectively, in a single step and in good yields (63–72%).

The structures of **3a**–**3c** and **5** were confirmed by elemental analysis and mass spectra and those of **3a** and **5** were further confirmed by their ^{1}H-NMR spectra. Thus, the ^{1}H-NMR spectrum of compound **3b** in DMSO-d$_6$ showed the following signals: two sharp singlets very close to each other at 2·1 and

2·2 attributed to 6H aliphatic of the two methyl groups at C-5 and C-7; a singlet at 5·9 (D_2O-exchangeable) attributed to 1H due to the —NH— group at N-1; a sharp singlet at 6·4 attributed to 1H of the proton at C-6; and two peaks at 7·2 attributed to 5H aromatic of the phenyl ring at C-3. The ^1H-NMR spectrum of compound **5** in trifluoroacetic acid showed the following signals: a triplet at 1·2 attributed to 3H of the methyl of the carbethoxy group at C-3; a broad signal indicating a singlet and a doublet appearing very close together between 2·2 and 2·8 attributed to 6H of the two methyl groups at C-5 and C-7; a quartet at 4·3 attributed to 2H of the —CH_2— of the carbethoxy group at C-3; and a sharp singlet at 6·5 attributed to 1H of the proton at C-6.

TABLE 1
Absorption and Fluorescence Emission Spectra of Pyridino-[1,2-*b*]pyrazol-2-ones

Compound	*Absorption maximum (nm) (in DMF)*	*Fluorescence emission maximum (nm)*	*log ε*
3a	346	414	4·28
3b	346	421	4·29
3c	347	422	4·27
5	339	416	4·25
Standard[a]	376	458	4·41

[a] The standard fluorescent compound was 7-*N*,*N*-diethylamino-4-methylcoumarin.

The fluorescent properties of the products **3a**–**3c** and **5** that were synthesised were studied in their DMF solutions. The absorption maxima and the fluorescence emission maxima in the electronic spectra of the compounds are listed in Table 1, together with that of the standard fluorescent compound *N*,*N*-diethylamino-4-methylcoumarin. It was observed that various groups such as cyano, phenyl, naphthyl and carbethoxy present in 3-position of the 4-cyano-5,7-dimethylpyridino[1,5-*a*]pyrazol-2-one had very little influence on the absorption and fluorescence emission maxima. Compounds **3a**–**3c** and **5** were colourless and they were applied to polyester fibres as fluorescent whiteners; **3a** and **5** gave good whitening effect of the polyester fibres, whereas **3b** and **3c** gave a brownish tint.

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 in DMF solutions were recorded on a Beckman Model 25 spectrophotometer and Aminco–Bowman spectrophotofluorimeter, respectively. The ^{1}H-NMR spectra were recorded on a Varian 60-MHz instrument EM-360-L using TMS as internal standard; the chemical shifts are given in δ (ppm).

3.1 Preparation of starting materials

The starting material *N*-amino-3-cyano-4,6-dimethylpyrid-2-one (1) was prepared by the known method.[6]

3.2 3,4-Dicyano-5,7-dimethylpyridino[1,2-*b*]pyrazol-2-one (3a)

Using a flask fitted with a reflux condenser and a calcium chloride guard tube, a mixture of *N*-amino-3-cyano-4,6-dimethylpyrid-2-one (**1**) (2·45 g, 0·015 mol), ethyl cyanoacetate (1·70 g, 0·015 mol), anhydrous sodium acetate (0·5 g) and *N*,*N*-dimethylformamide (8–10 ml) was heated to reflux and refluxing was continued until the reaction was completed (5 h, monitored by TLC). The reaction mixture was allowed to cool to room temperature and then slowly poured into ice–water (about 50 g) when **3a** separated. The crude product was filtered, washed with water, dried and recrystallised from DMF as colourless needles (65%), m.p. 179°C. Calculated for $C_{11}H_8N_4O$: C, 62·3; H, 3·8; N, 26·4. Found: C, 62·6; H, 3·6; N, 26·6%. P^+ at *m/e* 212. IR: 3240 cm^{-1} (NH); 2240 cm^{-1} (CN) and 1720 cm^{-1} (imido C═O).

The compounds **3b** and **3c** were synthesised in the same manner.

3.3 3-Phenyl-4-cyano-5,7-dimethylpyridino[1,2-*b*]pyrazol-2-one (3b)

Recrystallised from DMF as colourless needles (63%), m.p. 181°C. Calculated for $C_{16}H_{13}N_3O$: C, 73·0; H, 4·9; N, 16·0. Found: C, 72·9; H, 4·8; N, 15·8. P^+ at *m/e* at 263. IR: 3240 cm^{-1} (NH); 2240 cm^{-1} (CN) and 1720 cm^{-1} (imido C═O).

3.4 3-(1-Naphthyl)-4-cyano-5,7-dimethylpyridino[1,2-*b*]pyrazol-2-one (3c)

Recrystallised from DMF as colourless needles (68%), m.p. 175°C. Calculated for $C_{20}H_{15}N_3O$: C, 76·7; H, 4·8; N, 13·4. Found: C, 76·45; H, 4·7; N, 13·7. IR: 3240 cm^{-1} (NH); 2240 cm^{-1} (CN); 1720 cm^{-1} (imido C═O).

3.5 Ethyl 4-cyano-5,7-dimethylpyridino[1,2-*b*]pyrazol-2-one-3-carboxylate (5)

Using a flask fitted with a calcium chloride guard tube, a mixture of compound **1** (2·45 g, 0·015 mol), diethyl malonate (**4**) (2·4 g, 0·015 mol) and anhydrous sodium acetate (0·5 g) was heated with vigorous stirring, the temperature being gradually raised to 160°C over 1 h and maintained at 160°C until reaction was complete (3 h, monitored by TLC). The reaction mixture was stirred into ice–water (about 50 g) and the solid product was filtered, washed with water, dried and recrystallised from DMF as colourless needles (72%), m.p. 258°C. Calculated for $C_{13}H_{13}N_3O_3$: C, 60·2; H, 5·0; N, 16·2. Found: C, 60·1; H, 4·9; N, 16·2%. P^+ at m/e 259. IR: 3240 cm^{-1} (NH); 2240 cm^{-1} (CN); 1720 cm^{-1} (imido C=O); 1650 cm^{-1} and 1740 cm^{-1} (carboethoxy C=O).

ACKNOWLEDGEMENT

One of us (R.C.P.) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of Junior and Senior Research Fellowships.

REFERENCES

1. Rajadhyaksha, D. D. & Rangnekar, D. W., *J. Chem. Tech. Biotechnol.*, **36** (1986) 300.
2. Rajadhyaksha, D. D. & Rangnekar, D. W., *Dyes and Pigments*, **7** (1986) 365.
3. Rajadhyaksha, D. D. & Rangnekar, D. W., *Ind. J. Chem.*, **26B** (1987) 143.
4. Phadke, R. C. & Rangnekar, D. W., *Synthesis* (1986) 860.
5. Phadke, R. C. & Rangnekar, D. W., *Synthesis* (1987) 484.
6. Reid, W. & Meyer, A., *Chem. Ber.*, **90** (1957) 2841.

D. W. Rangnekar & R. C. Phadke
Dyes Research Laboratory,
Department of Chemical Technology,
University of Bombay, Matunga,
Bombay 400 019, India

(Received 1 December 1987; accepted 29 January 1988)