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Short Communication

Synthesis of 5-Arylazo-2,6-dichloro-3-cyano-4-methylpyridines and Their Application on Polyamide Fibre as Disperse Reactive Dyes

ABSTRACT

Diazotised arylamines were coupled to 3-cyano-4-methyl-6-hydroxy-2-pyridone to give 5-arylazo-3-cyano-4-methyl-6-hydroxy-2-pyridones, which on refluxing with phosphorus oxychloride yielded the corresponding 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridines. These dyes were applied to polyamide fibres as disperse reactive dyes and their fastness properties were evaluated.

1 INTRODUCTION

We have previously reported the synthesis of arylazohalogenopyrimidines and their application to polyamide fibres as disperse reactive dyes.[1] As a continuation of this study, we have investigated the synthesis of a number of heterocycles for use in similar disperse reactive dyes and we report here the synthesis of some 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridine dyes, their application to polyamide fibres and an evaluation of their fastness properties.

2 RESULTS AND DISCUSSION

Aromatic amines[*p*-toluidine (**1a**), *p*-anisidine (**1b**), *p*-chloroaniline (**1c**), *p*-nitroaniline (**1d**) and aniline (**1e**)] were diazotised and the diazonium compounds (**2a**–**2e**) were coupled to 3-cyano-4-methyl-6-hydroxy-2-

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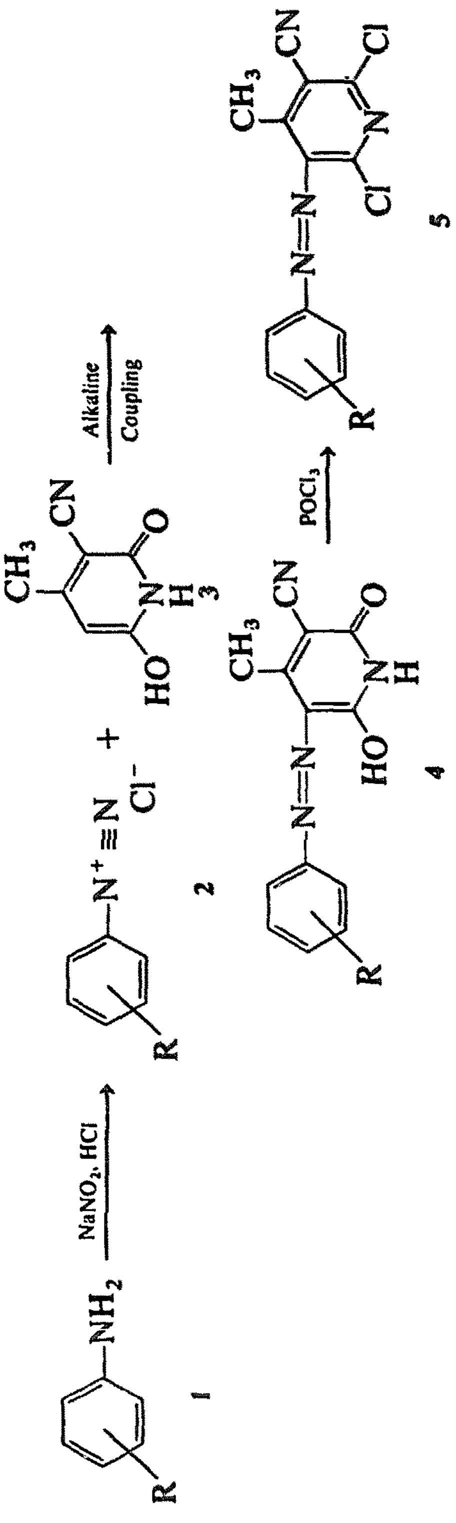

	R
1a, 2a, 4a, 5a	— CH$_3$
1b, 2b, 4b, 5b	— OCH$_3$
1c, 2c, 4c, 5c	— Cl
1d, 2d, 4d, 5d	— NO$_2$
1e, 2e, 4e, 5e	— H

Scheme 1

TABLE 1
Characterisation and Fastness Data for Pyridine Disperse Reactive Dyes **5a**–**5e** on Polyamide Fibres (1% shades)

Dye	*R*	*Physical appearance of dye*	*m.p. (°C)*	*Dyed polyamide fibres*		
				Hue	*Pick-up*	*Lightfastness*
5a	CH_3	Red crystals	201	Brilliant orange	4	4
5b	OCH_3	Rose crystals	177	Brilliant golden yellow	4	3
5c	Cl	Red crystals	191–194	Brilliant golden yellow	4	3
5d	NO_2	Orange crystals	221–224	Brilliant yellow	4	2–3
5e	H	Orange crystals	211	Brilliant yellow	2	5

pyridone (**3**) under alkaline coupling conditions to give the 5-arylazo-3-cyano-4-methyl-6-hydroxy-2-pyridone dyes (**4a**–**4e**) (Scheme 1). These dyes **4a**–**4e** were then refluxed in phosphorus oxychloride to yield the corresponding 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridine dyes (**5a**–**5e**).

The structure of the dyes was confirmed by IR and mass spectrometry and by satisfactory elemental analyses. The IR spectra of **4a**–**4e** showed characteristic absorptions for hydroxy, imino and keto residues, and these were not present in the spectra of dyes **5**, confirming that the replacement of the hydroxy groups had occurred.

The 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridine dyes **5a**–**5e** were applied on polyamide fibres as disperse reactive dyes and yielded brilliant yellow to orange level dyeings (see Table 1) of generally good lightfastness and pick-up.

Dyeings on polyamide were carried out using conventional disperse dyeing procedures and also by then adjusting the pH of the dye liquor to 10–10·5 with sodium carbonate and continuing the dyeing for a further 30 min. The dyeings obtained after the latter adjustment of the pH of the dye liquor had considerably greater depth than dyeings without it, indicating that the dyes were acting as disperse reactive dyes.

3 EXPERIMENTAL

All melting points are uncorrected and are in °C. Infrared spectra were recorded on a Perkin–Elmer Model 397 Spectrometer in Nujol mull.

3.1 Preparation of starting materials

3-Cyano-4-methyl-6-hydroxy-2-pyridone (**3**), m.p. 311°, (lit.[2] m.p. 311°) was prepared by known methods by condensation of cyanoacetamide with acetoacetic ester.

3.2 5-(4-Methylphenyl)azo-3-cyano-4-methyl-6-hydroxy-2-pyridone (4a)

A mixture of *p*-toluidine (2·14 g, 0·02 mol) and aqueous hydrochloric acid (4·8 ml of 1·6M, 0·05 mol) was warmed to obtain a clear solution. The solution was cooled to 5°C and sodium nitrite (1·38 g, 0·02 mol) in water (20 ml) was added with stirring over 15 min. The diazonium salt solution was then stirred for 30 min, after which excess nitrous acid was removed by the addition of urea (0·2 g). The diazonium salt solution thus obtained was clear. This clear diazo salt solution was run over 30 min at 0–5°C into a solution of 3-cyano-4-methyl-6-hydroxy-2-pyridone (2·72 g, 0·02 mol) in water (300 ml) made alkaline with sodium carbonate (6·4 g, 0·06 mol) in water (150 ml). The pH during the coupling was maintained at 10 and the mixture was stirred for 6 h at 0–5°C and then neutralised with dilute hydrochloric acid. The precipitated dye was filtered, washed with water, dried and recrystallised from acetone to yield red crystals (75%), m.p. 232–233°. Calculated for $C_{14}H_{12}N_4O_2$: C, 63·5; H, 4·4; N, 20·4. Found: C, 63·2; H, 4·1; N, 20·4%.

The other 5-arylazo-3-cyano-4-methyl-6-hydroxy-2-pyridone dyes (**4b–4e**) were prepared in a similar manner.

3.3 5-(4-Methoxyphenyl)azo-3-cyano-4-methyl-6-hydroxy-2-pyridone (4b)

Crystallised from acetone as red crystals (82%), m.p. 260°. Calculated for $C_{14}H_{12}N_4O_3$: C, 62·7; H, 4·5; N, 20·9. Found: C, 62·4; H, 4·2; N, 21·1%.

3.4 5-(4-Chlorophenyl)azo-3-cyano-4-methyl-6-hydroxy-2-pyridone (4c)

Crystallised from acetone as yellow crystals (78%), m.p. 211°. Calculated for $C_{13}H_9N_4O_2Cl$: C, 54·1; H, 3·1; N, 19·4; Cl, 12·3. Found: C, 53·8; H, 2·8; N, 19·6; Cl, 12·0%.

3.5 5-(4-Nitrophenyl)azo-3-cyano-4-methyl-6-hydroxy-2-pyridone (4d)

Crystallised from acetone as red crystals (80%), m.p. 218–219°. Calculated for $C_{13}H_9N_5O_4$: C, 52·2; H, 3·0; N, 23·4. Found: C, 51·8; H, 2·7; N, 23·0%.

3.6 5-Phenylazo-3-cyano-4-methyl-6-hydroxy-2-pyridone (4e)

Crystallised from acetone as orange crystals (76%), m.p. 240–244°. Calculated for $C_{13}H_{10}N_4O_2$: C, 61·4; H, 3·9; N, 22·05. Found: C, 61·5; H, 3·6; N, 21·7%.

3·7 5-(4-Methylphenyl)azo-2,6-dichloro-3-cyano-4-methylpyridine (5a)

A mixture of dye **4a** (2.5 g, 0·01 mol) was refluxed with phosphorus oxychloride (40 ml, s.g. 1·675, 0·432 mol). On addition of the phosphorus oxychloride, the colour changed from red to yellow and then to red after 1 h reflux. Refluxing was continued until the reaction was complete (10 h) (monitored by TLC). Most of the phosphorus oxychloride was then distilled under vacuum and the remaining mixture (about 10 ml) was added to ice–water (about 300 g) with vigorous stirring. The resulting dark oily compound yielded, on prolonged stirring, a red solid. The product was filtered and washed acid-free with water and dried at 40–50°C. It was recrystallised from benzene to yield red crystals (82%), m.p. 201°. Calculated for $C_{14}H_{10}N_4Cl_2$: C, 55·1; H, 3·3; N, 18·4; Cl, 23·3. Found: C, 54·7; H, 3·0; N, 17·9; Cl, 22·7%.

3.8 5-(4-Methoxyphenyl)azo-2,6-dichloro-3-cyano-4-methylpyridine (5b)

Crystallised from benzene as rose crystals (85%), m.p. 177°. Calculated for $C_{14}H_{10}N_4OCl_2$: C, 52·3; H, 3·1; N, 17·45; Cl, 22·1. Found: C, 52·6; H, 3·1; N, 17·3; Cl, 21·8%.

3·9 5-(4-Chlorophenyl)azo-2,4-dichloro-3-cyano-4-methylpyridine (5c)

Crystallised from benzene as red crystals (84%), m.p. 191–194°. Calculated for $C_{13}H_7N_4Cl_3$: C, 47·9; H, 2·15; N, 17·2; Cl, 32·7. Found: C, 48·15; H, 2·1; N, 17·1; Cl, 32·6%.

3.10 5-(4-Nitrophenyl)azo-2,4-dichloro-3-cyano-4-methylpyridine (5d)

Crystallised from benzene as brown crystals (84%), m.p. 221–224°. Calculated for $C_{13}H_7N_5O_2Cl_2$: C, 46·4; H, 2·1; N, 20·8; Cl, 21·1. Found: C, 46·2; H, 2·1; N, 20·6; Cl, 20·8%.

3.11 5-Phenylazo-2,6-dichloro-3-cyano-4-methylpyrimidine (5e)

Crystallised from benzene as orange crystals (82%), m.p. 211°. Calculated for $C_{13}H_8N_4Cl_2$: C, 53·6; H, 2·75; N, 19·2; Cl, 24·4. Found: C, 53·4; H, 2·6; N, 19·0; Cl, 24·2%.

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