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Pyrimidyl and Imidazolyl Coumarin Disperse Dyes

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SUMMARY

The synthesis of 7-diethylaminocoumarin derivatives containing pyrimidine and imidazole substituents at the 3-position is described. These have been evaluated as disperse dyes on polyester.

1. INTRODUCTION

We have recently described the synthesis of coumarins containing heterocyclic substituents such as furyl,[1] oxazolyl,[1] oxadiazolyl,[1] indolyl[2] and coumarinyl,[3] and have reported their dyeing properties. In recent years many patents have appeared wherein the 7-diethylamino-3-hetaryl coumarin system has been described as useful for fluorescent dyes. The present paper describes the synthesis of new coumarin derivatives substituted by pyrimidine and imidazole units at the 3-position.

A recent patent[4] describes the synthesis of the amidine derivative **3** by reaction of ethyl cyanoacetate (**2**) and 4-diethylaminosalicaldehyde[5] (**1**) in the presence of ammonium acetate. The resultant compound **3** is claimed to be a cationic dye. No further reactions of this amidine are mentioned in the literature. Cyclisation[6] is the most important reaction of amidines and it was therefore envisaged that the amidine **3** would be a useful intermediate for the synthesis of new 3-hetaryl coumarins.

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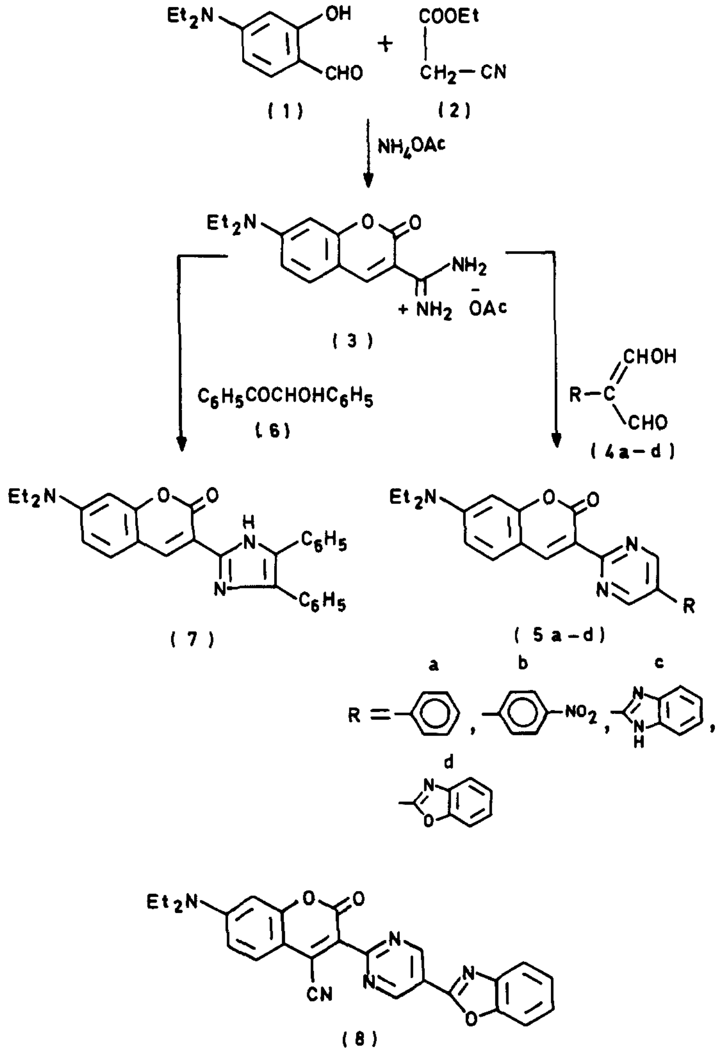
2. RESULTS AND DISCUSSION

Arylacetic acids and compounds having active methyl groups were diformylated by the Vilsmeier reaction and the resulting malondialdehydes were studied in the synthesis of various heterocyclic compounds (Scheme 1).[7] β-Dialdehydes[8] are known to react with



Scheme 1. Synthesis of pyrimidyl and imidazolyl coumarin derivatives.

amidines to give pyrimidine derivatives. The malondialdehydes synthesised were reacted with benzamidine hydrochloride to give the corresponding substituted pyrimidine derivatives. Thus, the amidine **3** was reacted with the malondialdehydes **4a–d** in dimethylformamide in the presence of piperidine to yield the pyrimidyl coumarins **5a–d**. The structures of the products were established on the basis of their elemental analyses and infrared spectra (absence of amino peaks). As a representative of the 3-pyrimidylcoumarins the PMR spectrum of compound **5d** was recorded in trifluoroacetic acid. It displayed a triplet at δ 1·3 corresponding to the six protons of the methyl groups, a quartet at δ 4·0 corresponding to the four protons of the methylene groups, a multiplet between δ 7·6 and 8·3 corresponding to seven aromatic protons and a sharp singlet at δ 9·4 corresponding to three protons (which could be due to the proton at C4 of the coumarin ring and the two protons of the pyrimidine ring). The mass spectrum of compound **5d** showed the molecular ion peak M^+ at m/e 412 corresponding to the molecular formula $C_{24}H_{20}N_4O_3$. With the exception of compound **5b** the compounds synthesised exhibited an intense green fluorescence in daylight and were evaluated on polyester as disperse dyes. The evaluation data are given in Table 1.

TABLE 1
Evaluation of 3-Hetaryl Coumarins on Polyester (100%)

Compound	*Colour on fibre*	*Pick-up*[a]	*Sublimation fastness*[b]	*Xenotest*
5a	Greenish yellow	1	2	<1
5b	Reddish yellow	4	2	<1
5c	Greenish yellow	3	2	<1
5d	Greenish yellow	4	3	<1
7	Greenish yellow	4	3	<1
8	Orange	3	3	<1

[a] Pick-up scale: 5, twice standard depth (excellent); 4, equals standard (very good); 3, half standard (good); 2, one-third standard (moderate); 1, one-sixth standard (very poor).
[b] Sublimation fastness scale: 5, excellent; 4, good; 3, fair; 2, poor; 1, very poor.

α-Hydroxyketones[9] react with amidines to yield imidazoles. Benzoin was therefore reacted with compound **3** under high-temperature fusion condition. The structure of the product was established on the basis of elemental analysis and mass spectrum (M^+ at *m/e* 435). This product showed an intense green fluorescence in daylight.

Moeckli[10] has reported the synthesis of deeply coloured 4-cyanocoumarins and it has also been reported that 3-(4′-pyridyl)coumarin does not undergo cyanation at the 4-position of the coumarin nucleus. It was anticipated that the introduction of an additional nitrogen atom in the ring (namely, by use of a pyrimidine residue) would increase the electron-withdrawing character of the 3-substituent, thus enabling attack of the cyanide ion at the 4-position to occur. Accordingly, compound **5d** was reacted with sodium cyanide in dimethylformamide, followed by oxidation with bromine. The structure of the resultant product (**8**) was established on the basis of its colour (on TLC), m.p. and elemental analysis. It was applied to polyester and the relevant evaluation data are given in Table 1.

3. EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 397 spectrophotometer using Nujol mull, PMR spectra on a Varian EM-360L spectrophotometer using TMS as internal standard and mass spectra on a Varian Mat CH-7 spectrometer. Ultraviolet spectra were recorded on a Perkin–Elmer double-beam spectrophotometer Model 124.

4-Diethylaminosalicaldehyde[5] (**1**) was prepared by the Vilsmeier formylation of 3-diethylaminophenol using dimethylformamide and phosphorus oxychloride. Phenyl (**4a**) and *p*-nitrophenyl (**4b**) malondialdehydes were prepared by the Vilsmeier reaction on the corresponding arylacetic acids following the procedure reported by Arnold.[12] Benzimidazolyl-[13] (**4c**) and benzoxazolyl-[14] (**4d**) malondialdehydes were obtained from 2-methylbenzimidazole and 2-acetamidophenol, respectively.

3.1. 7-Diethylaminocoumarin-3-amidine acetate (3)

A mixture of 4-diethylaminosalicaldehyde (**1**) (3·9 g, 0·02 mol), ethyl cyanoacetate (**2**) (2·3 g, 0·02 mol) and ammonium acetate (2·3 g, 0·03 mol) in absolute ethanol (15 ml) was refluxed for 3 h. The reaction mixture was cooled to room temperature and the yellow solid which separated was filtered, washed with a little ethanol and dried. Yield 4·5 g (70 %), m.p. 175–178 °C. As crystallisation from methanol did not improve the m.p. the crude amidine was used as such for further reactions without any purification.

3.2. Pyrimidylcoumarins (5a–d)

General procedure

A mixture of the amidine **3** (0·005 mol) and the appropriate malondialdehyde derivative (**4a–d**) (0·0055 mol) was refluxed in DMF (3–5 ml) containing a few drops of piperidine for 4 h. The reaction mixture was concentrated, cooled and diluted with a little ethanol. The solid which separated (in the case of **4c,d**) was filtered, washed with a little ethanol and dried. In the case of **4a,b**, the reaction mixture was poured into ice-cold water containing very dilute alkali (to remove unreacted malondialdehyde) and the solid which separated was filtered, washed with water and dried. The yield, m.p., crystallisation solvent, molecular formula and λ_{max} of the pyrimidylcoumarins thus prepared are shown in Table 2.

3.3. 2-(7′-Diethylaminocoumarin-3′-yl)-4,5-diphenylimidazole (7)

An equimolar mixture of compound **3** and benzoin was heated on an oil bath at 140 °C for 3–4 h. The reaction mixture was cooled and a little

TABLE 2
Physical Data of the Pyrimidylcoumarins (**5a–d**)

Compound	*Yield (%)*	*M.p. (°C)*	*Crystallisation solvent*	*Molecular formula*[a]	λ_{max} *(nm)*	*log ε*
5a	65	223–225	EtOH	$C_{23}H_{21}N_3O_2$	394	3·90
5b	67	312–314	EtOH–DMF (1:1)	$C_{23}H_{20}N_4O_4$	285 338	4·24 4·71
5c	68	295–298	DMF	$C_{24}H_{21}N_5O_2$	320 432	4·15 4·86
5d	78	268–269	DMF	$C_{24}H_{20}N_4O_3$	310 450	4·84 4·27

[a] Satisfactory elemental analyses were obtained.

ethanol was added. The solid which separated was filtered and dried. Yield 63%. It was crystallised from ethanol, m.p. 180–182°C; λ_{max}(log ε) 392 nm (3·74), in methanol. Found: N, 9·8; $C_{28}H_{25}N_3O_2$ requires N, 9·6%.

3.4 Preparation of compound 8 by cyanation of 5d

To a suspension of **5d** (0·005 mol) in DMF (3 ml), sodium cyanide (0·01 mol) was added with stirring. The reaction mixture was stirred for 1 h. Bromine (0·0055 mol) was added dropwise after cooling the reaction mixture to 0–5°C and stirring was continued for 1 h at room temperature. The dark reaction mixture was poured into ice-cold water containing a little sodium chloride and the product which separated was filtered, washed free of cyanide and dried. Yield 80%. It was crystallised from EtOH–DMF, m.p. 238–240°C. Found: N, 16·3; $C_{25}H_{19}N_5O_3$ requires N, 16·0%; λ_{max}(log ε) 460 nm (3·25) in methanol.

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