PREPARATION OF SOME NEW RED FLUORESCENT 4-CYANOCOUMARIN DYES†

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SUMMARY

The first fluorescent dyestuffs for polyester fibres appeared towards the end of the 1960s. These were coumarin derivatives, the shades of which, however, remained restricted to the greenish yellow region. Thus, it was repeatedly attempted to synthesise further fluorescent disperse dyes possessing longer wavelength absorptions. The introduction of a cyano group into the 4-position of the coumarin ring offers a surprisingly simple possibility of achieving the desired effect. The new dyestuffs are formed readily and in high yield. They may be used to dye polyester fibres in brilliant red shades, exhibiting strong fluorescence. The scope and limitations of the reaction are discussed and compared with similar reactions reported in the literature.

1. INTRODUCTION

In 1929 Krais discovered that the naturally occurring coumarin derivative esculin could be used to increase the whiteness of certain textiles.[1] The subsequent development of the optical whitening agents then led to an intensive study of this class of compounds. As a result, in 1958, Haeusermann and Voltz discovered the first class of dyestuffs based on the coumarin system (2), the synthesis of which is shown in Scheme 1.[2]

These new products enabled synthetic fibres to be dyed in greenish yellow shades possessing a previously unattained brilliance. The success of these so

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(a), X = −NH−   (2 a), 434 nm
(b), X = −O−   (2 b), 434 nm
(c), X = −S−   (2 c), 452 nm
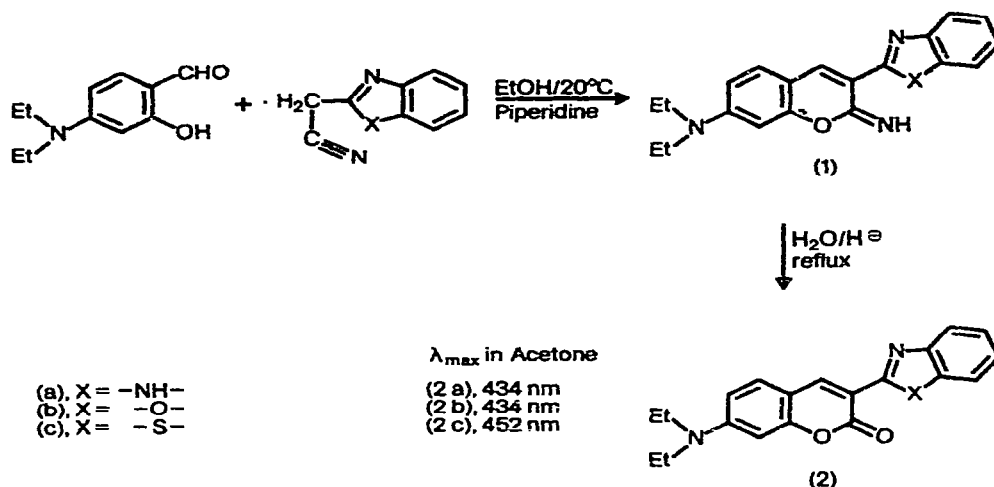
Scheme 1

called 'Shock Colours' in the late 1960s initiated world-wide research activity in this area. There followed the publication of many patents in which new coumarin derivatives, based principally on variations of the substituent in the 3-position, were suggested. The shades of these dyestuffs, however, remained in all cases restricted to the greenish yellows previously obtained. It was not until 1972 that Mach *et al.* reported the hitherto only red dyestuff based on the coumarin system (3), which they obtained by condensation of the iminocoumarin (1a) with malononitrile under simultaneous ring-closure.[3]


(3)
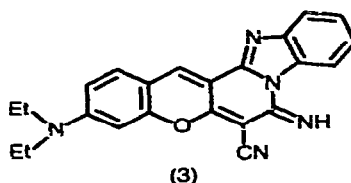
It has long been known that the cyanide ion can add to styryl dyes, and the resulting addition products then be oxidised to tricyanovinylanilines.[4] In the preparation of tricyanovinylanilines (Scheme 2) the introduction of a third cyano group causes the large bathochromic shift of 85 nm.

The process can readily be performed as a one-pot reaction, in which case dimethylformamide (DMF) is the solvent of choice. The excellent results that we obtained with this synthetic method prompted us to apply it to the previously mentioned coumarin dyes. It is apparent that such compounds are,

Scheme 2

(4) (5)
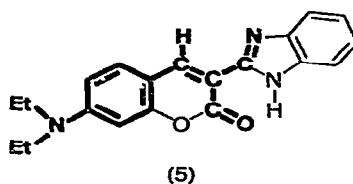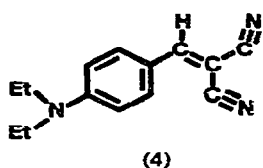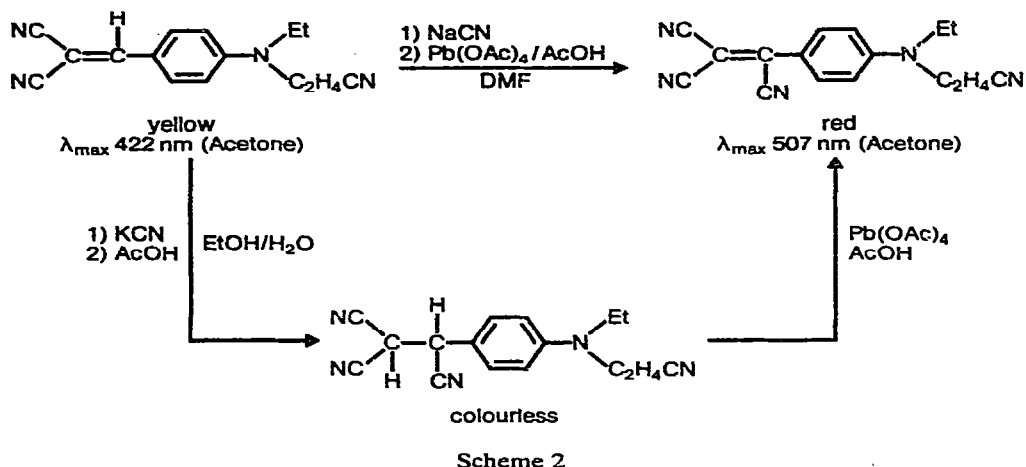
in fact, closely related to the styryl dyes in that they may be considered as possessing a ring-closed type of styryl structure (cf. (4) and (5)). Thus, we treated a suspension of the compound (2c) in DMF at room temperature with excess 30% aqueous sodium cyanide. Immediately a clear, brown solution resulted, which was cooled to 8–10°C and then oxidised directly with bromine, whereupon the 4-cyanocoumarin (6) precipitated, and was isolated in a yield of c. 90%.

Exactly as in the case of the styryl dyes, the introduction of the cyano group results in a large bathochromic shift (67 nm) from a greenish yellow to a bluish red shade. Along with this surprising similarity in the course of the reaction, and the correct elemental analysis, in particular, the NMR spectrum of the
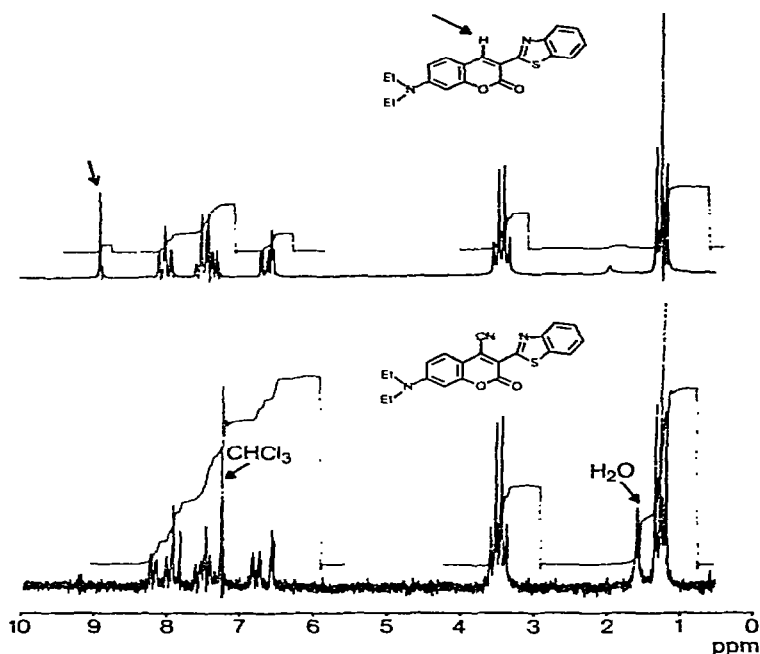

(6)
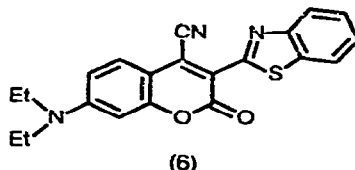
red; λ_{max} 519 nm (Acetone)

Fig. 1. ^{1}H-NMR-spectra of compounds (2c) and (6) in CDCl$_{3}$. The spectra were recorded using a Varian XL-100-12 spectrometer at 100 MHz and at room temperature. (*Note*: (6) is less soluble in CDCl$_{3}$ than (2c).)

product demonstrates the correctness of the assigned structure (6), the signal for the proton in the 4-position of the starting material being completely absent in the reaction product (Fig. 1).

As opposed to the cyanation of styryl dyes, which proceeds readily in alcoholic medium, it is necessary to use dipolar aprotic solvents, preferably DMF, in the case of the coumarins. In addition to the above mentioned bromine as oxidising agent, lead tetraacetate in acetic acid may also be used, but other oxidising agents were found to be less suitable.

The reaction is, however, not limited to the above example, but may also be applied to almost all known coumarin dyes. The resulting products are red dyestuffs, possessing more or less bluish hues, most of which exhibit a strong orange to red fluorescence. Consequently, dyeings of these dyestuffs show exceptional brilliance and brightness. This effect may be illustrated by a consideration of the reflectance spectra of such dyeings, with and without fluorescence excitation, as demonstrated in Fig. 2.

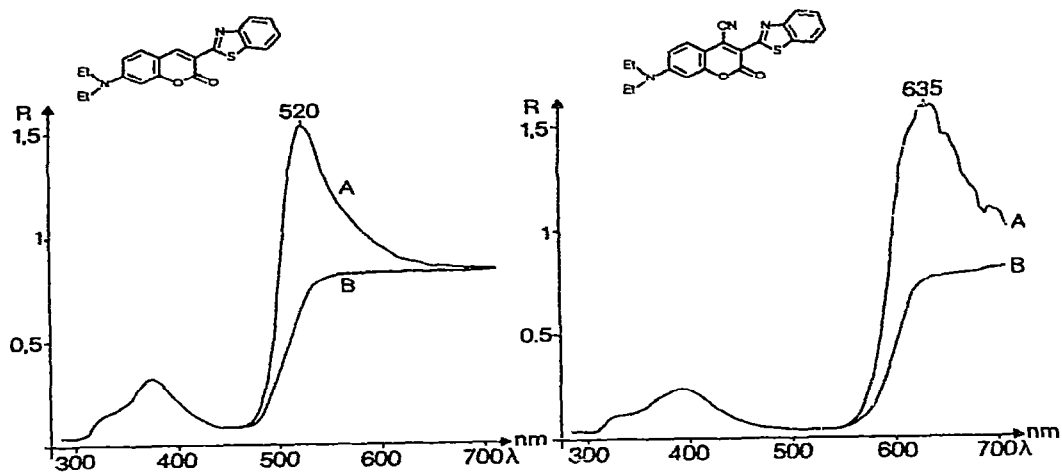The application and fastness properties of the new products are very similar
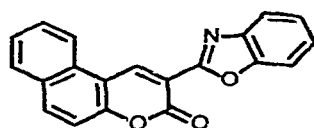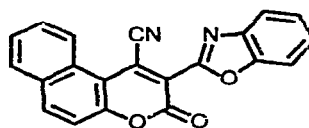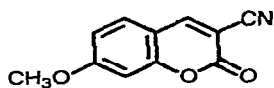
Fig. 2. Spectral reflectance (A) with and (B) without fluorescence excitation of Polyester dyeings of (2c) and (6) in standard depth. The spectra were recorded according to the method of Eitle and Ganz[5] using a Beckman Acta M-VI spectrophotometer.
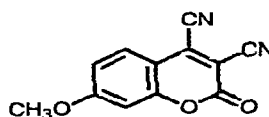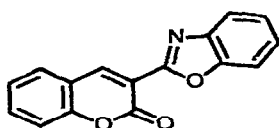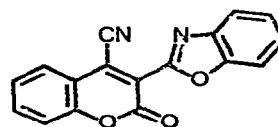
(7)
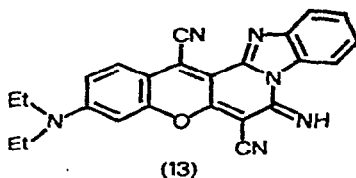almost colourless

(8)
strongly yellow

(9)
colourless

(10)
pale yellow

(11)
colourless

(12)
pale yellow

(13)

blue; λ_{max} 630 nm (Chloroform)

to those of the known unsubstituted dyestuffs, and both may also be readily used in combination with each other.

Furthermore, it was found that not only the 7-dialkylaminocoumarins undergo this reaction. Thus, compounds such as (7), (9) and (11) may also be converted into the corresponding 4-cyano derivatives (8), (10) and (12). Such cyanated products are, however, somewhat sensitive to hydrolysis, and are thus probably only useful for dry, thermal dyeing application.

The previously mentioned fluorescent red dye (3) has also been shown to undergo cyanation leading to the formation of (13). Here, once again, a large bathochromic shift results. The new product (13) is a greenish blue dyestuff exhibiting red fluorescence, the emission maximum being at 668 nm ir chloroform solution.

The 4-cyanocoumarins cannot, in general, be sulphonated without simultaneous attack at the cyano group occurring. It is, however, possible to sulphonate an unsubstituted coumarin derivate and then subsequently introduce the cyano substituent, as exemplified in Scheme 3. The compounds (15) and (17) may be used to dye polyamide fibres in fluorescent yellow and red shades, respectively, although the light stability of these dyeings is insufficient for practical textile application.

(14)   Oleum 24%, 60°C →   (15)

(16)   1) NaCN 2) Br$_2$ DMF →   (17)
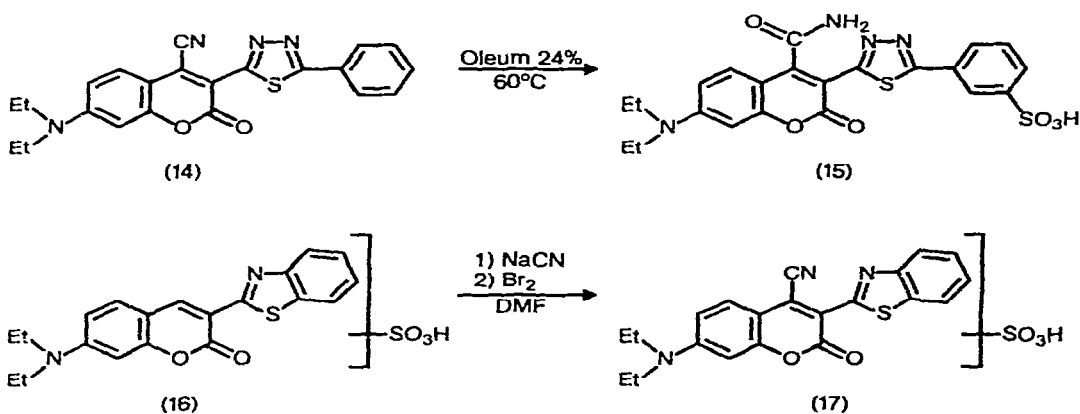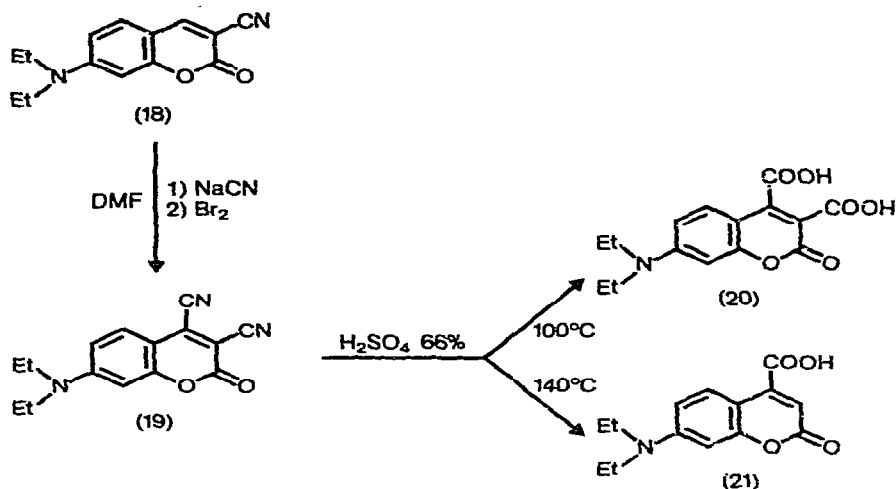
Scheme 3

Scheme 4

The cyano groups of the new compounds can also readily be hydrolysed to the corresponding carboxylic acids, an interesting example being shown in Scheme 4. Depending upon the temperature of hydrolysis, either the di- (20) or monocarboxylic acid (21) may be isolated.

The oxidative introduction of the nitrile group is apparently not only restricted to styryl dyes and coumarins, but would seem to be of a more general nature. In the literature, a number of further examples are reported which are exactly analogous to this type of reaction. Thus, the anthraquinone derivative (22) has been shown to add cyanide ion, in DMF, subsequent oxidation with m-nitrobenzenesulphonic acid resulting in the formation of the cyano compound (23) (Scheme 5).[6]
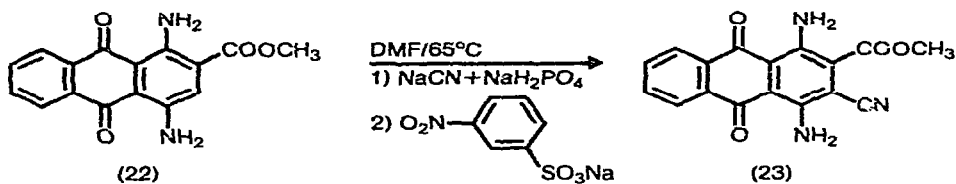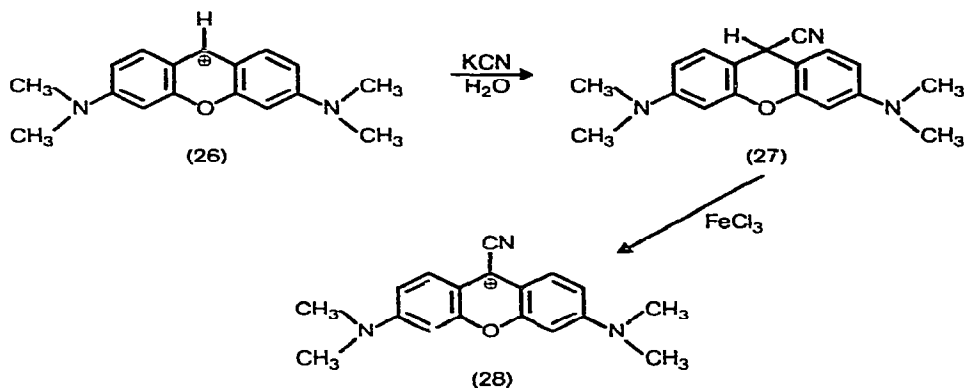

Scheme 5

Furthermore, the preparation of the violet dyestuff (24), as described by Stolle et al., should be mentioned at this point.[7] Presumably this one-pot reaction proceeds by way of the intermediate (25), which then undergoes oxidative cyanation, since the reaction may also be carried out on the isolated derivative (25), as shown in Scheme 6.
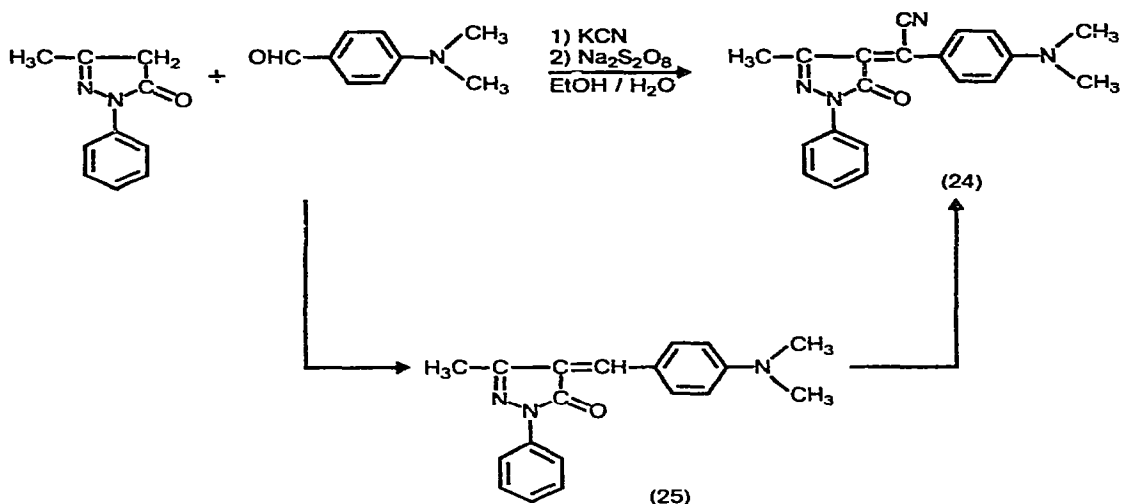
Scheme 6

Scheme 7

A further interesting example is the cyanation of the pyronine (26) reported by Ehrlich and Benda, as illustrated in Scheme 7.[8] The red pyronine initially undergoes addition of cyanide ion, resulting in the formation of the so-called 'pyronine leuco-cyanide' (27), which is almost colourless in the pure state. Oxidation then leads to the greenish blue dye (28).

The critical step in these oxidative cyanations appears to be the initial addition of cyanide ion, since we have experienced no difficulties in carrying out the subsequent oxidation. Thus, for example, cyanide ion does not add to the coumarin (29), whereas the quaternised analogue (30) readily undergoes
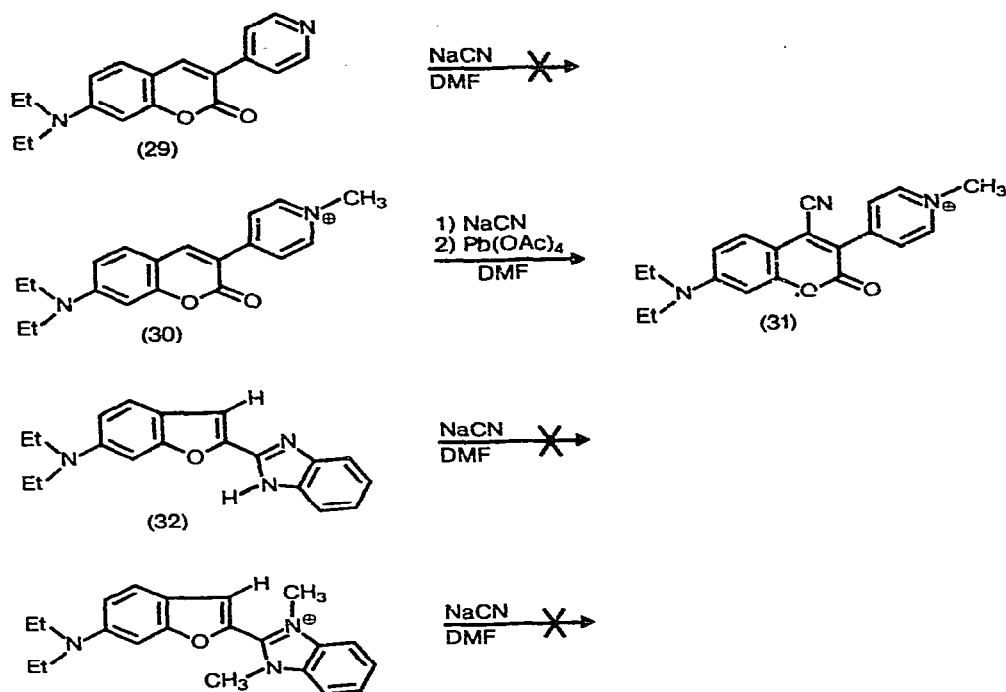
Scheme 8

oxidative cyanation, yielding the cationic coumarin dye (31). However, in the case of the benzofuran (32), quaternisation was found to be of no avail (Scheme 8).

The chief requirement for the addition of cyanide ion would thus appear to be the possibility for a sufficiently high degree of mesomeric stabilisation of the resulting addition product, as demonstrated in the examples of Scheme 9.

2.   EXPERIMENTAL

All melting points are uncorrected.

2.1. *General procedure for the introduction of a cyano group into the 4-position of the coumarin ring*

The coumarin (1·0 mol) was suspended in DMF (5–10 fold quantity) and treated, at room temperature, with sodium cyanide (2·0 mol), preferably in the form of a 30% aqueous solution. In general, a clear brownish yellow solution resulted, which was then cooled to 0–10°C and bromine (1·1 mol) carefully
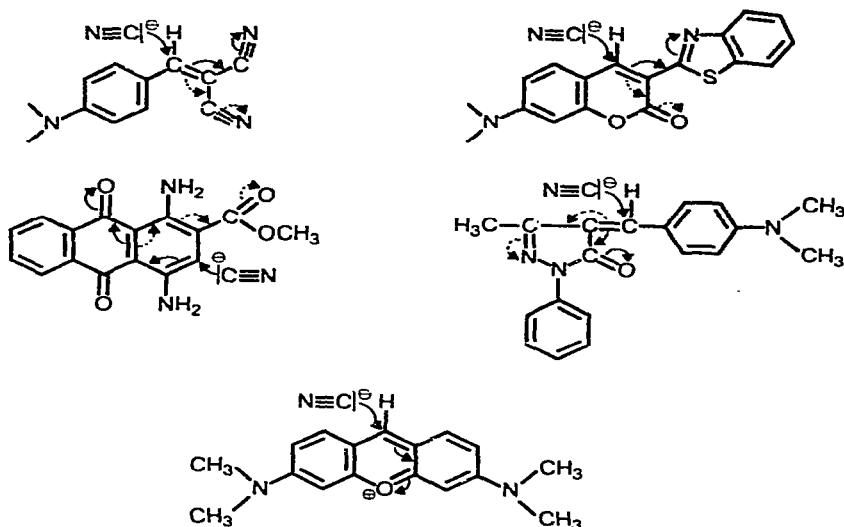
Scheme 9

added, when the product usually precipitated immediately. The mixture was then stirred for a further hour at room temperature, filtered and washed, first with a little DMF and then with alcohol. In order to remove the sodium bromide, the filter cake was slurried in water, filtered and washed salt-free with water.

The preparation of the dyestuffs (6), (13), (14) and (19) has been described in detail in a patent application which also describes the preparation of further 4-cyanocoumarins not mentioned in this paper.[9] The starting materials (11),[10] (29),[11], (30)[11] and (32)[12] are known compounds.

2.2. 3-(Benzoxazol-2-yl)-4-cyanobenzo[5,6]coumarin (8)

The compound was prepared in 85% yield, according to the general procedure; m.p. 203–208°C. Repeated recrystallisation from perchloroethylene yielded an analytically pure sample; m.p. 212–213°C. The starting material (7) was prepared by condensation of 3-carbethoxybenzo[5,6]coumarin[13] with o-aminophenol in polyphosphoric acid.

2.3. 3,4-Dicyano-7-methoxycoumarin (10)

Following the general procedure, the product was obtained in a yield of 66%; m.p. 204–208°C. The starting material (9) was prepared by condensation of 4-methoxy-salicylaldehyde with ethyl cyanoacetate, under the usual basic conditions.

2.4. 3-(*Benzoxazol-2-yl*)-4-*cyanocoumarin* (12)

The compound was obtained by the general procedure in 86% yield; m.p. 248–250°C. Repeated recrystallisation from methyl ethyl ketone gave an analytically pure sample; m.p. 251–252°C.

2.5. 3-[5-(3-*Sulphophenyl*)*thiadiazol-2-yl*]-4-*carbamoyl*-7-N,N-*diethylaminocoumarin* (15)

1·1 g (2·74 mmol) ot compound (14)[9] were dissolved in 6 ml 24% oleum, and stirred for 12 h at 50–60°C. The mixture was poured on to ice, when a red solution resulted from which golden yellow crystals precipitated after a few minutes. These were filtered and washed with a little water. Yield 1·2 g; 84%. The product was dissolved in 35 ml water and the solution adjusted to pH 7·5 by the addition of 27·4 ml 0·1N sodium hydroxide solution. The addition of 5·5 g sodium chloride resulted in the formation of an orange suspension, which was filtered and washed with 10% sodium chloride solution. After drying, 1·4 g of a chromatographically pure, yellow powder were obtained, the structure, (15), of which was assigned on the basis of the elemental analysis and ^{1}H and ^{13}C NMR spectroscopy.

The starting material for the dye (14) is a known compound.[14]

2.6. 3-(*Benzothiazol-2-yl*)-4-*cyano*-7-N,N-*diethylaminocoumarin*-x-*sulphonic acid* (17)

4·3 g (0·01 mol) compound (16) were suspended in 43 ml DMF and treated with 2·84 ml (0·02 mol) 30% aqueous sodium cyanide solution, when an almost colourless solution resulted. The traces of undissolved sodium cyanide were removed by filtration, the filtrate was cooled to 5°C and 0·52 ml (0·01 mol) bromine added dropwise. An intense violet solution was formed, which was diluted with 150 ml water and salted out by the addition of 110 ml brine to give 2·8 g of product.

The starting material (16) was prepared by sulphonation of (2c) in 8·5% oleum at 50°C.

2.7. 3,4-*Dicarboxy*-7-N,N-*diethylaminocoumarin* (20)

133·5 g (0·5 mol) compound (19) were dissolved in 1000 ml concentrated sulphuric acid and carefully treated with 500 ml water so that the temperature did not exceed 90°C. The mixture was stirred for 5 h at 100°C, cooled, and poured into 5 litres ice-water, when the product precipitated in the form of ochre yellow crystals, which were filtered and washed neutral with water, to yield 122·7 g (80%); m.p. 185°C (decomposition). Repeated recrystallisation from a 60-fold quantity of absolute alcohol furnished an analytically pure product.

2.8. 4-*Carboxy*-7-N,N-*diethylaminocoumarin* (21)

The preparation was performed as described for compound (20), with the exception that the reaction mixture was heated for 3 h at 140°C. A yield of 64% was obtained. Recrystallisation from ethyl acetate gave an analytically pure product; m.p. 195–196°C.

Since this monocarboxylic acid was not found to be identical to the 3-carboxylic acid, obtainable by hydrolysis of the nitrile (18), it was concluded that the reaction product possessed the 4-carboxylic acid structure (21).

2.9. 3-(1-*Methylpyridinium*-4-*yl*)-4-*cyano*-7-N,N-*diethylaminocoumarin chloride* (31)

To 1·75 g (5 mmol) of the chloride of compound (30),[11] suspended in 15 ml DMF, 0·75 ml (5 mmol) 30% sodium cyanide solution were added. The resulting brown suspension was then treated with 2·35 g (5 mmol) lead tetraacetate, when an intense red solution formed immediately. Traces of insoluble materials were filtered, and the filtrate slowly treated with ether, whereby an oil separated. The solvent was decanted off, the sticky residue dissolved in methanol and again treated with ether. There separated 2·1 g of a dark gum, with which polyacrylonitrile could be dyed in less brilliant, bluish red shades. The thin-layer chromatogram of this product showed it to consist of a single intense red compound, along with a small quantity of starting material.

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