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## Short Communication

# Synthesis of 1,1-Dicyano-2,4-diaryl-1,3-butadienes—A Novel Chromophore

*SUMMARY*

*A series of bright, attractive disperse dyes have been obtained by the condensation of acetophenone with malononitrile and reacting the resultant vinylogous reactive methyl compound with aldehydes. The resultant 1,1-dicyano-2,4-diarylbutadienes are bright strong colours with good dyeing properties on polyester. In one case the above product was submitted to oxidative cyanation to yield a novel chromophore, namely the tricyanobutadiene derivative, which has a deeper colour and improved dyeing properties.*

## 1. INTRODUCTION

Disperse dyes for hydrophobic fibres are usually based on small chromophores in order to facilitate entry of the dye molecule into the compact fibre structure. It is usually difficult to obtain violet and blue colours with very small structures and one of the smallest chromophores to yield very deep shades was the tricyanoethylene chromophoric system developed in the 1960s.[1,2] This concept was recently extended by Sandoz[3] who described the reaction of the active methylene function in the benzothiophene dioxide derivative **1** with aldehydes to yield bluish-violet disperse dyes **2**.

## 2. RESULTS AND DISCUSSION

The present paper describes the synthesis of disperse dyes based on the concept of the reactivity of a vinylogous active methyl group. The



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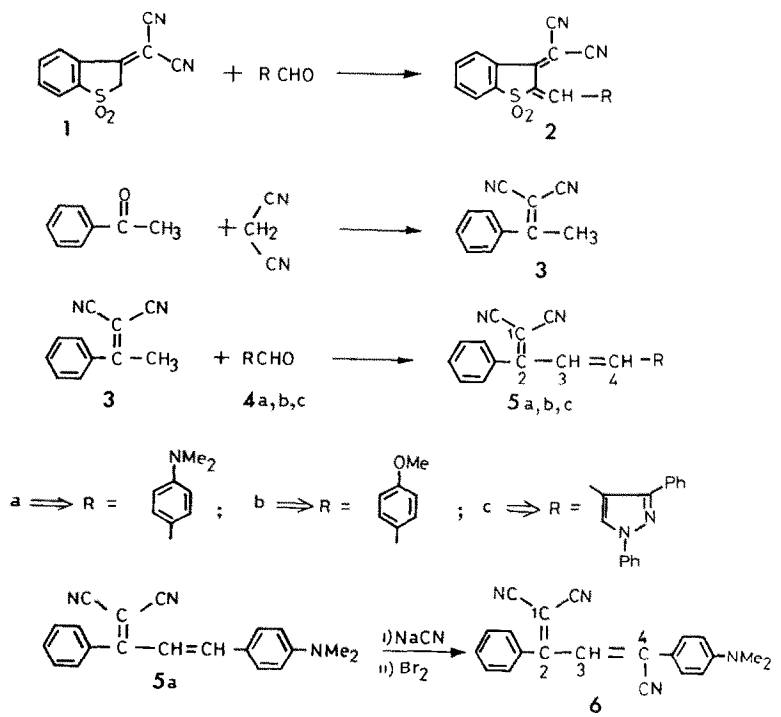
general approach is outlined in Scheme 1. Thus acetophenone was reacted with malononitrile to give the unsaturated dinitrile **3**. The methyl group is activated by the cyano groups and reaction takes place in a facile manner with aldehydes **4** such as *p*-dimethylaminobenzaldehyde to yield the dicyanobutadiene derivatives **5a,b,c**, which are bright and intense in colour. The structures of the compounds obtained were established by elemental analysis, PMR spectrum and mass spectral data.

Recently the colour range of the coumarin system has been extended beyond red by Moeckli,[4] who carried out cyanation of appropriately substituted coumarins to obtain deeply coloured 4-cyanocoumarin derivatives. On this basis the scarlet coloured dimethylaminophenyl derivative **5a** was treated with sodium cyanide in dimethyl formamide as previously reported[4] and the resultant dye **6** was a deep violet in colour. Surprisingly, however, the cyanation reaction failed in the case of the other dicyano compounds (**5b** and **5c**).



**Scheme 1**

The dyes were evaluated on polyester and the results are given in Table 1. It is apparent that the dyes have exceptionally good light and sublimation fastness properties. The colour value is also very good with the exception of dye **5c** derived from the pyrazolyl aldehyde.

This preliminary report thus describes the synthesis of a potentially good series of dyes derived from readily available intermediates and we are investigating the more general applicability of the reaction scheme to a wider range of colourants.

## 3. EXPERIMENTAL PROCEDURE

All melting points are uncorrected. Infrared spectra were recorded in Nujol mull on a Perkin-Elmer 397 spectrophotometer, PMR spectra on a Varian EM-360L spectrophotometer using TMS as internal standard, and mass spectra on a Varian Mat CH-7 spectrometer. The absorption spectra were recorded on a Bausch and Lomb-2000 spectrophotometer.

The starting materials malononitrile-α-methylbenzylidene (**3**),[5] *p*-dimethylaminobenzaldehyde (**4a**)[6] and 1,3-diphenylpyrazole-4-carboxaldehyde (**4c**)[7] were prepared by known methods.

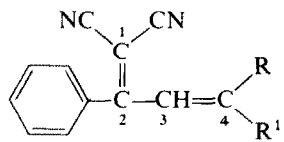
### 3.1. Preparation of 1,1-dicyano-2-phenyl-4-substituted-1,3-butadienes (5a,b,c): general procedure

A mixture of malononitrile-α-methylbenzylidene **3** (3·4 g; 0·02 mol), the appropriate aldehyde **4a,b,c** (0·02 mol), dry benzene (75 ml), dry ammonium acetate (0·300 g) and glacial acetic acid (0·8 ml) was stirred at reflux with continuous removal of water for about 8–9 h. The resultant products were purified as indicated in Table 1, which also gives melting points, molecular formulae, spectral data and dyeing properties.

### 3.2. Preparation of 4-(*p*-dimethylaminophenyl)-2-phenyl-1,1,4-tricyano-1,3-butadiene (6)

The dicyanobutadiene derivative **5a** (3·0 g; 0·01 mol) and finely powdered sodium cyanide (1·0 g; 0·02 mol) were stirred in DMF (20 ml) at room temperature for 3 h. The reaction mixture was then cooled to 0–5°C and bromine (1·6 g; 0·01 mol) was added dropwise during 20 min. The mixture was further stirred at 5–10°C for 1 h and then at room temperature for 2 h. It was poured into ice water (150 ml) containing

**TABLE 1**
1,1-Dicyano-2,4-diaryl-1,3-butadienes




| *No.* | $R^1$ | *R* | *Molecular formula* | *M.p.* (°C) | *Yield* (%) | *PMR* | | $\lambda_{max}$ (*nm*) | *log e* | *Dyeing properties on polyester (100%)* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *Solvent* | *Spectral data* | | | *PU*[d] | *Xeno*[e] | *SF*[f] |
| **5a** | H | *p*-Dimethyl-aminophenyl | $C_{20}H_{17}N_3$[a] | 142[b] | 66 | Acetone-$d_6$ | 3·0$\delta$, s, 6H($NMe_2$), 6·6–7$\delta$, t, 3H(1H C-3 and 2 Ar—H *ortho* to $NMe_2$), 7·2–7·6$\delta$, m, 8H(7 Ar—H and 1H C-3) | 502 | 4·73 | 5 | 7 | 5 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **5b** | H | *p*-Methoxy-phenyl | $C_{19}H_{14}N_2O^a$ | 125[c] | 50 | Acetone-$d_6$ | 3·9$\delta$, s, 3H($OCH_3$), 6·8–7·1$\delta$, t, (1H C-3 and 2H—Ar *ortho* to OMe), 7·3–7·9$\delta$, m, 8H(7Ar—H and 1H C-4) | 400 | 4·49 | 4 | 6 | 4 |
| **5c** | H | 1,3-Diphenyl-4-pyrazolyl | $C_{27}H_{18}N_4^a$ | 220[b] | 55 | | Insufficient solubility | 404 | 4·53 | 3 | 6 | 5 |
| **6** | CN | *p*-Dimethyl-aminophenyl | $C_{21}H_{16}N_4^a$ | 220[b] | 95 | DMSO-$d_6$ | 3·1$\delta$, d, 6H($NMe_2$), 6·8–7·1$\delta$, m, (2H—Ar *ortho* to $NMe_2$ and 1H at C-3), 7·9$\delta$, d 1H(Ar—H *meta* to $NMe^2$); 7·2–7·8$\delta$, m, 6H(Ar) | 551 | 4·19 | 5 | 8 | 5 |

[a] Satisfactory elemental analysis obtained.
[b] Crystallised from benzene.
[c] Chromatographed over silica (benzene–petroleum ether, 1:1).
[d] PU, pick-up: $5 \equiv 2 \times$ standard depth (excellent); $4 \equiv 1 \times$ standard (very good); $3 \equiv 1/2 \times$ standard (good); $2 \equiv 1/3 \times$ standard (moderate); $1 \equiv 1/6 \times$ standard (very poor).
[e] Xeno, light fastness: 8 = outstanding; 7 = excellent; 6 = very good; 5 = good; 4 = fairly good; 3 = fair; 2 = poor; 1 = very poor.
[f] SF, sublimation fastness: 5 = excellent; 4 = good; 3 = fair; 2 = poor; 1 = very poor.

salt (2·5 g). The violet coloured product (**6**) was filtered and washed well with water and dried. Yield, melting point, crystallisation solvent, molecular formula, spectral data and dyeing properties are given in Table 1.

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