Synthesis of 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines and their application on synthetic fibres as disperse dyes

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Four monoazo disperse dyes, 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines, were prepared and their dyeing performance on polyester and polyamide fibres was assessed. The dyeings had bright yellow shades with excellent pick-up and moderate light fastness on both the fibres and moderate sublimation fastness on polyester fibre.

Keywords: Azo disperse dyes, Dyeing, 4-Methylpyridines, Polyester fibre, Polyamide fibre

1 Introduction

Many heterocyclic compounds used as diazo and coupling components are being increasingly used in the synthesis of disperse dyes for synthetic fibres. The compactness of structure, low molecular size, linearity and intrinsic conjugation involved in the disperse dyes derived from heterocyclic compounds lead to improved dyeing properties.

We have earlier reported the synthesis and application of a variety of disperse dyes derived from heterocyclic compounds. In the present paper, we report the synthesis of 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines and their application to polyester and polyamide fibres.

2 Materials and Methods

p-Toluidine and p-anisidine were diazotized and coupled with 3-cyano-6-hydroxy-4-methyl-2-pyridone and the resulting monoazo dyes were refluxed with phosphorus oxychloride to get the corresponding 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridines (I), which have been reported earlier by us as disperse reactive dyes.

The pyridines were reacted with an equimolar quantity of n-butylamine (IIa) or n-propylamine (IIb) in acetone at 15°C. The resulting 2-alkylamino-5-arylazo-6-chloro-3-cyano-4-methylpyridines (III) were not isolated but the second chlorine atom in III was replaced in situ by using monoethanolamine (IV) to get 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines (V).

2.1 Preparation of 2,6-Dialkylamino-5-arylazo-3-cyano-4-methylpyridines (V)

A mixture of 5-arylazo-2,6-dichloro-3-cyano-4-methylpyridine (I, 0.01 mol) and acetone (100 ml) was cooled to 15°C. n-Butylamine (IIa, 0.73 g, 0.01 mol) or n-propylamine (IIb, 0.59 g, 0.01 mol) was then gradually added in 20 min with vigorous stirring and the mixture was further stirred...
until the reaction was complete (2-3 h, monitored by TLC). Acetone was vacuum distilled and xylene (120 ml) was added. The reaction mixture was stirred at room temperature and monoethanolamine (IVA, 1.22 g, 0.02 mol) and sodium acetate (0.82 g, 0.01 mol) were added. The reaction mixture was refluxed until the reaction was complete (12-15 h, monitored by TLC). Most of the xylene was removed by vacuum distillation and the concentrated reaction mixture on dilution with petroleum ether (b.p., 100-120°C) gave a yellow sticky product which was filtered and repeatedly washed with petroleum ether to get a bright yellow solid (V). The solid was filtered, washed with petroleum ether, dried and recrystallized from benzene.

3 Results and Discussion

The physical data of 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines (V) are given in Table 1. The dyes V were bright yellow in colour and were obtained in fairly good yield (61-68%). The structures of dyes Va-d were confirmed by their elemental analyses and further supported by the mass spectra of Va and Vd exhibiting molecular ion peaks at m/z 382 and 350 respectively.

It was, however, not possible to decide whether the chlorine atom in position 2 or 6 of the compound I was first replaced by alkylamine. To understand this, the dye IIIa or VI was reacted with hydrazine hydrate. The product obtained by the condensation of IIIa or VI with hydrazine hydrate may lead to the formation of either VII or VIII. However, if VIII is formed, it will cyclize to give a fused pyrazole derivative IX. The IR spectrum of the product isolated showed the presence of a sharp peak at 2200 cm⁻¹, corresponding to a cyano group, indicating that the product isolated was VII and not IX and further suggesting that the chlorine atom at 6-position in Ia is replaced first by the alkylamine. Thus, the correct structure of the product obtained on reaction of I with the first alkylamine (II) is III and not VI. In the replacement of chlorine atom in position 6 of the compound I with alkylamine, steric hindrance is exerted due to the presence of bulky arylazo group in position 5 whereas in the replacement of chlorine atom in position 2 of the compound I, no steric hindrance is exerted due to the presence of small size of cyano group in position 3. This further supports the fact that III is formed in preference to VI.

The λ_max values of the dyes Va-d were recorded in their DMF solutions and are given in Table 2. The dyes Va-d were applied on polyester and polyamide fibres as disperse dyes. Their dyeing properties are given in Table 2. All the dyes gave bright yellow shades on polyester and polyamide. The pick-up and light fastness of these dyes were excellent (4) and moderate (3) respectively. These dyes had moderate (3) sublimation fastness on polyester.

### Table 1 – Physical data of 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines (V)

<table>
<thead>
<tr>
<th>Dye</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Yield %</th>
<th>m.p. °C</th>
<th>Molecular formula</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Va</td>
<td>OCH₃</td>
<td>n-butyl</td>
<td>CH₂CH₂OH</td>
<td>66</td>
<td>140</td>
<td>C₂₀H₂₆N₆O₂</td>
<td>Yellow</td>
</tr>
<tr>
<td>Vb</td>
<td>OCH₃</td>
<td>n-propyl</td>
<td>CH₂CH₂OH</td>
<td>68</td>
<td>142</td>
<td>C₁₉H₂₄N₆O₂</td>
<td>Yellow</td>
</tr>
<tr>
<td>Vc</td>
<td>CH₃</td>
<td>n-butyl</td>
<td>CH₂CH₂OH</td>
<td>61</td>
<td>155</td>
<td>C₂₀H₂₆N₆O</td>
<td>Yellow</td>
</tr>
<tr>
<td>Vd</td>
<td>CH₃</td>
<td>n-propyl</td>
<td>CH₂CH₂OH</td>
<td>63</td>
<td>166</td>
<td>C₁₉H₂₄N₆O</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

*All dyes gave satisfactory elemental analyses.

*Melting points are uncorrected.

### Table 2 – Spectral data and fastness properties of 2,6-dialkylamino-5-arylazo-3-cyano-4-methylpyridines (V)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Shade on polyester/polyamide</th>
<th>Pick-up</th>
<th>Light fastness</th>
<th>Sublimation fastness</th>
<th>λ_max nm</th>
<th>log ε</th>
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</thead>
<tbody>
<tr>
<td>Va</td>
<td>Bright yellow</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>425</td>
<td>4.32</td>
</tr>
<tr>
<td>Vb</td>
<td>Bright yellow</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>430</td>
<td>4.40</td>
</tr>
<tr>
<td>Vc</td>
<td>Bright yellow</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>421</td>
<td>4.37</td>
</tr>
<tr>
<td>Vd</td>
<td>Bright yellow</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>419</td>
<td>4.43</td>
</tr>
</tbody>
</table>

*Sublimation fastness on polyester.
Acknowledgement
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References