Synthesis of 3-amino-2-arylazo-4,6-dimethylthieno[2,3-b]pyridines and their application on polyester fibres as disperse dyes

D W Rangnekar & P Y Kamat
Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India
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3-Cyano-4,6-dimethyl-2-(1H)-pyridone (III) was treated with phosphorus pentachloride in refluxing phosphorus oxychloride to give 2-chloro-3-cyano-4,6-dimethylpyridine (IV) which was reacted with thioglycolic acid in refluxing methanol in the presence of sodium methoxide to result sodium salt of 3-amino-4,6-dimethylthieno[2,3-b]pyridine-2-carboxylic acid (V). Various aryl diazonium compounds (VIa-d) were coupled with V to give 3-amino-2-arylazo-4,6-dimethylthieno[2,3-b]pyridines (VIIa-d) with the replacement of carboxylic acid group. The compounds VIIa-d when applied on polyester fibres gave orange to violet shades with excellent pick-up, low light fastness and good to very good sublimation fastness.

Keywords: 2-Arylazothieno[2,3-b]pyridines, Disperse dyes, Polyester fibre

1 Introduction
In search of new disperse dyes with improved dyeing characteristics and fastness properties on polyester, we have earlier developed a variety of novel azo heterocyclic disperse dyes1-13 including those based on pyridine and thiophene. In continuation of our work on the development of new disperse dyes derived from thienopyridines, we focused our attention on the structure of 3-amino-4,6-dimethylthieno[2,3-b]pyridine-2-carboxylic acid (V) which has been reported14 to undergo decarboxylation at room temperature under mild acidic conditions. It was observed that the compound V when coupled with aryl diazonium compounds undergo decarboxylation and coupling under mild acidic conditions. In the present paper, we report the synthesis of 3-amino-2-arylazo-4,6-dimethylthieno[2,3-b]pyridines and their dyeing performance on polyester fibres.

2 Materials and Methods
3-Cyano-4,6-dimethyl-2-(1H)-pyridone15 (III) prepared from cyanoacetamide (I) and acetylacetone (II) was treated with phosphorus pentachloride in refluxing phosphorus oxychloride to give 2-chloro-3-cyano-4,6-dimethylthieno[2,3-b]pyridine (IV). The compound IV was reacted with thioglycolic acid using sodium methoxide in refluxing methanol to get sodium salt of 3-amino-4,6-dimethylthieno[2,3-b]pyridine-2-carboxylic acid (V). The compound V was found to be stable as its sodium salt but decarboxylated in acidic conditions. Hence, V was isolated and stored as its sodium salt. The compound V was coupled at weakly acidic pH with four representative aryl diazonium compounds (VIa-d) derived from p-toluidine, p-nitroaniline, 2-methoxy-p-nitroaniline and 2,4-dinitroaniline to result 3-amino-2-(4-methylphenyl)azo-4,6-dimethylthieno[2,3-b]pyridine (VIIa), 3-amino-2-(4-nitrophenyl)azo-4,6-dimethylthieno[2,3-b]pyridine (VIIb), 3-amino-2-(2-methoxy-4-nitrophenyl)azo-4,6-dimethylthieno[2,3-b]pyridine (VIIc) and 3-amino-2-(2,4-dinitrophenyl)azo-4,6-dimethylthieno[2,3-b]pyridine (VIIId) (Scheme 1).

The structures of the compounds VIIa-d were confirmed by their elemental analyses and infrared spectra. The infrared spectrum of V showed two characteristic peaks at 3350 and 3450 cm\(^{-1}\) due to the presence of a primary amino group, a peak at 1670 cm\(^{-1}\) corresponding to carbonyl of carboxylic acid group but was devoid of a peak between 2200 cm\(^{-1}\) and 2220 cm\(^{-1}\) characteristic of a cyano group. The infrared spectra of VIIa-d, recorded in Nujol mull, exhibited two characteristic peaks at 3340 and 3450 cm\(^{-1}\) due to the presence of a primary amino group and did not show any peak characteristic of a carbonyl of carboxylic acid group. The IR spectra of compounds V and VIIa-c are shown in Fig. 1. The structure of the compound VIIc was further confirmed by its mass spectrum, which
showed m/e + peak at 357 corresponding to its molecular weight.

2.1 Preparation of Sodium Salt of 3-Amino-4,6-dimethylthieno[2,3-b]pyridine-2-carboxylic acid (V)

The compound IV (16.65 g, 0.1 mol) and thioglycolic acid (9.6 g, 0.1 mol) were added to a clear solution of sodium (9.2 g, 0.4 atom) dissolved in absolute methanol (100 ml). The mixture was gently refluxed till the reaction was complete (8 h, monitored by tlc). The sodium salt of compound V separated as a solid was filtered, washed with ether and dried, yield 22 g (90%); m.p. > 360°C.

2.2 Preparation of 3-Amino-2-aryazo-4,6-dimethylthieno[2,3-b]pyridine (VIIa-d)

p-Toluidine, p-nitroaniline or 2-methoxy-p-nitroaniline (0.01 mol) was dissolved in dil. hydrochloric acid (12.5 ml, 2N) by warming. The solution was then cooled to 0-5°C and sodium nitrite solution (10 ml, 1N) was gradually added in 20 min with stirring at 0-5°C. The mixture was stirred for further 1 h at 0-5°C and the excess nitrous acid was destroyed using urea (0.2 g). The mixture was filtered and the clear diazo solution was kept at 0-5°C and used for coupling.

2,4-Dinitroaniline (1.83 g, 0.01 mol) was gradually added in 30 min to cold nitrosyl sulphuric acid, previously prepared by dissolving anhydrous sodium nitrite (0.76 g, 0.011 mol) in conc. sulphuric acid (10 ml) by heating to 70°C and then cooling to 10°C. Stirring was continued at 10°C for further 2 h and the diazo solution was diluted with cold glacial acetic acid (100 ml). The excess of nitrous acid was destroyed by adding urea and the mixture was filtered to get a clear diazo solution which was kept at 10°C and used for coupling.

The compound V (2.44 g, 0.01 mol) was dissolved in water (50 ml) and glacial acetic acid (10 ml) and the solution was cooled to 10-15°C. The diazo solution (VI) was then gradually added with vigorous stirring in 30 min at 10-15°C and the mixture was stirred for further 2 h. The mixture was diluted with ice cold water (50 ml) and the pH of the mixture was carefully adjusted to 5-6 using sodium hydroxide solution (8%), maintaining the temperature at 10-15°C. The mixture was further stirred for 2 h at pH 5-6 and 10-15°C and the solid separated was filtered, washed with water, dried and recrystallized from DMF. The characterization data of compounds VIIa-d are given in Table 1.
Table 1—Characterization data of 3-amino-2-arylazo-4,6-dimethylthieno[2,3-b]pyridines (VIIa-d)

<table>
<thead>
<tr>
<th>Compd</th>
<th>Ar</th>
<th>Yield</th>
<th>m.p.</th>
<th>Absorption λ&lt;sub&gt;max&lt;/sub&gt;, nm</th>
<th>log ε</th>
<th>Mol. formula</th>
<th>Found (Calcd), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIIa</td>
<td>4-Methylphenyl</td>
<td>79</td>
<td>185</td>
<td>410</td>
<td>4.32</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>48.56 (48.39)</td>
</tr>
<tr>
<td>VIIb</td>
<td>4-Nitrophenyl</td>
<td>77</td>
<td>207</td>
<td>475</td>
<td>4.50</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>53.55 (53.78)</td>
</tr>
<tr>
<td>VIIc</td>
<td>2-Methoxy-4-nitrophenyl</td>
<td>76</td>
<td>202</td>
<td>510</td>
<td>4.51</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>54.68 (55.05)</td>
</tr>
<tr>
<td>VIIId</td>
<td>2,3-Dinitrophenyl</td>
<td>78</td>
<td>&gt;360</td>
<td>505</td>
<td>4.53</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>64.52 (64.86)</td>
</tr>
</tbody>
</table>

*Crystallization solvent used, DMF.
*Melting points are uncorrected.

2.3 Dyeing
The compounds VIIa-d were applied on polyester fibres as reported earlier.

2.4 Determination of Fastness Properties
The pick-up, light fastness and sublimation fastness were determined as reported earlier.

3 Results and Discussion
The compounds VIIa-d were dark red in colour and were obtained in excellent yield (76-79%) (Table 1). The absorption maxima of these dyes, recorded in their DMF solutions, was in the range of 410-510 nm. The absorption maxima of VIIb-d with one or two electron withdrawing nitro groups showed remarkable bathochromic shifts as compared to that of VIIa with a methyl group. The logarithm of molar extinction coefficient of these compounds varied from 4.32 to 4.53, indicating that their intensity of absorption has surpassed even some of the standard disperse dyes.

The compounds VIIa-d when applied on polyester fibres as disperse dyes gave bright orange to red violet shades (Table 2). The pick up of the compounds VIIa, VIIc and VIIId was excellent (4) and that of VIIb, very good (3). The light fastness of these compounds was moderate to good (2-3) which may be due to the presence of a primary amino group in 3-position in the structure of these compounds. Considerable improvement in light fastness may result by converting the primary amino group to a tertiary amino group such as dimethylamino group, since the primary amino group in the dye structure is attacked by photons exposure from sunlight or an equivalent light source, whereas the tertiary amino groups are not attacked. The sublimation fastness of the compounds VIIa-d was good to very good (3-4).

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References