SYNTHESIS OF SOME STYRYL DYES FROM 3-ETHYL-2-ThIO-4-SELENAZOLIDONE

T. K. RAJA, S. ANANTHAPADMANABHAN, R. GOPALAKRISHNAN and K. M. VIMALA
Research and Development, Hindustan Photo Films Manufacturing Co. Ltd., Ootacamund 643 005, India.

The body of information found in chemical literature on the synthesis of 2-thio-4-selenazolidones\(^1\)\(^2\) is meagre. A literature search was undertaken to synthesize some styryl dyes using thioselezanolidones. Surprisingly, no report has appeared hitherto on the syntheses of styryl dyes using the above mentioned selenium heterocycle. Incidentally the synthesis of thioselezanolidone itself appears to be accomplished by a circuitous method\(^1\)\(^2\) which involves the reduction of diselenodiglycolic acid and a subsequent reaction of the resulting selenoglycolic acid with alkylaryl isothiocyanates. As the above method involves three steps viz. the preparation of diselenodiglycolic acid, its reduction to selenoglycolic acid and the final reaction of the same with appropriate isothiocyanates, we focussed our attention on the preparation of selenoglycolic acid through a simpler procedure. In this context, it is worth mentioning that the facile and easy preparation of sodium hydroselanenide\(^3\) \textit{in situ} in ethanol solution and its reaction on organic compounds containing replaceable chlorine atoms have given impetus to numerous nucleophilic displacement reactions involving hydroselanenide anion. Extending the above methodology to chloroacetic acid, selenoglycolic acid was prepared \textit{in situ} which in turn was reacted with ethylisothiocyanate in the same pot to get 3-ethyl-2-thio-4-selenazolidone (1) in moderate yield.

Having achieved the one pot synthesis of the thioselezanolidone (1) our subsequent interest was to prepare some styryl dyes (2). They were synthesized by reacting thioselezanolidone with appropriate aldehydes in the presence of sodium hydroxide. The structures of the products were fully attested by elemental analysis and PMR spectral data.

Cl-CH\(_2\)-COOH \(\text{NaHS}_2\text{Se} / \text{C}_2\text{H}_5\text{OH}\) \[\text{HSe-CH}_2\text{-COOH}\]

\[\text{R'}\text{NCS} / \text{C}_2\text{H}_5\text{OH} \xrightarrow{50\% \text{ H}_2\text{SO}_4} \begin{array}{c}
\text{Se} \\
\text{S}
\end{array} \begin{array}{c}
\text{R'} \\
\text{CH}
\end{array} \begin{array}{c}
\text{Se} \\
\text{S}
\end{array}
\]

\[R' = \text{C}_2\text{H}_5\]

\[\begin{align*}
2a, & \text{ R} = \\
2b, & \text{ R} = \\
2c, & \text{ R} =
\end{align*}\]

\[\begin{align*}
\text{CH}_3 & \text{--N} \\
\text{CH}_3 & \text{--CH} = \text{CH} \\
\text{O} & \text{--CH} = \text{CH} \\
\text{O} & \text{--CH} = \text{CH}
\end{align*}\]

\textbf{Synthesis of 3-ethyl-2-thio-4-selenazolidone (1)}

Chloroacetic acid (94.5 g, 1 mol) taken in ethanol (50 ml) was added dropwise to a freshly prepared sodium hydroselenenide\(^3\) solution, \textit{in situ} in ethanol under nitrogen cover and was refluxed on a water bath for 2 h. After adjusting the pH of the solution to about 2 by adding 50% sulphuric acid, ethylisothiocyanate (85 g, 1 mol) was added in one lot and refluxed for 5 h. The reaction mixture was cooled, poured onto ice and extracted with chloroform. The chloroform layer was washed with water and dried (anhyd. Na\(_2\)SO\(_4\)). The solvent was removed under reduced pressure to get an oily liquid of thioselezanolidone which was further purified by vacuum distillation.

Yield: 83 g (40%); b.p. 120-125°C/12 mm;
PMR: (CCl\(_4\)) 81.25 (t, 3H, CH\(_2\)-CH\(_3\), J = 6 Hz), 3.28 (S, 2H, Ring CH\(_2\)) and 4.13 (q, 2H, CH\(_2\)-CH\(_3\), J = 6 Hz).

\textbf{General procedure for the preparation of styryl dyes (2)}

To a mixture containing equimolar quantities of 3-ethyl-2-thio-4-selenazolidone and appropriate aldehyde in ethanol (10 ml) was added 5 M aqueous sodium hydroxide (0.5 ml). The solution was left at room temperature for 2 h with occasional stirring. After the removal of ethanol the residue was extracted with ether. The ether layer was washed with saturated sodium bisulphite solution to remove the unreacted aldehyde and then with water and dried (anhyd. Na\(_2\)SO\(_4\)). Removal of ether gave crude styryl dye which was further purified by passing through a silica gel column. The styryl dyes were recrystallised from appropriate solvents. The yield, m.p. and PMR data are given in table 1.
Table 1 Yield, m.p. and PMR data

<table>
<thead>
<tr>
<th>Styril dyes</th>
<th>Yield %</th>
<th>M.p. °C (solvent)</th>
<th>PMR (CDCl₃) δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>54</td>
<td>102–103 (Benzene)</td>
<td>1.23 (t, 3H, CH₂–CH₃, J = 6 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.00 (q, 2H, CH₂–CH₃, J = 6 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.06–7.86 (m, 5H, aromatic protons)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.85 (s, 1H, C₆H₅–CH=)</td>
</tr>
<tr>
<td>2b</td>
<td>59</td>
<td>115–116 (Chloroform)</td>
<td>1.25 (t, 3H, CH₂–CH₃, J = 6 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.17 (q, 2H, CH₂–CH₃, J = 7.5 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.70 (d, 1H, C₆H₅–CH=CH₂, J = 12 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.84 (d, 1H, C₆H₅–CH=, J = 15 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.40–7.57 (m, 5H, aromatic protons) and 7.92 (d, 1H, –CH=CH–, J = 12 Hz)</td>
</tr>
<tr>
<td>2c</td>
<td>62</td>
<td>126–127 (Chloroform)</td>
<td>1.25 (t, 3H, CH₂–CH₃, J = 7.5 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.95 (S, 6H, –N(CH₃)₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.00 (q, 2H, CH₂–CH₃, J = 6 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.20–6.55 (m, 3H, C₆H₅–CH=CH–)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.00–7.30 (m, 3H, C₆H₅–CH = CH–)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.20 (d, 1H, –CH = CH–, J = 9 Hz)</td>
</tr>
</tbody>
</table>

All the m.ps are uncorrected. Satisfactory elemental analysis were obtained for all compounds. NMR spectra were recorded on a spectrometer (Varian-90 MHz) with TMS as internal standard. The authors are grateful to Shri P. R. S. Rao for encouragement.

9 November 1987; Revised 4 January 1988


EUGNONE, A NEW ANTHRAQUINONE FROM THE STEM BARK OF SAPIUM EUGNIFOLIUM

KALPNA RUSIA and S. K. SRIVASTAVA
Department of Chemistry, Dr H. S. Gour University, Sagar 470 003, India.

SAPIUM EUGNIFOLIUM Linn. (Euphorbiaceae) is used in the Indian system of medicine1. Anthraquinone has not been reported so far from this plant. We report here the isolation of a new anthraquinone eugnone (3-hydroxy-1, 6, 7-trimethoxy-2-methyl anthraquinone) and its characterization by colour reactions, spectral data and chemical methods. The powdered stem bark of S. eugnifolium (3 kg) was extracted with ethanol under reflux from 180 h on a water bath. The ethanol from the percolates (201) was removed under reduced pressure on a water bath to get a syrupy mass which was then successively extracted with petroleum ether, benzene, chloroform and ethyl acetate. The excess of solvent was removed from the ethyl acetate extract under reduced pressure to get a yellowish solid mass which on TLC examination showed the presence of a single entity. It was loaded on a column of neutral alumina, eluted with CHCl₃–EtOAc (8:2) and crystallized as yellow coloured crystals from CHCl₃–MeOH (8:2): eugnone. (1), (yield 900 mg).

Eugnone (1), m.p. 278–280°C, C₁₉H₁₂O₆ (M⁺328), showed UV-visible absorption maxima at 225, 250, 380, 405 nm and gave a positive Borntrager reaction2 characteristic for an anthraquinone. The IR (KBr) spectrum of (1) showed characteristic absorptions for hydroxyl (3250–3350 cm⁻¹), methoxyl (2900), methyl (2830 and 1470) and carbonyl (1690) groups. The ¹H NMR spectrum (DMSO-d₆, 8, 90 MHz) of (1) showed a signal for an unchelated hydroxyl (11.20), three methoxyls (4.0) and one methyl group (2.40)³. Further, (1) showed two separate singlets (δ 8.16, 7.50 and 7.66) corresponding to one proton, at positions C-5 and C-8, and C-4, respectively.