A convenient one pot synthesis of some novel benzothiazole and its derivatives

S. G. Badne\textsuperscript{a*}, S. V. Kuberkar\textsuperscript{b}, K. N. Puri\textsuperscript{b}, V. W. Banewar\textsuperscript{c} and G. H. Murhekar\textsuperscript{c}

\textsuperscript{a}Shri Shivaji College of Arts, Commerce and Science, Shivaji Nagar, Akola, Mahatrashtira, India
\textsuperscript{b}P G Department of Chemistry, Yashwant Mahavidalaya, Nanded, M S, India
\textsuperscript{c}Organic Synthesis Division, PG Department of Chemistry, Govt. Vidarbha Institute of Science and Humanities, Amravati, M.S., India

Abstract

The one pot synthesis of 3-amino-4-imino-8-methoxy- (2H) Pyrazolo [3’,4’:4,5] pyrimido[2,1-b] benzothiazole and its 2-substituted derivatives is convenient over traditional rout of synthesis of this organic compound. The novel compound are prepare by condensation of 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-b] benzothiazole with 80% Hydrazine hydrate and other reagent. The structure of the compound was verified by $^1$H NMR and other spectroscopic techniques.

Keywords: Benzothiazole, Hetrocyles, One pot synthesis, Pyrazoles.

Introduction


Material and Methods

The chemical used in this work where reagent grade including hydrazine hydride (Aldrich 99.99%), N,N-Dimethylformamide (Merck, 99.99%), pyridine (Merck, 99.90%), ethanol (Merck, 99%), potassium carbonate (Merck, 99.00%), and distilled water were used.

A mixture of 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-b] benzothiazole (1 mmol) and 80% Hydrazine hydrate 3a, 2-hydrazinobenzothiazole 3b, 6-methyl-2-hydrazinobenzothiazole 3c, 6-chloro-2-hydrazinobenzothiazole 3d, 6-methoxy-2-hydrazinobenzothiazole 3e (2 mmol) were reflux in the presence of N,N-Dimethylformamide (5 ml) and catalytic amount of Potassium Carbonate for 4 hrs. After cooling the solid that appeared were collected by filtration and recrystallised from mixture solvent of DMF and ethyl alcohol to afford crystalline solid of 3a-e.

**Scheme –I**

![Scheme](image)

**Table – 1**

<table>
<thead>
<tr>
<th>R</th>
<th>R’</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-OCH₃</td>
<td>H₂N –N H₂</td>
<td>3 a</td>
</tr>
<tr>
<td>-OCH₃</td>
<td></td>
<td>3 b</td>
</tr>
<tr>
<td>-OCH₃</td>
<td></td>
<td>3 c</td>
</tr>
<tr>
<td>-OCH₃</td>
<td></td>
<td>3 d</td>
</tr>
<tr>
<td>-OCH₃</td>
<td></td>
<td>3 e</td>
</tr>
</tbody>
</table>
Scheme-II

Reflux
Anhydrous K₂CO₃
DMF
3-4 hrs

MeO\-S\-N\-CS\-N\-N\-NH₂

H₂N\-NH₂

Reflux
Anhydrous K₂CO₃
DMF
3-4 hrs

MeO\-S\-N\-CS\-N\-N\-NH₂

H₂N\-N\-S\-C₃H₃

Reflux
Anhydrous K₂CO₃
DMF
3-4 hrs

MeO\-S\-N\-CS\-N\-N\-NH₂

H₂N\-N\-S\-C₃H₃

Reflux
Anhydrous K₂CO₃
DMF
3-4 hrs

MeO\-S\-N\-CS\-N\-N\-OMe

H₂N\-N\-S\-C₃H₃
Tentative mechanism for the formation of compound (3a-e)

The melting points were determined in open capillary tube, and were found to be uncorrected. $^1$H NMR spectra were measured on Gemini 200 MHz spectrometer with TMS as an internal standard. $^{13}$C NMR spectrums were measured on Brucker DPX-400 at 100 MHz with TMS as an internal standard. IR spectrums were recorded in Nujol / KBr palates on Bomen MB 104 FT IR spectrometer. Elemental analyses were performed using a Heraus C, H, N, O rapid analyzer. All reactions were carried out under ambient atmosphere and monitored by Thinlayer Chromatography carried out on 0.2 mm Silica Gel-G-plate using iodine vapor for detection. Mass spectrums were recorded on FT VG-7070 µH Mass spectrophotometer using the EI technique at 70 ev.

Result and Discussion

When 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-b] benzothiazole were reflux independently with 80% Hydrazine hydrate (3a), 2-hydrazinobenzothiazole (3b), 6-methyl-2-hydrazinobenzothiazole (3c), 6-chloro-2-hydrazinobenzoiazole (3d), 6-methoxy-2-hydrazinobenzothiazole (3e), in the presence of N, N-Dimethylfarmamide and catalytic amount of Potassium Carbonate to obtained 2-substituted derivative of 3-amino-8-methoxy-4-imino-2-(2’-benzthiazolyl) (5a-e) respectively.
Table-2: Characterization benzothiazole

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>R</th>
<th>R’</th>
<th>Formula</th>
<th>W_i(calc.) / W_i (found) %</th>
<th>M.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-OCH₃</td>
<td>H₂N-NH₂</td>
<td>C₁₂H₁₀N₆OS</td>
<td>50.34/3.49</td>
<td>29.37</td>
</tr>
<tr>
<td>2</td>
<td>-OCH₃</td>
<td></td>
<td>C₁₉H₁₃N₇OS₂</td>
<td>54.41/3.10</td>
<td>23.38</td>
</tr>
<tr>
<td>3</td>
<td>-OCH₃</td>
<td></td>
<td>C₂₀H₁₅N₇OS₂</td>
<td>55.40/3.46</td>
<td>22.63</td>
</tr>
<tr>
<td>4</td>
<td>-OCH₃</td>
<td></td>
<td>C₁₉H₁₂N₇S₂OCl</td>
<td>50.33/2.64</td>
<td>21.63</td>
</tr>
<tr>
<td>5</td>
<td>-OCH₃</td>
<td></td>
<td>C₂₀H₁₅N₇O₂S₂</td>
<td>53.45/3.34</td>
<td>21.82</td>
</tr>
</tbody>
</table>

Spectroscopic Characterization

1) 3-amino-4-imino-8-methoxy (2H)-pyrazolo[3',4';4,5] pyrimido[2,1-b] benzothiazole [3a]
   (KBr/cm⁻¹) 3317-3250 cm⁻¹(bs), 3168-2914, 1635, 1571, 1456, 1282, 1047; δ_H(200 MHz, DMSO-D6) δ: 3.7 (s, 3H), δ: 3.4 (bs, 2H), δ: 6.9-7.7 (m, 3H), δ: 7.9 (s, 1H), δ: 8.3 (s, 1H), m/z (EI, 70ev) 286 (M⁺), 258, 229, 176, 138.

2) 3-amino-4-imino-8-methoxy-2-(2'-benzothiazolyl)pyrazolo[3',4';4,5]pyrimido[2,1-b] benzothiazole [3b]
   (KBr/cm⁻¹) 3481-3363, 3240, 2948, 1629, 1562, 1462, 1278, 1180 cm⁻¹; δ_H(200 MHz, DMSO-D6) δ: 3.3 (s, 3H), δ: 3.5 (s, 2H), δ: 6.6-7.7 (m, 7H), δ: 8.1 (s, 1H); m/z (EI, 70ev) 419(M⁺).

3) 3-amino-4-imino-8-methoxy-2-(6'-methyl-2'-benzothiazolyl)pyrazolo[3',4';4,5]pyrimido[2,1-b] benzothiazole [3c]
   (KBr/cm⁻¹) 3342-3309 (bs), 3140, 2943, 1649, 1521, 1461, 1292, 1112; δ_H(200 MHz, DMSO-D6) δ: 3.0 (s, 3H), δ: 3.6 (s, 2H), δ: 7.0-7.9 (m, 3H), δ: 8.1 (s, 1H); m/z (EI, 70ev) 433 (M⁺ 100%).


385
(KBr/cm$^{-1}$) 3370-3255 (bs), 3190, 2929, 1609, 1516, 1432, 1278, 1184; $\delta_H$(200 MHz, DMSO-D6) $\delta$2.3 (s, 3H), $\delta$2.5 (s, 3H), $\delta$3.5 (s, 2H), $\delta$6.9-7.7 (m, 3H); $\delta$8.2 (s, 1H).

(KBr/cm$^{-1}$) 3390-3267, 3182, 2960, 1625, 1543, 1440, 1274, 1125; $\delta_H$(200 MHz, DMSO-D6) $\delta$2.4 (s, 3H), $\delta$3.4 (bs, 2H), $\delta$3.9 (s, 3H), $\delta$6.9-7.8 (m, 6H); $\delta$8.4 (s, 1H).

Acknowledgements
Authors are thankful to University Grants Commission, New Delhi, for their financial support for this work under Minor Research Project.

References