SIGMATROPIC REARRANGEMENTS OF ALKENYL BENZOFURYL AND BENZOTHIENYL SULFIDES

A. V. Anisimov, V. S. Babaitsev, T. A. Kolosova, and E. A. Viktorova

The thio Claisen rearrangement of 2-butenyl 2-benzofuryl sulfide, cyclopenten-2-yl 2-benzofuryl sulfide, 2-butenyl 2-benzothonienyl sulfide, and cyclopenten-2-yl 2-benzothonienyl sulfide was investigated. The rates, energies, and entropies of activation of the process were calculated, and the effect of the structure of the sulfide, the polarity of the solvent, and the temperature was demonstrated by comparison of these values. The 1,3-thioallyl rearrangement of 1-methylallyl 3-methyl-2-benzothonienyl sulfide was studied, and it was shown that this reaction competes with the thio Claisen rearrangement.

Transformations of allyl thienyl and allyl sulfides via a scheme involving a concerted [3,3]-sigmatropic shift lead to the formation of alkenylliophenethiols and furanathiols [1], which undergo cyclization to condensed derivatives of thiophene and thiopyran [2]. The extension of this reaction to sulfides of the benzofuran and benzothiophene series makes it possible to expect the production of difficult-to-obtain benzofuranathiols and benzothiophene-thiols, as well as benzothielenothiophenes and benzothielenothiopyrans.

When alkenyl 2-benzofuryl and alkenyl 2-benzothonienyl sulfides Ia-d are heated in the presence of solvents with various polarities and without a solvent, they undergo rearrangement to isomeric thiolis IIa-d (Table 1):

<table>
<thead>
<tr>
<th></th>
<th>Ia-d</th>
<th>IIa-d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Structural formula" /></td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>Ia-c</td>
<td>R'=H, R''=CH3; b-d</td>
<td>R'+R''=(CH2)2;</td>
</tr>
<tr>
<td>a,b</td>
<td>x=O; c,d</td>
<td>x=S</td>
</tr>
</tbody>
</table>

In a number of cases thiolis IIa-d are formed in significant yields (up to 19%) even when sulfides Ia-d are allowed to stand for a long time (10 days) at room temperature.

The rearrangement of all of the investigated sulfides proceeds irreversibly as a first-order reaction with inversion of the allyl group; this follows from the structures of thiolis IIa-cand the methyl derivatives IIIa-c, which were isolated in the transformations of sulfides Ia-c.

A comparison of the kinetic parameters Eact and ΔS for the rearrangement of sulfides Ia-d indicates the absence of an effect of the heteroatom (S or O) on their resistance to rearrangement.

TABLE 1. Results of Experiments on the Rearrangement of Sulfides

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Solvent</th>
<th>Exptl. time, min</th>
<th>Yields of thiols, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>110°</td>
</tr>
<tr>
<td>l c</td>
<td>m-Xylene</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Dibutyl ether</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td>l b</td>
<td>m-Xylene</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Dibutyl ether</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>l a</td>
<td>m-Xylene</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Dibutyl ether</td>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>l d</td>
<td>m-Xylene</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Dibutyl ether</td>
<td>20</td>
<td>—</td>
</tr>
</tbody>
</table>

TABLE 2. Kinetic Parameters of the Rearrangement of the Sulfides

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Solvent</th>
<th>T, °C</th>
<th>(K_o \cdot 10^4) sec(^{-1})</th>
<th>(E_{act}), kcal/mole, ±0.5</th>
<th>(\Delta S,) deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>l a</td>
<td>m-Xylene</td>
<td>120</td>
<td>0.64</td>
<td>3.04</td>
<td>34.0</td>
</tr>
<tr>
<td>l b</td>
<td>Dibutyl ether</td>
<td>120</td>
<td>2.26</td>
<td>11.8</td>
<td>43.0</td>
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<tr>
<td>The same</td>
<td>m-Xylene</td>
<td>130</td>
<td>6.67</td>
<td>12.8</td>
<td>43.0</td>
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<tr>
<td>l c</td>
<td>Dibutyl ether</td>
<td>130</td>
<td>1.15</td>
<td>13.7</td>
<td>44.5</td>
</tr>
<tr>
<td>l d</td>
<td>m-Xylene</td>
<td>130</td>
<td>0.93</td>
<td>14.6</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>Dibutyl ether</td>
<td>130</td>
<td>0.33</td>
<td>11.7</td>
<td>46.5</td>
</tr>
</tbody>
</table>

TABLE 3. Results of Experiments on the Mutual Isomerization of 1-Methylallyl 3-Methyl-2-benzothienyl Sulfide (V) and 2-Butenyl 3-Methyl-2-benzothienyl Sulfide (VI)

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>t, °C</th>
<th>Exptl. time, h</th>
<th>V : VI ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>20</td>
<td>336</td>
<td>90 : 10</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1604</td>
<td>55 : 45</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1</td>
<td>80 : 20</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1</td>
<td>56 : 24</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1</td>
<td>35 : 65</td>
</tr>
<tr>
<td>200*</td>
<td>1</td>
<td>5 : 95</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>20</td>
<td>0.5</td>
<td>5 : 95</td>
</tr>
<tr>
<td></td>
<td>200*</td>
<td>1</td>
<td>5 : 95</td>
</tr>
</tbody>
</table>

*Partial destruction of the sulfide with cleavage of the C–S bond is observed.

The slight change in the \(K_o\) rate constants calculated in the initial sections of the kinetic curves from a first-order equation and the \(E_{act}\) values on passing from m-xylene to dibutyl ether constitutes evidence for a small degree of separation of the charges in the transition state; the large negative \(\Delta S\) values also indicate the high symmetry of the latter.

According to the IR spectroscopic data, thiols IIa–d formed as a result of the reaction are stabilized due to the formation of associates with the solvent (a broad band at 2400–2550 cm\(^{-1}\) in the case of dibutyl ether) or undergo cyclization to give difficult-to-separate mixtures of derivatives of thiendo[2,3-b]thiophene and thiendo[2,3-b]thiopyran in the case of IIa–c. Unstable ammonium salts of the corresponding thiols are formed when the reaction is carried out in nitrogenous bases.

The cyclization of thiol IIId proceeds selectively to give cyclopentano-2,3-dihydrobenzothieno[2,3-b]thiophene, since in this case the formation of an isomeric sulfide with a six-