Dipolarophilic Behaviour of Propadienyl Sulfides towards 3,5-Dichloro-2,4,6-trimethylbenzonitrile Oxide

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We report an exploratory study aimed at shedding light on the site selectivity and regioselectivity of nitrile oxide cycloadditions to propadienyl sulfides.

The growing interest towards 1,3-dipolar cycloadditions to allenes arises from the fact that the resulting cycloadducts still contain an ethylenic bond susceptible to a variety of further transformations. However, the site and regiochemical outcomes of these cycloadditions depend on the complex interplay of several factors, which are far from being thoroughly elucidated. Hence, we devised the opportunity of studying the behaviour of propadienyl sulfides 2a-e towards 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide 3 (Scheme 1). To our knowledge, the only previous report on this kind of allene deals with the reaction of phenylthiopropadiene with 2,6-dichlorobenzonitrile oxide.5

<table>
<thead>
<tr>
<th>Allene</th>
<th>Time (t/h)</th>
<th>Eluant</th>
<th>Products*</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>21</td>
<td>Et₂O</td>
<td>12, 9a, 8, 4a</td>
<td>10, 5, 5, 12</td>
</tr>
<tr>
<td>2b</td>
<td>20</td>
<td>light petroleum–EtOAc (1:1)</td>
<td>4b, 10, 9b</td>
<td>20, 5, 13</td>
</tr>
<tr>
<td>2c</td>
<td>24</td>
<td>PhMe–EtOAc (1:1)</td>
<td>4c, 9c, 8</td>
<td>41, 24, 4</td>
</tr>
</tbody>
</table>

*In order of elution. \(^{*}\)B.p. 45–60°C.

The allenes 2a–e, which were readily available upon base-promoted isomerisation of the corresponding propargyl derivatives 1a–c, were treated with an equimolar amount of 3 in boiling tetrachloromethane. Reaction times, products and yields are reported in Table 1. The lack of isolation of the primary cycloadducts 5 can be accounted for by the pronounced acidity of the isoxazoline hydrogens in position 4, which facilitates the prototropic rearrangement to 9. On the other hand, the lability of 6 is not surprising, since 4-methylene-4,5-dihydroisoxazoles are known to be good dipolarophiles generating spiro diadducts. However, the conversion of 6 into 12 must be stressed as a peculiar example of a thio-Claisen rearrangement followed by a 1,3-addition of the so-formed thiol group onto the nitrile oxide dipole.

In conclusion, the above results demonstrate that nitrile oxides cycloadd preferably (or exclusively) to the external

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double bond of propadienyl sulfides. The degree of regio-
selectivity of this cycloaddition is rather modest, but favours
the formation of 4-alkylidene- over 5-alkylidene-4,5-di-
hydroisoxazoles.

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Techniques used: IR, $^1$H NMR, $^{13}$C NMR, MS, elemental analysis

Schemes: 2

References: 12

Table 1: Reaction of allenes 2a-c with nitrile oxide 3

Table 2: Elemental analyses of new compounds

Table 3: Physical and spectral data for compounds 4, 9, 10 and 12

References cited in this synopsis