A Novel Phase-Transfer Catalysed Cycloaddition of Carbonyl-Stabilized Sulfur Ylides to Vinlyc Sulfones


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In our current studies on the chemistry and synthetic utility of carbonyl stabilized sulfur ylides, we have found that the cycloaddition of dimethylsulfonium phenacylides to aryl vinyl sulfones to be a useful general approach to 1-arylsulfonyl-2-arylcyclopropanes.

Although phase-transfer conditions have been exploited for very many reactions, their application to cyclopropanation reactions of sulfonyl activated double bonds is not well explored. Stabilized sulfur ylides and the more reactive non-stabilized ylides have both been utilized for cyclopropanations, whereby rigorous reaction conditions have often been employed which often result in poor yields. The reaction of vinylic sulfones with carbonyl stabilized sulfur ylides, whether in a two-phase system or not, has not to our knowledge been reported, even though a few instances of the cycloaddition of sulfur ylides to chalcones under phase-transfer conditions are known.

Hence, we now wish to report the application of phase-transfer catalysis to the synthesis of a variety of 1-arylsulfonyl-2-arylcyclopropanes by the cycloaddition reaction of aryl vinyl sulfones with dimethylphenacyl sulfonium bromides in dichloromethane with 50% aqueous sodium hydroxide in the presence of benzyltriethyl ammonium chloride (BTEAC) (Table).

![Cyclopropanation Reaction Scheme]

Cyclopropanation to the activated double bond was done earlier by generating the ylide in situ from the salt or by preparing the stable ylide first. Both procedures, however, require perfectly anhydrous conditions and are time consuming. These difficulties have been overcome by adopting phase-transfer conditions, which avoids the obvious problem of...
<table>
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<tr>
<th>Product</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Yield (%)</th>
<th>m.p.&lt;sup&gt;a&lt;/sup&gt; (°C)</th>
<th>Molecular Formula&lt;sup&gt;b&lt;/sup&gt;</th>
<th>IR (KBr) (cm&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>¹H-NMR (CDCl&lt;sub&gt;3&lt;/sub&gt;/TMS)&lt;sup&gt;d&lt;/sup&gt; (ppm)</th>
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<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>H</td>
<td>153-154</td>
<td>1140, 1200</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (286.3)</td>
<td>1025 1320, 1200</td>
<td>2.30-2.66 (2H, CH₂), 3.40-3.80 (2H, CH₂)</td>
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<td>b</td>
<td>H</td>
<td>Cl</td>
<td>164-165</td>
<td>1155</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (326.8)</td>
<td>1020 1320, 1200</td>
<td>2.46-2.88 (2H, CH₂)</td>
</tr>
<tr>
<td>c</td>
<td>H</td>
<td>Br</td>
<td>198-200</td>
<td>1165</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (364.2)</td>
<td>1010 1305, 1135</td>
<td>3.52-3.88 (2H, CH₂)</td>
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<tr>
<td>d</td>
<td>4-Cl</td>
<td>Cl</td>
<td>167-168</td>
<td>1140</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (355.2)</td>
<td>1025 1305, 1200</td>
<td>2.38-2.80 (2H, CH₂)</td>
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<tr>
<td>e</td>
<td>4-Cl</td>
<td>Br</td>
<td>203-205</td>
<td>1140</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;BrCl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (399.7)</td>
<td>1020 1315, 1170</td>
<td>2.40-2.76 (2H, CH₂)</td>
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<td>f</td>
<td>4-Br</td>
<td>Cl</td>
<td>155-156</td>
<td>1140</td>
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<td>1015 1310, 1170</td>
<td>2.56-2.90 (2H, CH₂)</td>
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<tr>
<td>g</td>
<td>4-Br</td>
<td>CH₃</td>
<td>140-142</td>
<td>1135</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Br₂O&lt;sub&gt;3&lt;/sub&gt;S (379.3)</td>
<td>1015 1315, 1135</td>
<td>2.38 (2H, CH₂)</td>
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<td>h</td>
<td>4-CH₃</td>
<td>Cl</td>
<td>183-184</td>
<td>1135</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (334.8)</td>
<td>1025 1315, 1135</td>
<td>2.38 (2H, CH₂)</td>
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<td>i</td>
<td>3,4-Cl₂</td>
<td>H</td>
<td>211-212</td>
<td>1160</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (355.2)</td>
<td>1020 1310, 1160</td>
<td>2.22-2.68 (2H, CH₂)</td>
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<td>3,4-Cl₂</td>
<td>Br</td>
<td>191-192</td>
<td>1170</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;ClBr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (434.1)</td>
<td>1020 1315, 1170</td>
<td>3.44-3.82 (2H, CH₂)</td>
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<tr>
<td>k</td>
<td>3,4-Cl₂</td>
<td>CH₃</td>
<td>145-146</td>
<td>1145</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;S (369.2)</td>
<td>1020 1310, 1145</td>
<td>2.38-2.82 (2H, CH₂)</td>
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<sup>a</sup> Melting points are uncorrected.  
<sup>b</sup> Satisfactory microanalyses obtained: C ± 0.22, H ± 0.15.  
<sup>c</sup> Recorded on a Beckman Model 18-A spectrophotometer.  
<sup>d</sup> 89 MHz spectra recorded on a Bruker Spectrospin spectrometer.

*Table 1* - Arylsulfonyl-2-arylcyclopropanes 3 Prepared.

The IR spectra (2 max in cm<sup>−1</sup>) of compounds 3 display medium to strong intensity bands in the region 1040–1010, characteristic of the cyclopropane deformation mode of the ring<sup>a</sup> (Table). They also exhibit strong bands in the regions 1320–1305 and 1170–1135 (ν SO₃)<sup>c</sup> and 1680–1655 cm<sup>−1</sup> (ν C=O).<sup>a</sup>

The ¹H-NMR spectra of the compounds in the present investigation exhibited complex multiplets for the cyclopropyl methyl and methine protons. The deshielding effect of the sulfonyl and the carbonyl group is almost the same at the carbon atoms to which they are attached. Hence, the two methine protons can be considered as chemically equivalent and magnetically non-equivalent. Thus the four protons (methylene and methine) of the 1,2-disubstituted cyclopropane shows an AA' BB' pattern, which may be regarded as typical for the trans configuration.<sup>a</sup>

All the cyclopropyl keto sulfones (3) obtained are new products. The procedure herein described constitutes an elegant and simple method for obtaining 1-arylsulfonyl-2-arylcyclopropanes under mild reaction conditions.

**1-Arylsulfonyl-2-arylcyclopropanes 3: General Procedure:**
A mixture of aryl vinyl sulfone<sup>10</sup> (10 mmol), dimethylphenacylsulfonyl bromide<sup>11</sup> (11 mmol), dichloromethane (6 ml) and 50% aqueous sodium hydroxide (4 ml) are placed in a flask equipped with a magnetic stirrer. The contents of the flask are stirred for 20 to 30 min. Benzyltriethylammonium chloride (500 mg) is added and stirring is continued for 3-5 h at room temperature. The reaction mixture is diluted with water (50 ml). The organic layer is separated, washed with water, brine and dried over sodium sulfate. Evaporation of solvent under reduced pressure yields a crude solid, which is filtered through a column of silica gel (60-120 mesh, BDH, with hexane/ether; 3:2, as eluent) to give 3 as a crystalline solid, the purity of which is checked by TLC (Table).

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