Synthesis and characterisation of diastereomeric (E & Z) vinylsulfides and vinylsulfones from p-tollyphenylacetylene

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The addition of p-methylbenzenethiol to p-tollyphenylacetylene results in the formation of a mixture of diastereomeric (E & Z)-1-(4-methylphenyl)-2-phenyl-1-[(4-methylphenyl)thio] ethylenes (1 and 2) and (E & Z)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes (3 and 4). The configurations of these compounds have been established by $^1$H NMR studies, by their preparation from benzyl p-tolyl ketone and p-methylbenzyl phenyl ketone, and by the oxidation of the thioethylenes 1, 2, 3 and 4 to the corresponding sulfonylethylenes 5, 6, 7 and 8 respectively.

Keywords: p-Tollyphenylacetylene, vinylsulfides, vinylsulfones, p-methylbenzenethiol

Vinylene sulfonyl compounds$^1$ and a few mercapto halo ethylene sulfone derivatives$^2$ have been used as effective fungicides. Di-vinyl sulfone and hydroxy diethylsulfone are used to obtain crease-resistant finishes, and there are other sulfones that can be used as fuel additives, plasticizers and anti-icing additives$^3$. This article describes the preparation of (E) & (Z)-1-(4-methylphenyl)-2-phenyl-1-[(4-methylphenyl)thio] ethylenes (1 and 2) and (E & Z)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes (3 and 4) and their corresponding sulfones 5, 6, 7 and 8. The configurations of these compounds have been established by $^1$H NMR studies and synthesis.

Results and Discussion

Unlike the addition of arenethiols to diphenylacetylene, where only a pair of (E) & (Z)-1-arylthio-stilbenes are formed, the addition of p-methylbenzenethiol to p-tollyphenylacetylene resulted in the formation of two pairs of diastereoisomeric (E) & (Z)-1-(4-methylphenyl)-2-phenyl-1-[(4-methylphenyl)thio] ethylenes (1 and 2) and (E & Z)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes (3 and 4) (Scheme I).

They were separated by fractional crystallisation. The (E) isomers 1 and 3 were formed selectively when compared to their respective (Z) isomers 2 and 4. The addition of thiols to acetylenes were reported$^4-8$ to yield primarily the cis-addition products, and the trans-addition products were obtained in minor portion. The (E) isomers 1 and 3 in the present investigation are also sterically preferred over the corresponding (Z) isomers 2 and 4. The formation of two pairs of diastereomeric (E) and (Z) isomers in the present investigation are possible because the two acetylenic carbons in p-tollyphenylacetylene are dissimilar, where both the acetylenic carbons can be attacked independently by the thio radical, and the addition can be both cis and trans. The cis-addition of thiols leads to (E) isomers and the trans-addition leads to (Z) isomers. Out of four isomers 1, 2, 3 and 4, the diastereoisomers 3 and 4 together are formed in higher proportion when compared to the diastereomers 1 and 2. This may be attributed to the stabilities of the intermediate radicals involved. The formation of compounds 3 and 4 involves the intermediate radical I and formation of compounds 1 and 2 involves the intermediate radical II. The radical I is expected to be more stable than II due to the contribution of a greater number of resonance structures (Scheme II). Hence, compounds 3 and 4 together are formed in higher proportion when compared to 1 and 2. Compounds 1 and 2 are also prepared from benzyl p-tolyl ketone, while 3 and 4 are prepared from p-methylbenzyl phenyl ketone.

Benzy1 phenyl ketone is known$^9$ to react with benzenethiol, forming a mixture of (E) and (Z)-1-phenyl thiostilbenes in which the (E) isomer predominates. Similarly, the reaction of p-methylbenzenethiol with benzyl p-tolyl ketone in the present investigation gave a mixture of (E) & (Z)-1-(4-methylphenyl)-2-phenyl-1-[(4-methylphenyl)thio] ethylenes in which (E) isomer predominates$^{10}$. The (E) isomer has the same melting point as 1 obtained earlier, and there is no depression in the mixed melting point. The (Z) isomer has the same melting point as 2, and their IR spectra were also identical. On the other hand, the reaction of p-methylbenzenethiol...
with \( p \)-methylbenzyl phenyl ketone gave a mixture of \((E) \) & \((Z)\)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl)thio] ethylenes (Scheme I). The \((E)\) isomer was found to be identical with 3 from their melting point and mixed melting point, and \((Z)\) isomer was found to be identical with 4 from its melting point and IR spectra. All the compounds 1, 2, 3 and 4 on oxidation with hydrogen peroxide gave the corresponding sulfones 5, 6, 7 and 8 respectively (Scheme III).

The IR spectra of all the compounds showed a weak band in the region of 1625-1644 cm\(^{-1}\) due to the C=\(C\) stretching frequency (Table I). All the compounds 1-8 showed a prominent band in the region of 1071-1087 cm\(^{-1}\) for the S-aryl group and the sulfones 5-8 showed sharp asymmetric and symmetric stretching frequencies in the region 1301-1311 cm\(^{-1}\) and 1141-1144 cm\(^{-1}\) respectively due to sulfone group. Because the compounds 1-8 are tri-substituted ethylenes, in \(^1\)H NMR spectra chemical shifts are used rather than the coupling constants, to differentiate between \((E)\) and \((Z)\) isomers. The chemical shifts of vinyl protons of \textit{cis } (E) thio-ethylenes 1 and 3 occur at a lower field strength (\( \delta \) 7.1
and 7.4) than their corresponding trans (Z) thio ethylenes 2 and 4 (δ 6.7 and 6.9). Similar observations were made for β-croponates by Peeran and colleagues¹⁶ in sulphide-sulfone by Stirling¹⁷ and in monosulfides by Peeran and colleagues. On the other hand, the chemical shifts of the vinyl protons of cis (E) sulfonyl ethylenes 5 and 7 occur at a higher field strength (δ 7.0 and 7.1) than their corresponding trans (Z) sulfonyl ethylenes 6 and 8 (δ 7.9 and 7.9). The characterisation data of all the newly prepared compounds are presented in Table I.

**Experimental Section**

Melting points were determined on Mel-temp apparatus, Laboratory Devices, Cambridge, MA, USA and are uncorrected. IR spectra were recorded using KBr pellets on Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. ¹H NMR spectra were recorded at 400 MHz on a Bruker-400 spectrometer.

**Reaction of p-methylbenzenethiol with p-tolylphenylacetylene**

A solution of 23.0 g (0.12 mol) of p-tolylphenylacetylene in 150 mL of n-heptane was heated to its boiling point and 6.2 g (0.05 mol) of p-methylbenzenethiol was added. The reaction mixture was refluxed for 24 hr. The solution was washed with 2% NaOH solution and water and dried over anhyd. CaCl₂. The residue left after the evaporation of the

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**Table I — Characterisation data of various thio ethylenes and sulfonyl ethylenes**

<table>
<thead>
<tr>
<th>Compd</th>
<th>m.p. °C</th>
<th>Mol. Formula</th>
<th>Found % (Calcd)</th>
<th>¹H NMR, CDCl₃ =C-H (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96-98</td>
<td>C₂₂H₂₀S</td>
<td>83.38 (83.50) 6.30 (6.37) 10.06 (10.13)</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>68-70</td>
<td>C₂₂H₂₀S</td>
<td>83.36 (83.50) 6.29 (6.37) 10.01 (10.13)</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>78-80</td>
<td>C₂₂H₂₀S</td>
<td>83.35 (83.50) 6.25 (6.37) 10.03 (10.13)</td>
<td>7.4</td>
</tr>
<tr>
<td>4</td>
<td>52-54</td>
<td>C₂₂H₂₀S</td>
<td>83.34 (83.50) 6.29 (6.37) 10.08 (10.13)</td>
<td>6.9</td>
</tr>
<tr>
<td>5</td>
<td>150-52</td>
<td>C₂₂H₂₀S₂</td>
<td>75.69 (75.83) 5.66 (5.79) 9.11 (9.20)</td>
<td>7.0</td>
</tr>
<tr>
<td>6</td>
<td>140-42</td>
<td>C₂₂H₂₀S₂</td>
<td>75.72 (75.83) 5.68 (5.79) 9.05 (9.20)</td>
<td>7.9</td>
</tr>
<tr>
<td>7</td>
<td>111-14</td>
<td>C₂₂H₂₀S₂</td>
<td>75.70 (75.83) 5.67 (5.79) 9.09 (9.20)</td>
<td>7.1</td>
</tr>
<tr>
<td>8</td>
<td>197-201</td>
<td>C₂₂H₂₀S₂</td>
<td>75.69 (75.83) 5.65 (5.79) 9.07 (9.20)</td>
<td>7.9</td>
</tr>
</tbody>
</table>
The first fraction having needle shaped crystals weighed 5.8 g (18.7%) \((E)-1-((4\text{-methylphenyl})-2\text{-phenyl-1-[(4-methylphenyl)thio]}\) ethylene 1 was purified by recrystallization from absolute alcohol, m.p. 96-98°C.

The mother liquor which was obtained after removal of first fraction on further cooling also formed a solid. It was purified by recrystallization from methanol to give colourless crystals of \((E)-2-(4\text{-methylphenyl})-1-phenyl-1-[(4-methylphenyl)thio]\) ethylene 3 weighing 13.4 g (43.2%), m.p. 78-80°C.

The third fraction weighed 2.8 g (9.0%) and was obtained as a solid on fractional crystallization which gave \((Z)-1-((4\text{-methylphenyl})-2\text{-phenyl-1-[(4-methylphenyl)thio]}\) ethylene 2, m.p. 68-70°C.

The fourth fraction obtained on cooling gave needle shaped crystals which weighed 2.9 g (9.35%) identified as \((Z)-2-(4\text{-methylphenyl})-2\text{-phenyl-1-[(4-methylphenyl)thio]}\) ethylene 4, m.p. 52-54°C.

**Preparation of \((E)\) and \((Z)\)-1-(4-methylphenyl)-2-phenyl-1-[(4-methyl phenyl) thio] ethylenes (1 and 2) from benzyl p-tolyl ketone**

To a solution of 10.5 g (0.05 mol) of benzyl p-tolyl ketone in 100 mL of dichloromethane, 15.52 g (0.125 mol) of p-methylbenzenethiol was added. The solution was stirred with a magnetic stirrer at RT and 2.26 g (0.017 mol) of anhyd. AlCl\(_3\) was added in small portions over a period of 10 min. The reaction mixture turned turbid as the reaction proceeded. After the addition, the mixture was further stirred for another 30 min and poured into 75 mL of water. The resulting mixture was extracted with 150 mL of dichloromethane, washed with 200 mL of brine, and dried over anhyd. Na\(_2\)SO\(_4\); the solvent was evaporated to give a light yellow oil which solidified on cooling and weighed 22.1 g. The solid was subjected to fractional crystallisation from 95% ethanol to yield 9.5 g (43%) of \((E)-2-(4\text{-methylphenyl})-1-phenyl-1-[(4-methylphenyl)thio]\) ethylene 3, m.p. 78-80°C. The melting point of this compound was not depressed on admixture with 3 prepared earlier from p-tolyl phenylacetylene.

After separating the \((E)-2-(4\text{-methylphenyl})-1-phenyl-1-[(4-methyl phenyl)thio]\) ethylene 3 the remaining fraction was cooled to get a solid which on recrystallisation gave 9.6 g (41%) of \((Z)-2-(4\text{-methylphenyl})-2\text{-phenyl-1-[(4-methylphenyl)thio]}\) ethylene 4, m.p. 52-54°C. The melting point and IR spectrum of this compound was identical to that of 4 obtained earlier. The purity of all the compounds was determined using HPLC.

**General procedure for the oxidation of 1 and 2 to \((E)\) and \((Z)\)-1-(4-methylphenyl)-2-phenyl-1-[(4-methylphenyl)sulfonyl] ethylenes (5 and 6) and 3 and 4 to \((E)\) and \((Z)\)-2-(4-methylphenyl)-1-phenyl-1-[(4-methylphenyl) sulfonyl] ethylenes (7 and 8)**

A solution of 1 or 2 or 3 or 4 (0.002 mol) in acetic acid (25 mL) was heated to its boiling point and 30% of hydrogen peroxide (8 mL) was added and refluxed for 2 hr. The solid which separated on cooling was filtered and purified by recrystallization from 95% ethanol. The yields varied from 71-82% and the melting points of the sulfones thus obtained are given in Table I.

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References