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Investigation of the Addition of Benzenethiol to *p*-Chlorophenylphenylacetylene

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The addition of benzenethiol to p-*chlorophenylphenylacetylene results in the formation of a mixture of two pairs of diastereomeric (*E*)- and (*Z*)-1-*p-*chlorophenyl-2-phenyl-1-phenylthioethylenes (**1** and **2**) and (*E*)- and (*Z*)-1-*p-*chlorophenyl-2-phenyl-2-phenylthioethylenes (**3** and **4**). The configurations of these compounds have been established by ^1H NMR studies, by their preparation from benzyl* p-*chlorophenyl ketone and* p-*chloro-benzylphenyl ketone, and by the oxidation of the thioethylenes **1**,**2**, **3**, and **4** to the corresponding sulphonylethylenes **5**, **6**, **7**, and **8**, respectively.*

Keywords (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylenes; (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylenes; (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-1-phenylsulphonylethylenes; (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylsulphonyl-ethylenes

INTRODUCTION

Vinylene sulphonyl compounds[1] and a few mercapto haloethylene sulphone derivatives[2] have been used as effective fungicides. Divinyl sulphone and hydroxydiethyl sulphone are used to give crease-resistant finishes, and there are other sulphones that can be used as fuel additives, plasticisers, and anti-icing additives.[3] This article describes the preparation of (*E*)- and (*Z*)-1-*p*-chlorophenyl–2–phenyl-1-phenylthioethylenes (**1** and **2**), and (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylenes (**3** and **4**) and their corresponding sulphones (**5**,

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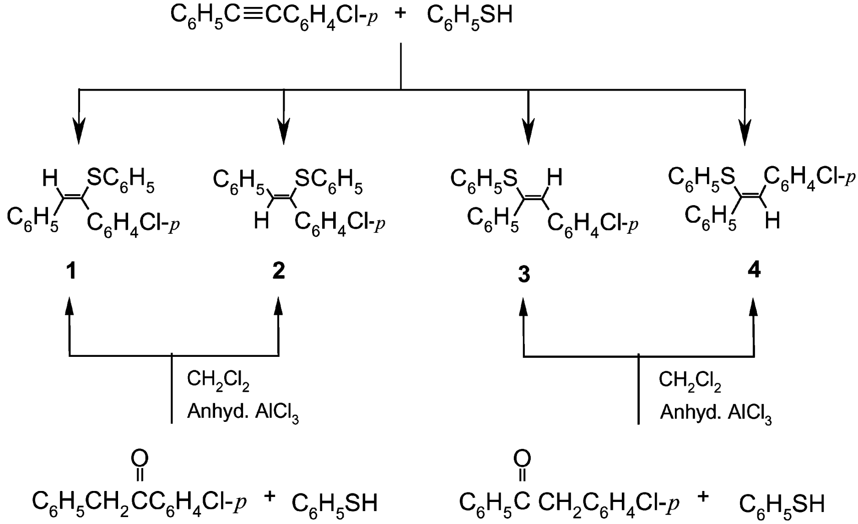
6, **7**, and **8**). The configurations of these compounds have been established by ^{1}H NMR studies.

DISCUSSION

Unlike the addition of arenethiols to diphenylacetylene, where only a pair of (*E*)- and (*Z*)-1-arylthiostilbenes are formed, the addition of benzenethiol to *p*-chlorophenylphenylacetylene resulted in the formation of two pairs of diastereomeric (*E*)- and (*Z*)-1-*p*-chloro-phenyl-2-phenyl-1-phenylthioethylenes (**1** and **2**), and (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylenes (**3** and **4**) (Scheme 1).



SCHEME 1

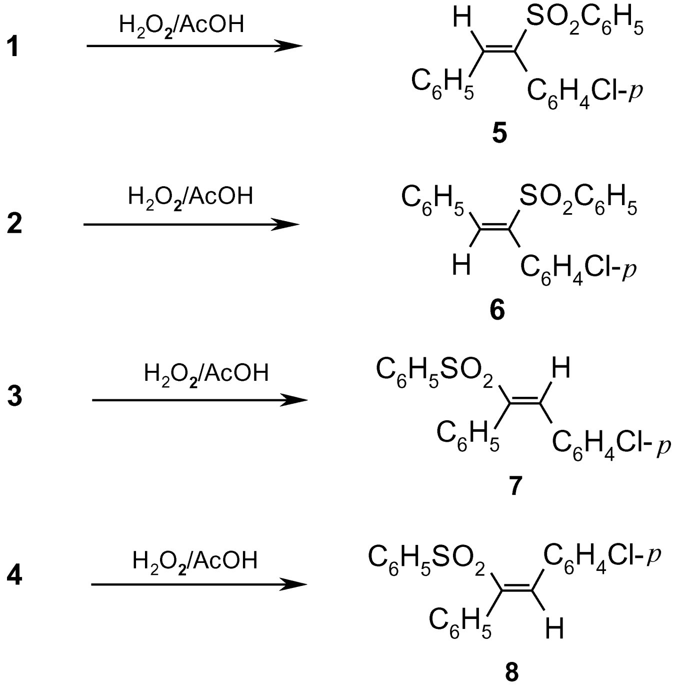
They were separated by fractional distillation under reduced pressure. The (*E*)- isomers **1** and **3** were formed selectively when compared to their respective (*Z*)- isomers (**2** and **4**). The addition of thiols to acetylenes were reported[4–8] to yield primarily the *cis*- addition products, and the *trans*- addition products were obtained in minor proportion. 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 in *p*-chlorophenylphenylacetylene the two acetylenic carbons 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 thiol leads to (*E*)- isomers and the *trans*- addition leads to (*Z*)- isomers. Out of four isomers, **1**, **2**, **3**, and **4**, the diastereomers **3** and **4** together are formed in a higher proportion when compared to the diastereomers **1** and **2**. This may be attributed to the stabilities of the intermediate radicals involve. The formation of compounds **3** and **4** involves the intermediate radical **I**, and compounds **1** and **2** involve the intermediate radical **II**. The radical **I** is expected to be more stable than **II** due to the contribution of more of a number of resonance structures (Scheme 2). 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*-chlorophenyl ketone, and **3** and **4** are prepared from *p*-chlorobenzyl phenyl ketone.

I **II**

SCHEME 2

Benzylphenyl ketone is known[9] to react with benzenethiol forming a mixture of (*E*)- and (*Z*)-1-phenylthiostilbenes in which the (*E*)- isomer predominates. Similarly, the reaction of benzenethiol with benzyl *p*-chlorophenyl ketone in the present investigation gave a mixture of (*E*)- and (*Z*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylenes in which the (*E*)- isomer predominates. The (*E*)- isomer has the same m.p. as **1** obtained earlier, and there is no depression in the mixed melting point. The (*Z*)- isomer has the same b.p. as **2**, and their IR spectra were also identical. On the other hand, the reaction of benzenethiol with *p*-chlorobenzylphenyl ketone gave a mixture of (*E*)- and (*Z*)- 1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylenes (Scheme 1). The (*E*)- isomer was found to be identical with **3** from their melting points and mixed melting point, and (*Z*)-isomer was found to be identical with (**4**) from their b.p. and IR spectra. All the compounds, **1**, **2**, **3**, and **4**, on oxidation with hydrogen peroxide gave the corresponding sulphones, **5**, **6**, **7**, and **8**, respectively. This is shown in Scheme 3.

In the UV region, the (*E*)- isomers absorb at a longer wavelength than their corresponding (*Z*)- isomers. The $\varepsilon_{\max}$ of the (*E*)- isomers are also higher than those of their (*Z*)- counterparts. This is in accordance with the generally accepted view that the (*E*)- isomers absorb at a longer wavelength and $\varepsilon_{\max}$ is also higher than the corresponding (*Z*)- isomers. The IR spectra of all the compounds showed a weak band[10] in the



SCHEME 3

region of 1621–1679 cm^{-1} due to the C=C stretching frequency (Table I). All the compounds **1–8** showed a prominent band[11] in the region of 1083–1090 cm^{-1} for the S-aryl group, and the sulphones **5–8** showed sharp asymmetric and symmetric stretching frequencies[12] in the region 1298–1305 and 1139–1148 cm^{-1}, respectively, due to sulphone group. Because the compounds **1–8** are trisubstituted ethylenes, in ^{1}H NMR spectra chemical shifts[13,14] are used, rather than coupling constants, to differentiate between (*E*)- and (*Z*)- isomers. The chemical shifts of vinyl protons of *cis*- (*E*)- thioethylenes **1** and **3** occur at a lower field strength (δ 7.3 and 7.4) than their corresponding *trans*- (*Z*)- thioethylenes **2** and **4** (δ 6.9 and 7.0). Similar observations were made in β-crotonates by Peeran and colleagues,[15] in sulphide-sulphones by Stirling[16] and in monosulphides by Peeran and colleagues. On the other hand, the chemical shifts of the vinyl protons of *cis*- (*E*)-sulphonylethylenes **5** and **7** occur at a higher field strength (δ 7.3 and 7.2) than their corresponding *trans*- (*Z*)-sulphonylethylenes **6** and **8** (δ 8.0 and 7.9). A similar observation was made in disulphones by Stirling.[16] The characterisation data of all the newly prepared compounds are presented in Table I.

TABLE I Characterization Data of Various Thioethylenes and Sulphonylethylenes

			Found (%)/Calc			UV (EtOH)		IR (KBr/ neat) cm^{-1}				
Compound	M.P./B.P.($^\circ$C)	Molecular formula	C	H	S	λ_{max} nm	ε_{max}	$\nu_{C{=}C}$	ν_{S-aryl}	ν_{SO_2}		^{1}H NMR $CDCl_3$ $=$CH- δ(ppm)
1	80–81	$C_{20}H_{15}ClS$	74.19 (74.40)	4.34 (4.68)	9.78 (9.93)	315	8,225	1658	1087	—	—	7.3
2	162–163/5 mm	$C_{20}H_{15}ClS$	74.10 (74.40)	4.52 (4.68)	9.85 (9.93)	304	8,010	1677	1090	—	—	6.9
3	41–42	$C_{20}H_{15}ClS$	74.20 (74.40)	4.58 (4.68)	9.75 (9.93)	320	11,201	1679	1090	—	—	7.4
4	191–192/5 mm	$C_{20}H_{15}ClS$	74.14 (74.40)	4.63 (4.68)	9.68 (9.93)	305	8,860	1677	1086	—	—	7.0
5	101–102	$C_{20}H_{15}ClO_2S$	67.48 (67.69)	4.13 (4.26)	8.95 (9.04)	275	14,404	1621	1083	1298	1139	7.3
6	169–170	$C_{20}H_{15}ClO_2S$	67.45 (67.69)	4.17 (4.26)	8.93 (9.04)	273	12,746	1631	1086	1304	1142	8.0
7	111–112	$C_{20}H_{15}ClO_2S$	67.35 (67.69)	4.26 (4.26)	9.18 (9.04)	283	19,456	1629	1085	1305	1148	7.2
8	237–238	$C_{20}H_{15}ClO_2S$	67.46 (67.69)	4.17 (4.26)	9.03 (9.04)	277	14,837	1629	1085	1302	1146	7.9

EXPERIMENTAL

Melting points were determined on Mel-Temp. apparatus, Laboratory Devices, Cambridge, MA, USA, and are uncorrected. UV spectra were recorded on Shimadzu Model 160A UV-visible recording Spectrophotometer. IR spectra on were recorded a Perkin-Elmer Infrared Spectrophotometer Model 983G. ^{1}H NMR were recorded at 400 MHz with a Bruker AVANCE instrument.

Reaction of Benzenethiol With *p*-Chlorophenylphenylacetylene

A Solution of 21.24 g of (100 mmole) of *p*-chlorophenylphenylacetylene in 150 mL of *n*-heptane was heated to its b.p., and 16.5 g (150 mmole) of benzenethiol was added. The reaction mixture was refluxed for 24 h. The solution was washed successively with 200 mL of 2% sodium hydroxide solution and water (250 mL) and dried over anhydrous calcium chloride. The residue left after the evaporation of the solvent was subjected to fractional distillation under reduced pressure. Four fractions were obtained.

The first fraction upon cooling solidified and weighed 7.3 g (18.8%). It was recrystallized from acetic acid to give needle-shaped crystals of (*E*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylene (**1**), m.p. 80–81°C.

The second fraction on cooling became a pasty mass and because solidified on treatment with *n*-heptane and weighed 17.8 g (45.4%). It was recrystallized from methanol to give colorless crystals of (*E*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylene (**3**), m.p. 41–42°C.

The third fraction weighed 3.7 g (9.7%) and did not solidify even on cooling or trituration with *n*-heptane or methanol. It was distilled under reduced pressure, and the distillate was collected at 162–163°C/5 mm, which gave (*Z*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylene (**2**).

The fourth fraction was obtained as a brown viscous oil, weighed 3.9. g (10%), and was redistilled under reduced pressure. The distillate collected at 191–192°C/5 mm gave (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylene (**4**).

Preparation of (*E*)- and (*Z*)-1-*p*-Chlorophenyl-2-phenyl-1-phenylthioethylenes (1 and 2) from Benzyl *p*-Chlorophenyl Ketone

To a solution of 11.55 g (50 mmol) of benzyl *p*-chloro-phenyl ketone in 100 mL of chloroform, 13.75 g (125 mmol) of benzenethiol was added.

The solution was stirred with a magnetic stirrer at r.t., and 2.26 g (17 mmol) of anhydrous aluminium chloride 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 100 mL of methylene chloride, washed with 200 mL of saturated brine, and dried over anhydrous $MgSO_4$; the solvent was evaporated to give 12.9 g of a light yellow oil. The light yellow oil was treated with *n*-heptane, and the solid separated was filtered and recrystallized from acetic acid yielding 6.8 g (42.1%) of (*E*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylene **(1)**, m.p. 80–81°C. The melting point of this compound was not depressed on admixture with **1** prepared earlier from *p*-chlorophenyl-phenylacetylene.

The *n*-heptane solution obtained after separating **1** on evaporation of the solvent gave 6.1 g (37.7%) of (*Z*)-1-*p*-chlorophenyl-2-phenyl-1-phenylthioethylene **(2)** as a yellow liquid. It was distilled under reduced pressure at a b.p. of 161–162°C/5 mm. Its b.p. and IR spectra were identical with that of **2** obtained earlier.

Preparation of (*E*)- and (*Z*)-1-*p*-Chlorophenyl-2-phenyl-2-phenylthioethylenes (3 and 4) from p-Chlorobenzylphenyl Ketone

A solution of 16.5 g (150 mmol) of benzenethiol and 13.85 g (60 mmol) of *p*-chlorobenzylphenyl ketone in chloroform (150 ml) was stirred at r.t., and 3 g (23 mmol) of anhydrous aluminium chloride was added in small portions over a period of 15 min. The reaction mixture turned turbid after the addition. The mixture was stirred further for another 45 min and poured into 100 mL of water. The resulting mixture was extracted with 150 mL of methylene chloride, washed with 200 mL of saturated brine, and dried over anhydrous $MgSO_4$; the solvent was evaporated to give 17.2 g of a light yellow oil. The light yellow oil was treated with *n*-heptane, and the solid separated was filtered and recrystallized from methanol to yield 7.96 g (41.0%) of (*E*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylene **(3)**, m.p. 41–42°C. The melting point of this compound was not depressed on admixture with **3** prepared earlier from *p*-chlorophenyl-phenylacetylene.

After separating the (*E*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylene (3), the *n*-heptane solution on evaporation of the solvent gave 8.3 g (43.0%) of (*Z*)-1-*p*-chlorophenyl-2-phenyl-2-phenylthioethylene **(4)** as a yellow liquid. It was distilled under reduced pressure, b.p. 191–192°C/5 mm. The b.p. and IR spectra of this compound was same as that of **4** obtained earlier.

General Procedure for the Oxidation of 1 and 2 to (*E*)- and (*Z*)-1-*p*-Chlorophenyl-2-phenyl-1-phenylsulphonylethylenes (5 and 6) and 3 and 4 to (*E*)- and (*Z*)-1-*p*-Chlorophenyl-2-phenyl-2-phenylsulphonylethylenes (7 and 8)

A solution of **1** or **2** or **3** or **4** (2 mmol) in acetic acid (25 mL) was heated to its b.p., and 30% hydrogen peroxide (5 mL) was added and refluxed for 2 h. The solid separated on cooling was filtered and recrystallized from 95% ethanol. The yields varied from 78–95% and melting points of the sulphones thus obtained are given in Table I.

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