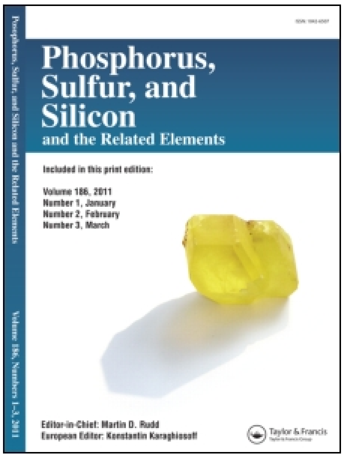

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# SYNTHESIS AND MASS SPECTRAL REARRANGEMENTS OF SOME NEW MIXED VINYL SULPHIDE-SULPHONES AND DISULPHONES

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# SYNTHESIS AND MASS SPECTRAL REARRANGEMENTS OF SOME NEW MIXED VINYL SULPHIDE-SULPHONES AND DISULPHONES

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Stererospecifically prepared (*E*)-1-chloro-2-*p*-chlorophenylsulphonylstilbene (**1**) and (*Z*)-1-bromo-2-*p*-chlorophenylsulphonylstilbene (**6**) on reaction with sodium alkyl thiolates in abs. ethanol underwent nucleophilic displacement of halogens leading to the formation of (*E*)- and (*Z*)-1-alkylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**2** and **7**). The sulphide-sulphones **2** and **7** on oxidation afforded the corresponding disulphones (**3** and **8**). Mass spectra of (*E*)- and (*Z*)-isomers of 1-butylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**2c** and **7c**) and their corresponding disulphones **3c** and **8c** are examined at 70 eV. Smiles type rearrangement is noticed only in **2c** and **7c** but not in **3c** and **8c**. McLafferty type rearrangement involving migration of hydrogen from aryl and/or alkyl groups to ethylenic carbon is observed both in sulphide-sulphones and in disulphones. Sulphonyl-sulphinate rearrangement with vinyl migration as the predominant pathway is a noted feature in both sulphide-sulphones and disulphones.

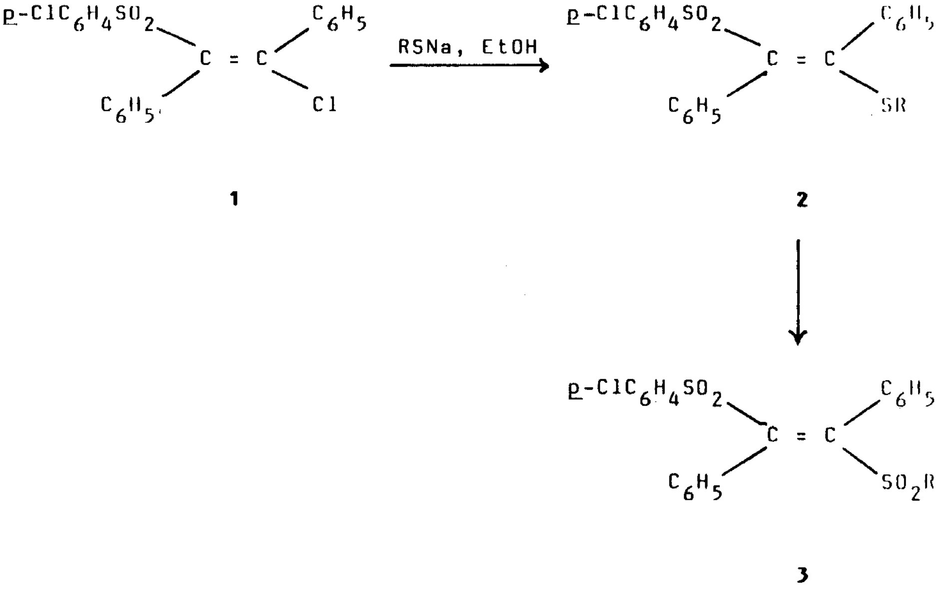
*Key words:* (E)-1-*p*-chlorophenylsulphenylstilbene; (E)-1-chloro-2-*p*-chlorophenylsulphonylstilbene; (Z)-1-bromo-2-*p*-chlorophenylsulphonylstilbene; (E)- and (Z)-1-alkylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes; (E)- and (Z)-1-alkylsulphonyl-2-*p*-chlorophenylsulphonylstilbenes.

## INTRODUCTION

Bis(organo sulphonyl)ethylenes,[1,2] vinylene sulphonyl compounds[3] are best known for their fungicidal activity to protect seeds. Further, activity is found to vary depending on geometry and the substituents present in the compounds. Even though some reports[4–8] have appeared on synthesis of unsaturated sulphide-sulphones and disulphones, mass spectral characterisation data available on these compounds is very scanty. Previously we have reported[9,10] the syntheses and mass spectral rearrangements of unsaturated bis-sulphides and bis-sulphones. Herein, we report the synthesis of some new (*E*)- and (*Z*)-1-alkylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**2** and **7**) and their corresponding disulphones (**3** and **8**) and mass spectral study of (*E*)- and (*Z*)-1-butylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**2c** and **7c**) and their corresponding disulphones (**3c** and **8c**).

## DISCUSSION

(*E*)-1-Chloro-2-*p*-chlorophenylsulphonylstilbene (**1**),[7,11] on reaction with sodium salt of different alkyl thiols in abs. ethanol underwent nucleophilic displacement of chlorine to furnish (*E*)-1-alkylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**2**) with retention of configuration[12,13] (Scheme I). Compound **2** on oxidation with



**2** and **3a**: R = $CH_3CH_2$
**b**: R = $CH_3CH_2CH_2$
**c**: R = $CH_3(CH_2)_2CH_2$
**d**: R = $(CH_3)_2CHCH_2$

SCHEME I

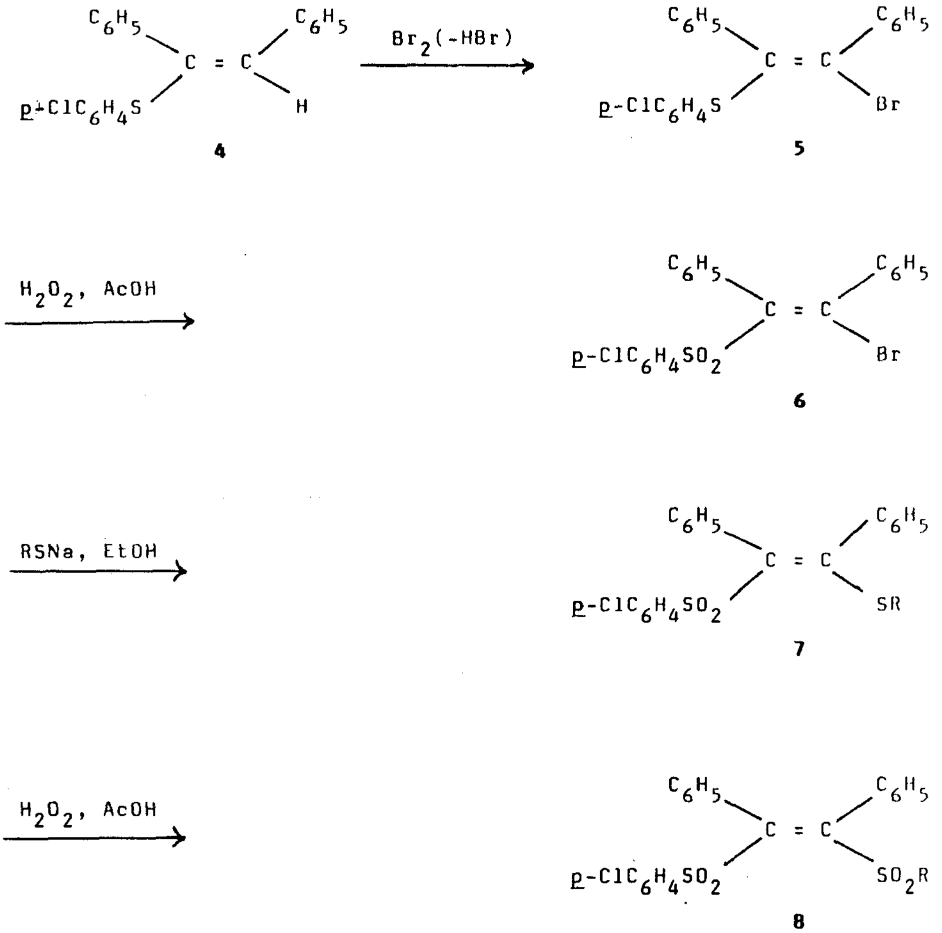
excess of 30% $H_2O_2$ afforded (*E*)-1-alkylsulphonyl-2-*p*-chlorophenylsulphonylstilbenes (**3**).

Similar reactions of (*Z*)-1-bromo-2-*p*-chlorophenylsulphonylstilbene (**6**) gave (*Z*)-1-alkylsulphenyl-2-*p*-chlorophenylsulphonylstilbenes (**7**) and their corresponding disulphones (**8**). (Scheme II). Compound **6** is prepared by the oxidation of the product obtained by the bromination[4,5] of (*E*)-1-*p*-chlorophenylsulphenylstilbene (**4**).[7]

The UV, $\lambda_{max}$ of the conjugation band for (*E*)-sulphide-sulphones **2** observed around 305–315 nm region and for their corresponding (*Z*)-isomers **7** around 298–305 nm region. The (*E*)-isomers of disulphones **3** exhibited the conjugation band around 246–251 nm region and the corresponding (*Z*)-isomers **8** around 243–245 nm region.

The IR $\nu_{max}$ for all the compounds (**2**, **3**, **7** and **8**) exhibited sharp bands around 1305–1332 and 1126–1160 $(SO_2)$[13] and 1080 and 1099 $cm^{-1}$ (C—S)[14,15].

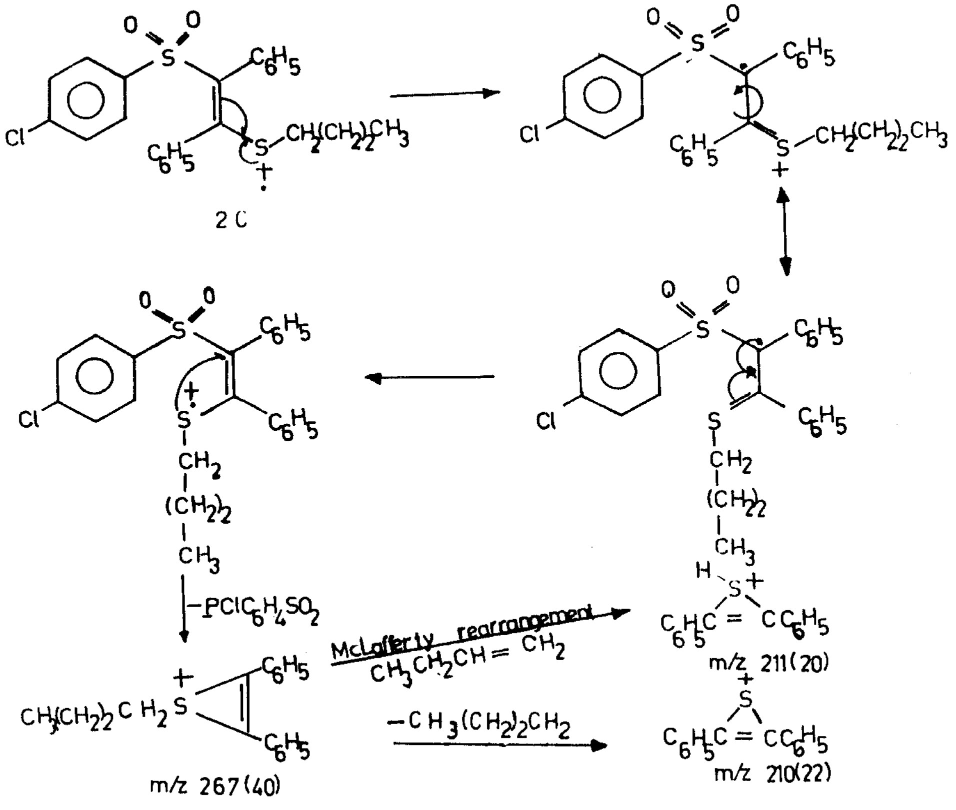
The low resolution mass spectral features of (*E*)- and (*Z*)-isomers of sulphide-sulphones (**2c** and **7c**) are found to be almost identical and so also those of the corresponding disulphones (**3c** and **8c**). The $M^+$ ion peak followed by $M^+ + 1$ and $M^+ + 2$ peaks is noticed both in sulphide-sulphones and disulphones. The



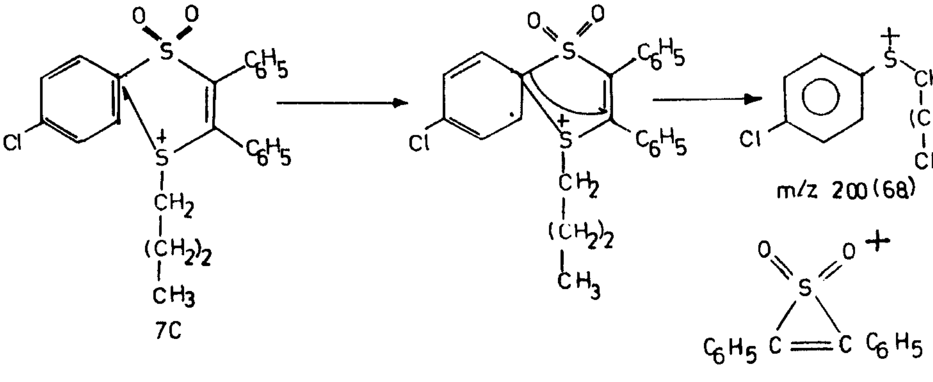
**7** and **8a**: $R = CH_3CH_2$
**b**: $R = CH_3CH_2CH_2$
**c**: $R = CH_3(CH_2)_2CH_2$
**d**: $R = (CH_3)_2CHCH_2$

SCHEME II

base peaks in sulphide-sulphones and disulphones are constituted by diphenylacetylene radical ion (m/z 178)[16] and $C_7H_5O^+$ ion (m/z 105) respectively. The fragment ion, $C_7H_5O^+$ which also constitutes a prominent peak in sulphide-sulphones is assumed to be formed via thiobenzil intermediate (m/z 226) in **2c** and **7c** and via benzil intermediate (m/z 210) in **3c** and **8c** through sulphonyl sulphinate rearrangement from $M^+$ ion. A proposed structure[16] for the fragment ion at m/z 267 in **2c** and **7c** which is believed to be resulted by the loss of p-$ClC_6H_4SO_2$ radical from $M^+$ ion is shown in Scheme III. The initial ionisation of sulphide-sulphone permits the rotation of *trans*- into *cis*-geometry and hence the corresponding peak (m/z



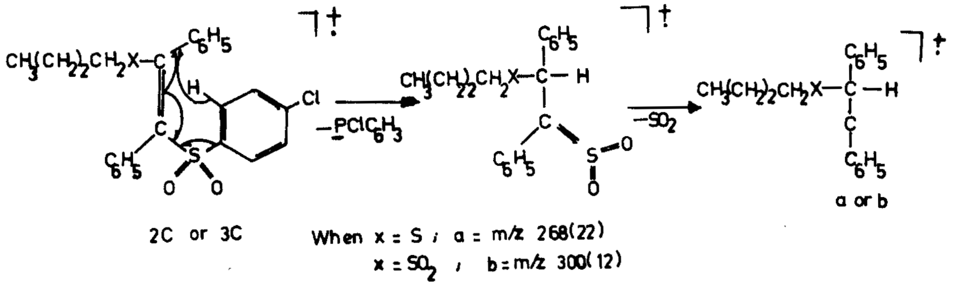
SCHEME III



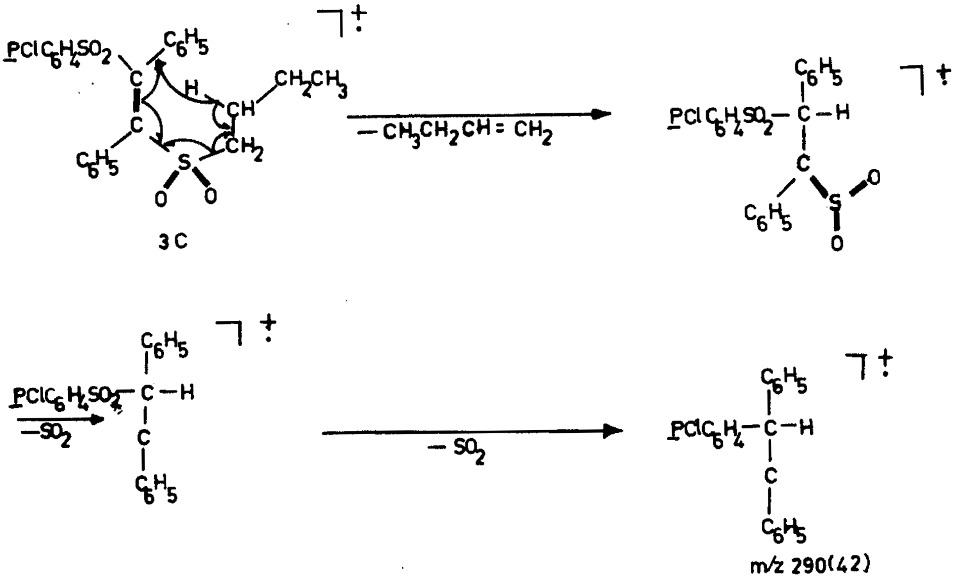
SCHEME IV

267) is seen in *trans*-isomer also. A conspicuous peak at m/z 211 is assumed to be due to the ion formed from fragment ion (m/z 267), undergoing McLafferty rearrangement. This ion (m/z 267) is further believed to be cleaved to afford a fragment ion at m/z 210 by the expulsion of $CH_3(CH_2)_2CH_2$ radical. Smiles type rearrange-

ment,[16] furnishing aryl alkyl sulphide radical ion at m/z 200 is noticed in **2c** and **7c** (Scheme IV). This is totally absent in **3c** and **8c** and explained as being due to the higher oxidation state of sulphur which has no lone pair of electrons to initiate the rearrangement to occur. An interesting feature observed in both sulphide-sulphones and disulphones is the presence of McLafferty type rearrangement,[17] involving migration of hydrogen from aryl group in **2c** and **7c** and from alkyl and aryl groups in **3c** and **8c**, to the ethylenic carbon via a six membered transition state. This is shown in Schemes V and VI respectively. The well known sulphonyl-sulphinate rearrangement[18] with subsequent cleavages furnishing $p$-$ClC_6H_4SO^+$ or $CH_3(CH_2)_2CH_2SO^+$ and/or $p$-$ClC_6H_4S^+$ or $CH_3(CH_2)_2CH_2S^+$ as the case may be, in both sulphide-sulphones and disulphones. Vinyl migration[10] is the predominant pathway, with no evidence of $p$-$ClC_6H_4O^+$ or $CH_3(CH_2)_2CH_2O^+$ to indicate an aryl or alkyl migration.



SCHEME V



SCHEME VI

## EXPERIMENTAL

The melting points were determined on a Mel Temp apparatus and are uncorrected. UV spectra were recorded in 95% EtOH on a Beckman Model DU-2 UV spectrophotometer ($\lambda_{max}$ in nm) and IR spectra in KBr pellets on a Perkin Elmer IR spectrophotometer 983 G ($\nu_{max}$ in $cm^{-1}$).

Diphenylacetylene, *p*-chlorophenylsulphenylchloride,[19] (*E*)-1-chloro-2-*p*-chlorophenylsulphonylstilbene (**1**)[7,10] and (*E*)-1-*p*-chlorophenylsulphenylstilbene (**4**)[7] were prepared as described.

*(Z)-1-Bromo-2-p-chlorophenylsulphenylstilbene* (**5**). To well stirred solution of (*E*)-1-*p*-chlorophenylsulphenylstilbene (**4**) (12 g, 0.03 mol) in gl. acetic acid (200 ml), a solution of bromine (2.4 g, 0.03 mol) in gl. acetic acid (25 ml) was added dropwisely. The addition took about 15 min and stirring was continued for 1 hr. The precipitated solid was filtered to yield 11 g (87.6%) and recrystallised thrice from methanol to afford **5** as light yellow crystals, m.p. 171–72° (Found: C, 59.63; H, 3.40. Calcd. for $C_{20}H_{14}ClBrS$: C, 59.85; H, 3.49%). UV: 322 ($\varepsilon$ 6,998), 268 (15,081), 227 (26,000), 202 (40,111); IR: 1080m (S-aryl) and 1650w $cm^{-1}$ (C=C).

*(Z)-1-Bromo-2-p-chlorophenylsulphonylstilbene* (**6**). To a boiling solution of **5** (2.0 g, 0.005 mol) in gl. acetic acid (30 ml), 30% $H_2O_2$ (10 ml) was added and resultant mixture was refluxed for 1 hr. The product separated on cooling, was filtered to yield 1.8 g (83.8%) and recrystallisation of which afforded **6** as colourless needle shaped crystals, m.p. 136–37° (Found: C, 55.63; H, 3.27; Calcd. for $C_{20}H_{14}ClBrO_2S$: C, 55.43; H, 3.23%); UV: 269 ($\varepsilon$ 15,547), 210 (38,983); IR: 1092s (S-aryl), 1132s ($SO_2$), 1317s ($SO_2$) and 1648w $cm^{-1}$ (C=C).

*(E)- And (Z)-1-alkylsulphenyl-2-p-chlorophenylsulphonylstilbenes* (**2** *and* **7**)*: General Method.* To a solution of sodium ethoxide prepared by dissolving sodium (230 mg, 0.01 mol) in abs. ethanol (25 ml), an appropriate alkane thiol (0.01 mol) was added. The resulting sodium thiolate was mixed with a solution of **1** or **5** (0.01 mol) in abs. ethanol (30 ml) and heated at reflux for 5–7 hr in different cases. The solid **2** or **7** separated on cooling was filtered and recrystallised from an appropriate solvent (Table I).

*(E)- And (Z)-1-alkylsulphonyl-2-p-chlorophenylsulphonylstilbenes* (**3** *and* **8**)*: General Method.* A boiling solution of **2** or **7** (0.005 mol) in gl. acetic acid was treated with 30% $H_2O_2$ (10 ml) and the reaction mixture heated at reflux for 1 hr. The solid **3** or **8** separated on cooling was collected and recrystallised from an appropriate solvent (Table I).

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