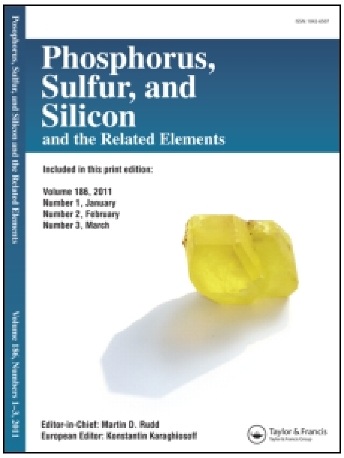

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SYNTHESES AND MASS SPECTRAL REARRANGEMENTS OF UNSATURATED BIS-SULPHIDES AND BIS-SULPHONES

S. G. Peeran[a]; G. Hanumantha Reddy[a]
[a] Department of Chemistry, Sri Krishnadevaraya University, Anantapur, India

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SYNTHESES AND MASS SPECTRAL REARRANGEMENTS OF UNSATURATED BIS-SULPHIDES AND BIS-SULPHONES

S. G. PEERAN[†] and G. HANUMANTHA REDDY
Department of Chemistry, Sri Krishnadevaraya University,
Anantapur 515 003, India

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The synthesis of (*E*)- and (*Z*)-1,2-bis(*p*-fluorophenylsulphenyl)stilbenes (**2a** and **2b**) and 1,2-bis(*p*-fluorophenylsulphonyl)stilbenes (**3a** and **3b**) was carried out and their configurations were consistent with their stereospecific synthesis. The isomeric 1,1-bis(*p*-fluorophenylsulphenyl)- and 1,1-bis(*p*-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylenes (**8** and **9**) were also synthesised and configurations were established by degradative oxidation. Mass spectral rearrangements of all these compounds were examined. Mass spectra of 1,1-bis-sulphide and 1,1-bis-sulphone bears close relationship with those of (*E*)- and (*Z*)-isomeric counterparts. Smiles-type rearrangement observed in 1,2-bis-sulphides was absent in 1,2-bis-sulphones. McLafferty-type rearrangement involving hydrogen migration, from aryl group was noticed in both bis-sulphides and bis-sulphones. Vinyl migration to the sulphone oxygen predominates over aryl migration in three isomeric bis-sulphones.

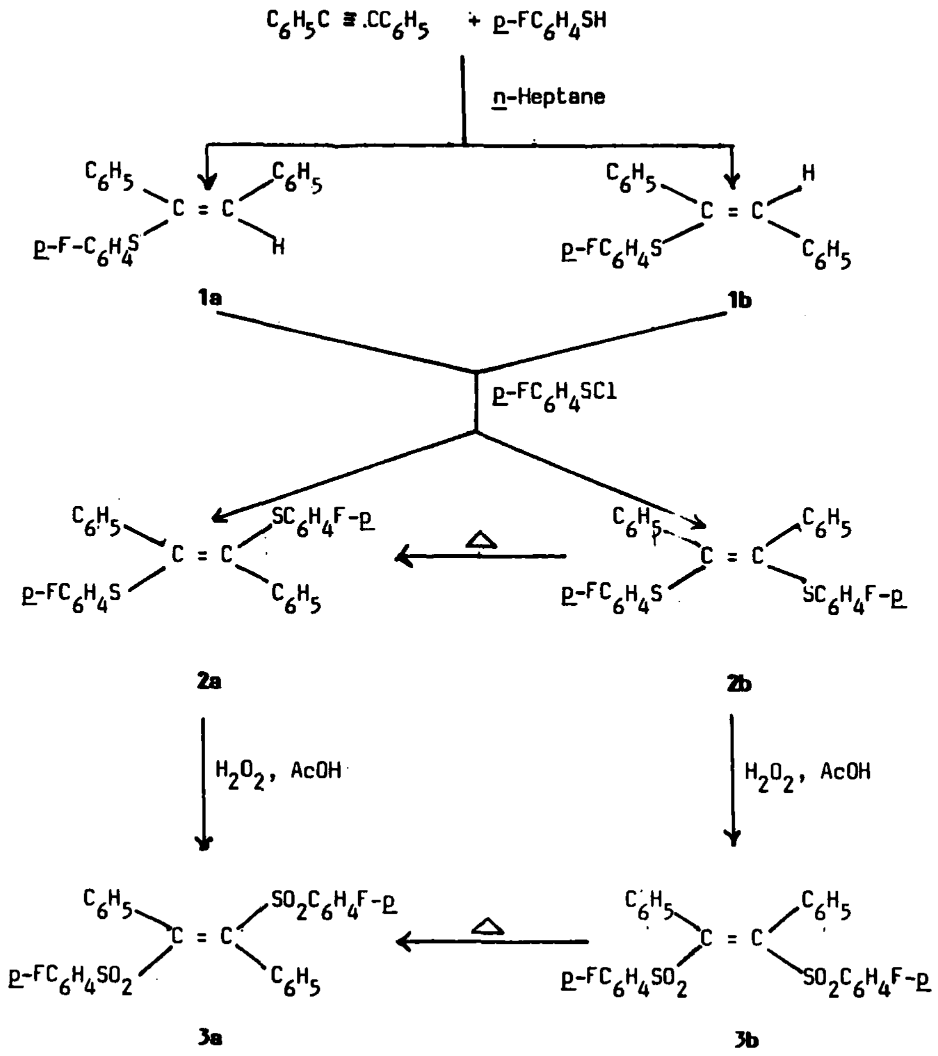
Key words: (*E*)- and (*Z*)-1-*p*-fluorophenylsulphenylstilbenes; (*E*)- and (*Z*)-1,2-bis(*p*-fluorophenylsulphenyl)stilbenes; (*E*)- and (*Z*)-1,2-bis(*p*-fluorophenylsulphonyl)stilbenes; (*E*)- and (*Z*)-1-*p*-fluorophenylsulphenyl-2-*p*′-fluorophenylsulphonylstilbenes; 1,1-Bis(*p*-fluorophenylsulphenyl)-2,2-bis(phenyl)ethylene; 1,1-Bis(*p*-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylene

INTRODUCTION

Biological studies carried out on bis(organosulphenyl and sulphonyl)ethylenes[1,2] have revealed that these compounds play a promising role as fungicides to protect seeds and against mildew on cotton-cloth, paint and various plant foliage diseases. So far the work reported on the synthesis and mass spectral studies of (*E*)- and (*Z*)-unsaturated bis-sulphides and bis-sulphones is not much,[3–5] and no attempt has been made to prepare unsaturated 1,1-bis-sulphides and 1,1-bis-sulphones. Hence, we report herewith the syntheses and electron impact-induced rearrangements of (*E*)- and (*Z*)-isomers of 1,2-bis(*p*-fluorophenylsulphenyl and sulphonyl)stilbenes (**2** and **3**) and their isomeric 1,1-bis(*p*-fluorophenylsulphenyl and sulphonyl)-2,2-bis(phenyl)ethylenes (**8** and **9**).

DISCUSSION

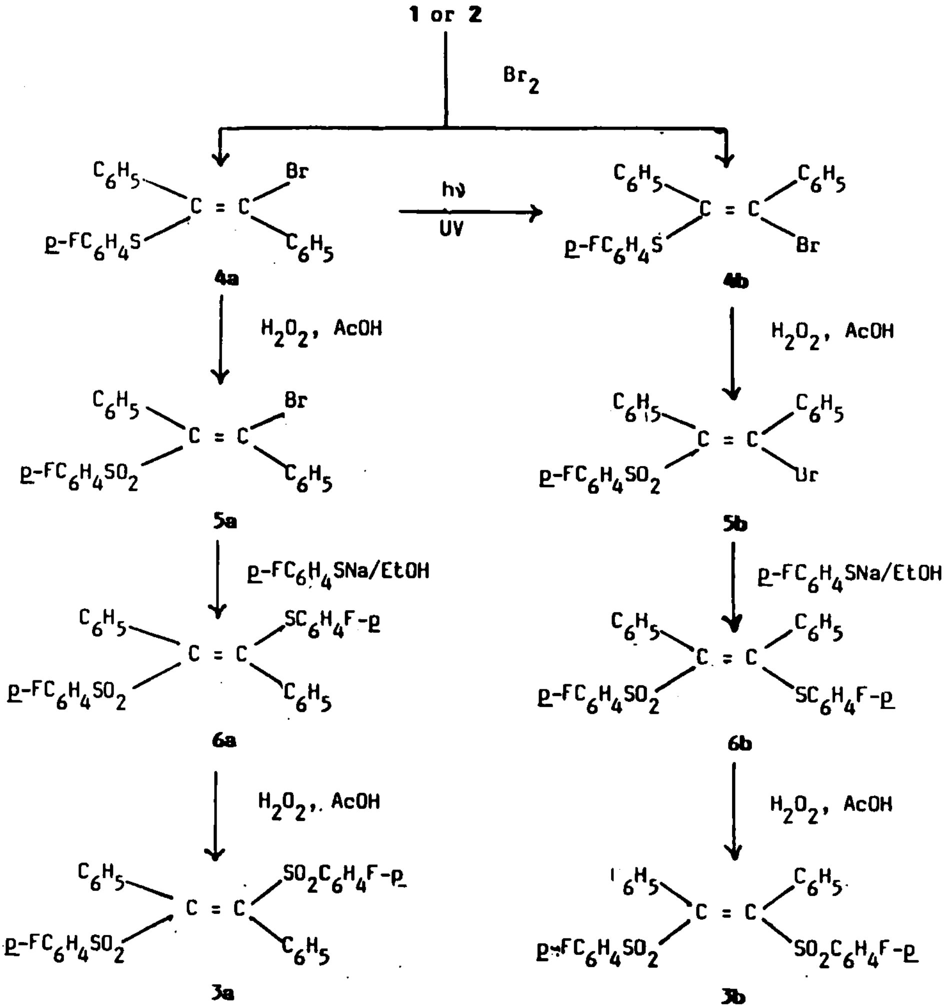
Addition of *p*-fluorobenzenethiol to diphenylacetylene resulted in the formation of a mixture of (*E*)- and (*Z*)-1-*p*-fluorophenylsulphenylstilbenes (**1a** and **1b**). They were separated by fractional crystallisation from methanol. The (*E*)-isomer **1a** was obtained as a major product and the (*Z*)-isomer **1b** constitutes the minor product. Addition of thiols to *t*-butylacetylene was reported to yield primarily the *cis*-addition product[6,7] and the *trans*-addition product was obtained in minor proportion. Sim-



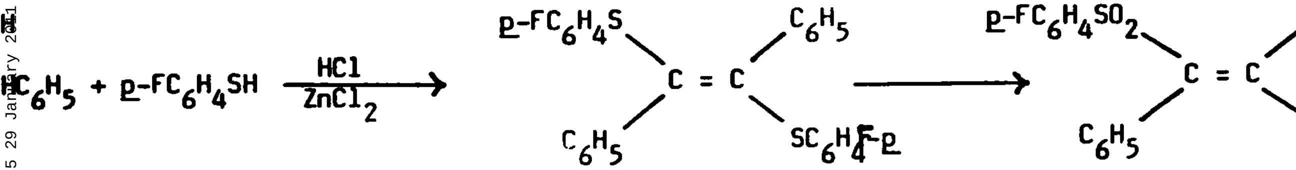
Scheme 1

ilarly, the addition of aromatic thiols to diphenylacetylene was also reported[4,5] to yield mainly (*E*)-1-arylsulphenylstilbenes. Hence in the present investigation also, the *cis*-addition product **1a** predominates over the *trans*-addition product **1b**, which probably due to a free radical addition. Further the *cis*-addition product **1a** is sterically preferred to **1b**. The configurations of these compounds were established by ^{1}H NMR studies. Since **1a** and **1b** being trisubstituted ethylenes chemical shifts[8,9] rather than coupling constants are utilized to differentiate between (*E*)- and (*Z*)-isomers. The chemical shift of vinylic proton of (*Z*) (*trans*)-isomer (δ 6.73) occurs at a lower field strength than of its corresponding (*E*) (*cis*)-isomer (δ 6.81). Similar observation was made in disulphones by Sterling[10] and β-crotonates by Jones et al.[11] Compounds **1a** and **1b** on reaction with *p*-fluorobenzenesulphenyl chloride at room temperature afforded a mixture of **2a** and **2b** (Scheme 1). They were separated by fractional crystallisation from methanol. Compound **2b** on heating above its m.p. isomerized into **2a**. Compound **2a** on oxidation afforded the bis-sulphone **3a** and oxidation of **2b** under mild conditions gave the bis-sulphone **3b** which on heating above its m.p. isomerised into **3a**.

Bromination[3] of **1** in gl. acetic acid furnished a mixture of (*E*)- and (*Z*)-1-bromo-2-*p*-fluorophenylsulphenylstilbenes (**4a** and **4b**) (Scheme 2). Compound **4a** on irradiation[4] with UV light in benzene for about 20 hr resulted in the formation of a compound which was found to be identical with **4b**, from its m.p., m.m.p. and other spectral studies. Compounds **4a** and **4b** on oxidation gave the corresponding (*E*)- and (*Z*)-1-bromo-2-*p*-fluorophenylsulphonylstilbenes (**5a** and **5b**). Compounds **5a** and **5b** underwent nucleophilic displacement of bromine when heated with the sodium salt of *p*-fluorobenzenethiol and gave (*E*)- and (*Z*)-1-*p*-fluorophenylsulphenyl-2-*p*′-fluorophenylsulphonylstilbenes (**6a** and **6b**) respectively, with retention of configuration.[3,12,13] Oxidation of **6a** and **6b** led to the formation of-



Scheme 2



2a

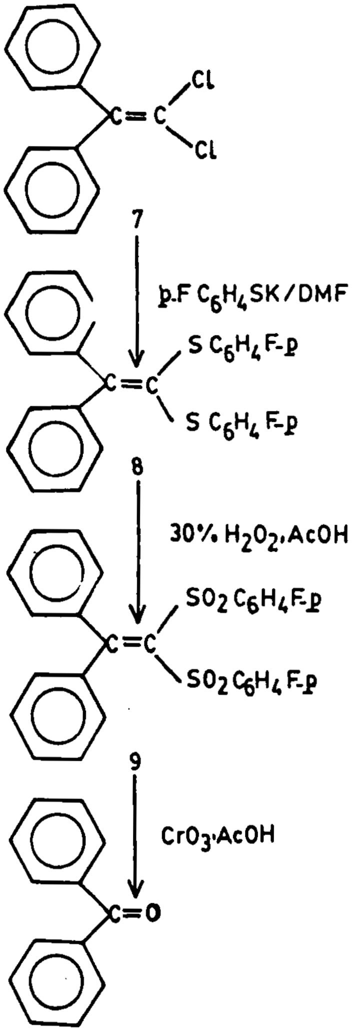
3a

Scheme 3

(*E*)- and (*Z*)-1,2-bis(*p*-fluorophenylsulphonyl)stilbenes which were found to be identical with **3a** and **3b** prepared earlier.

Compound **2a** was also prepared by the reaction of benzoin[3-5] with *p*-fluorobenzenethiol in presence of anhyd $ZnCl_2$ and dry HCl gas (Scheme 3).

The isomeric 1,1-bis-sulphide **8** and 1,1-bis-sulphone **9** were prepared starting from 1,1-dichloro-2,2-bis(phenyl)ethylene (**7**). Compound **7** when heated with the potassium salt of *p*-fluorobenzenethiol in dry DMF underwent nucleophilic displacement of chlorines to furnish 1,1-bis(*p*-fluorophenylsulphenyl)-2,2-bis(phenyl)ethylene (**8**), which on oxidation yielded 1,1-bis(*p*-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylene (**9**) (Scheme 4). The structure of **9** was established as it forms benzophenone on oxidation with chromic acid.



Scheme 4

TABLE I
Characterisation Data of Various Sulphides and Sulphones

				Found (%)/(Calc)			IR (KBr) cm^{-1}			
pound	Yield (%)	MP(°C)	Molecular formula	C	H	S	$^{\nu}$C=C	$^{\nu}$S-aryl		$^{\nu}$
	84	97–98	$C_{20}H_{15}FS$	78.56 (78.40)	5.07 (4.94)	— —	1628w	1078s	—	-
	7	67–68	$C_{20}H_{15}FS$	78.60 (78.40)	5.12 (4.94)	— —	1630w	1074s	—	-
	21	136–137	$C_{26}H_{18}F_2S_2$	72.47 (72.20)	4.42 (4.19)	14.41 (14.82)	1638w	1088m	—	-
	39	87–88	$C_{26}H_{18}F_2S_2$	72.10 (72.20)	4.45 (4.19)	14.63 (14.82)	1637w	1088m	—	-
	81	267–268	$C_{26}H_{18}F_2O_4S_2$	63.10 (62.89)	3.86 (3.65)	12.94 (12.91)	1636w	1081s	1332s	11
	81	163–165	$C_{26}H_{18}F_2O_4S_2$	62.99 (62.89)	3.89 (3.65)	12.82 (12.91)	1639w	1081s	1325s	11
	34	110–111	$C_{20}H_{14}FBrS$	62.55 (62.34)	3.79 (3.66)	— —	1628w	1070s	—	-
	55	135–136	$C_{20}H_{14}FBrS$	62.61 (62.34)	3.52 (3.66)	— —	1629w	1068s	—	-
	86	134–135	$C_{20}H_{14}FBrO_2S$	57.76 (57.56)	3.69 (3.38)	— —	1630w	1090s	1322s	11
	84	168–169	$C_{20}H_{14}FBrO_2S$	57.23 (57.56)	3.53 (3.38)	— —	—	1075s	1312s	11
	72	179–180	$C_{26}H_{18}F_2O_2S_2$	67.17 (67.22)	4.17 (3.91)	— —	—	1078s	1312s	11
	75	183–184	$C_{26}H_{18}F_2O_2S_2$	67.52 (67.22)	3.60 (3.91)	— —	—	1082s	1317	11
	49	86–87	$C_{26}H_{18}F_2S_2$	72.34 (72.20)	4.42 (4.19)	14.71 (14.82)	—	1093s	—	-
	81	128–129	$C_{26}H_{18}F_2O_4S_2$	63.17 (62.84)	3.80 (3.65)	12.79 (12.91)	—	1087s	1336s	11

The IR spectra of **2a**, **2b**, **3a** and **3b** showed a weak band[14] in the region 1639–1636 cm^{-1} due to the C═C stretching frequency, but this band is absent in **8** and **9** (Table 1). Bis-sulphones show sharp asymmetric and symmetric stretching frequencies[15] in the region of 1336–1325 and 1154–1140 cm^{-1} (SO_2), and bis-sulphides and bis-sulphones show a prominent frequency in the region of 1091–1081 cm^{-1} (S-aryl).[16]

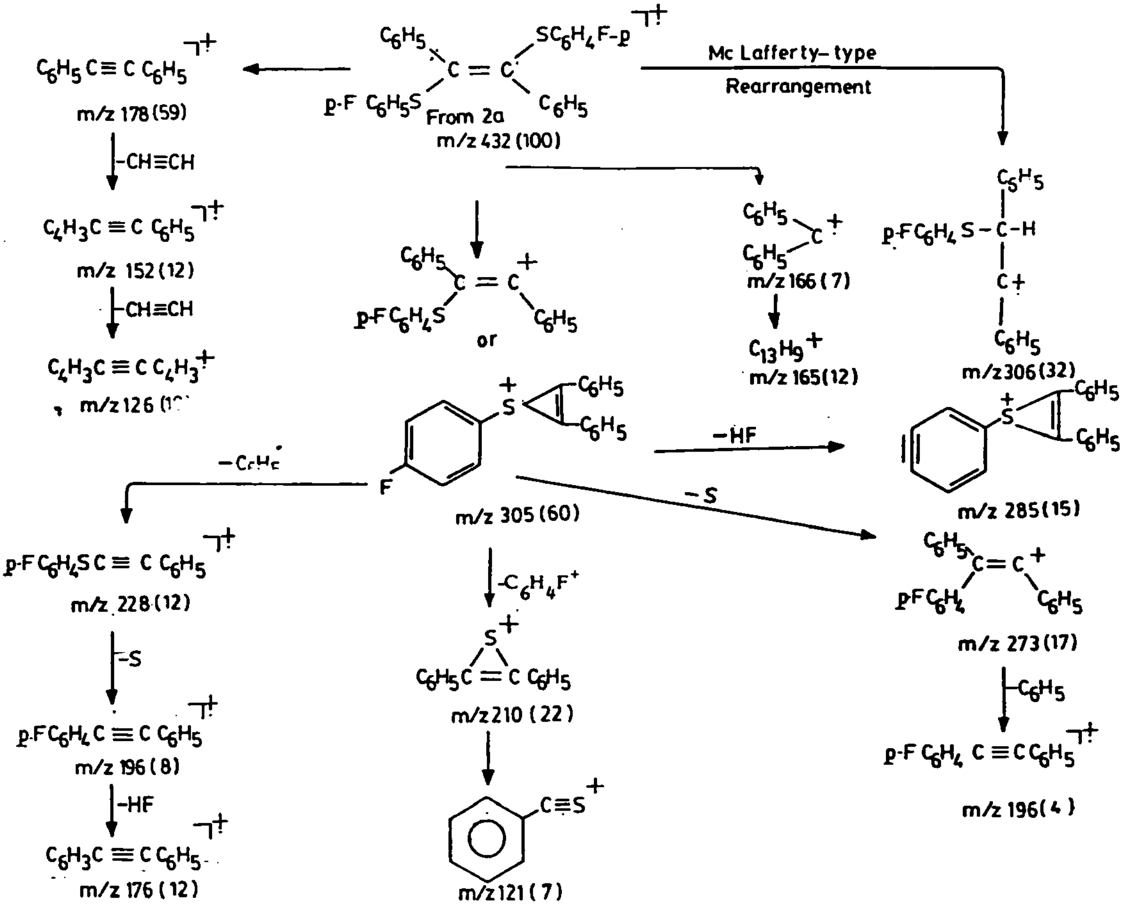
The mass spectra of all the isomeric bis-sulphides and bis-sulphones at 70 eV were examined. The fragmentation pattern of (*E*)- and (*Z*)-bis-sulphides **2a** and **2b** were almost identical. So also was fragmentation of bis-sulphones **3a** and **3b**.

The M^+ ion peaks were followed by $M^+ + 1$ and $M^+ + 2$ peaks in **2**. The M^+ ion peak of **2a** itself constituted the base peak. In **2b**, the base peak was observed at m/z 178 which is assigned to diphenylacetylene radical ion. A peak at m/z 305 in **2** is believed to be due to the fragment ion produced by the loss of SC_6H_4F-*p*· radical from the M^+ ion. The other significant peaks observed at m/z 285 and m/z 210 are assumed to be produced by the loss of HF molecule and C_6H_4F-*p* radical respectively from the fragment (m/z 305) ion, which is further believed to be cleaved to afford the ions at m/z 273 and 228 by the expulsion of sulphur and C_6H_5 radical respectively (Scheme 5).

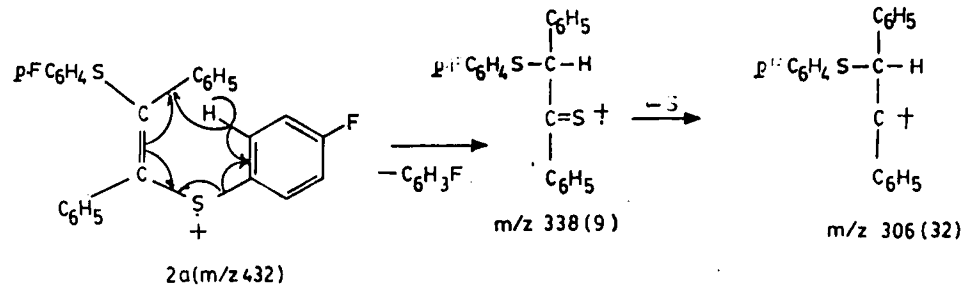
An interesting feature observed in **2** was the presence of a prominent peak at m/z 306 which is assumed to be due to the ions formed from the M^+ ions involving McLafferty-type rearrangement where migration of ortho hydrogen from aryl group to the ethylenic carbon is taking place (Scheme 6).

Another notable feature observed in both **2a** and **2b** was the presence of an electron impact-induced Smiles-type rearrangement leading to the formation of diarylsulphide ion (*p*-$FC_6H_4SC_6H_4F$-*p*) at m/z 222. This proposed rearrangement mechanism involves (Scheme 7) initial ionisation of the sulphide which permits rotation into a *cis* geometry which is a pre-requisite for such a rearrangement and hence was observed in (*E*)-isomer **2a** also. Similar rearrangement was reported in sulphenyl-sulphones by Hill et al.[17] Other prominent peaks observed at m/z 166 and 165 are assigned to the $C_{13}H_{10}^{+}$ and $C_{13}H_9^{+}$ ions respectively (Scheme 5). Similar ions are ascribed to the corresponding peaks by Dittmer and Kuhlmann[18] in their study of fragmentation reactions of thiobenzophenone. The peaks with significant intensity at m/z 152 and 126 are assumed due to the ions formed by the two successive losses of acetylene molecules from the diphenylacetylene radical ion (Scheme 5).

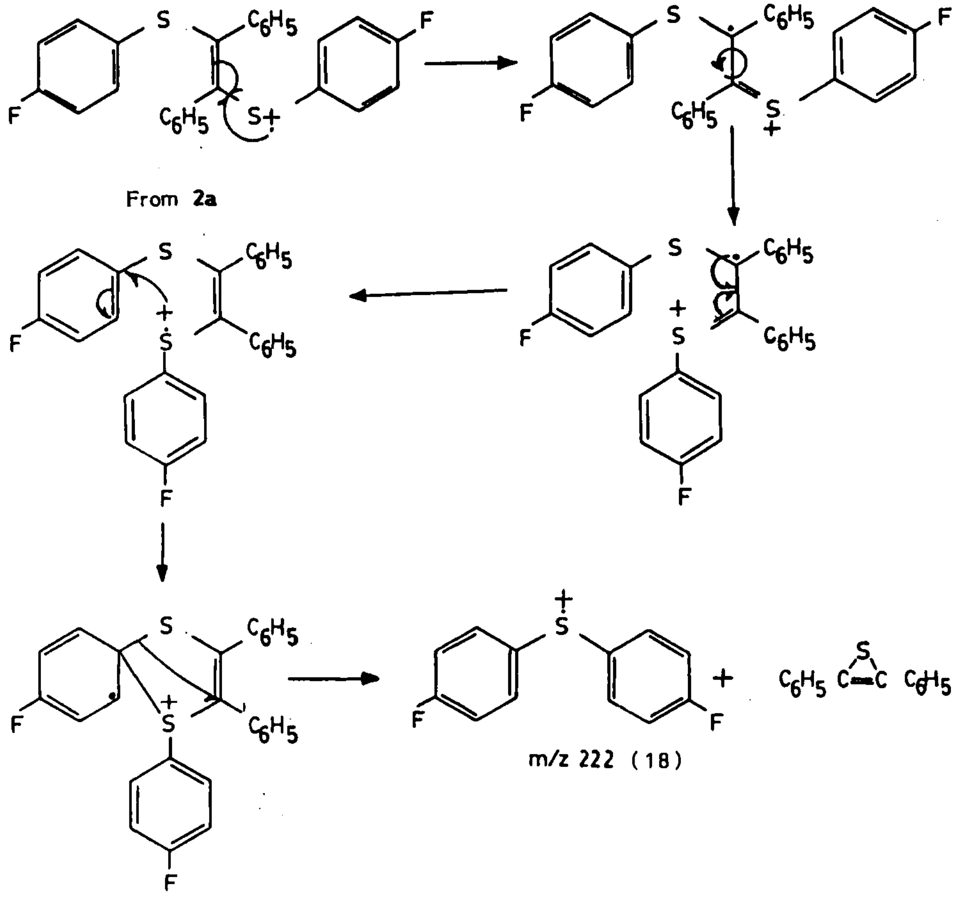
In bis-sulphones **3**, M^+ ions were not observed and this absence is attributed to the low thermal stability of the **3**. The base peaks in **3a** and **3b** were observed at m/z 105 ($C_7H_5O^+$) and 178 ($C_6C_5C{\equiv}CC_6H_5^{+}$) respectively. The formation of $C_7H_5O^+$ is depicted in Scheme 8 through sulphonyl-sulphinate rearrangement. Unlike in bis-sulphides **2**, a Smiles-type rearrangement was totally absent in bis-sulphones **3** and has been explained as being due to the loss of the unshared electron pair on the sulphur which is necessary for this rearrangement to occur. The well known rearrangement observed was the sulphonyl-sulphinate rearrangement[19] which on further cleavages resulting in *p*-$FC_6H_4SO^+$ and/or *p*-$FC_6H_4S^+$. The (*E*)- and (*Z*)-bis-sulphones **3** also underwent McLafferty-type rearrangement similar to that observed in bis-sulphides and gave a fragment ion at m/z 274. This is shown in Schemes


From 2a
m/z 432 (100)
m/z 178 (59)
-CH≡CH
m/z 152 (12)
-CH≡CH
m/z 126
Mc Lafferty- type Rearrangement
m/z 166 (7)
m/z 165 (12)
m/z 306 (32)
or
m/z 305 (60)
-HF
m/z 285 (15)
-S
m/z 273 (17)
-C6H5
m/z 196 (4)
m/z 228 (12)
-S
m/z 196 (8)
-HF
m/z 176 (12)
-C6H4F
m/z 210 (22)
m/z 121 (7)

Scheme 5



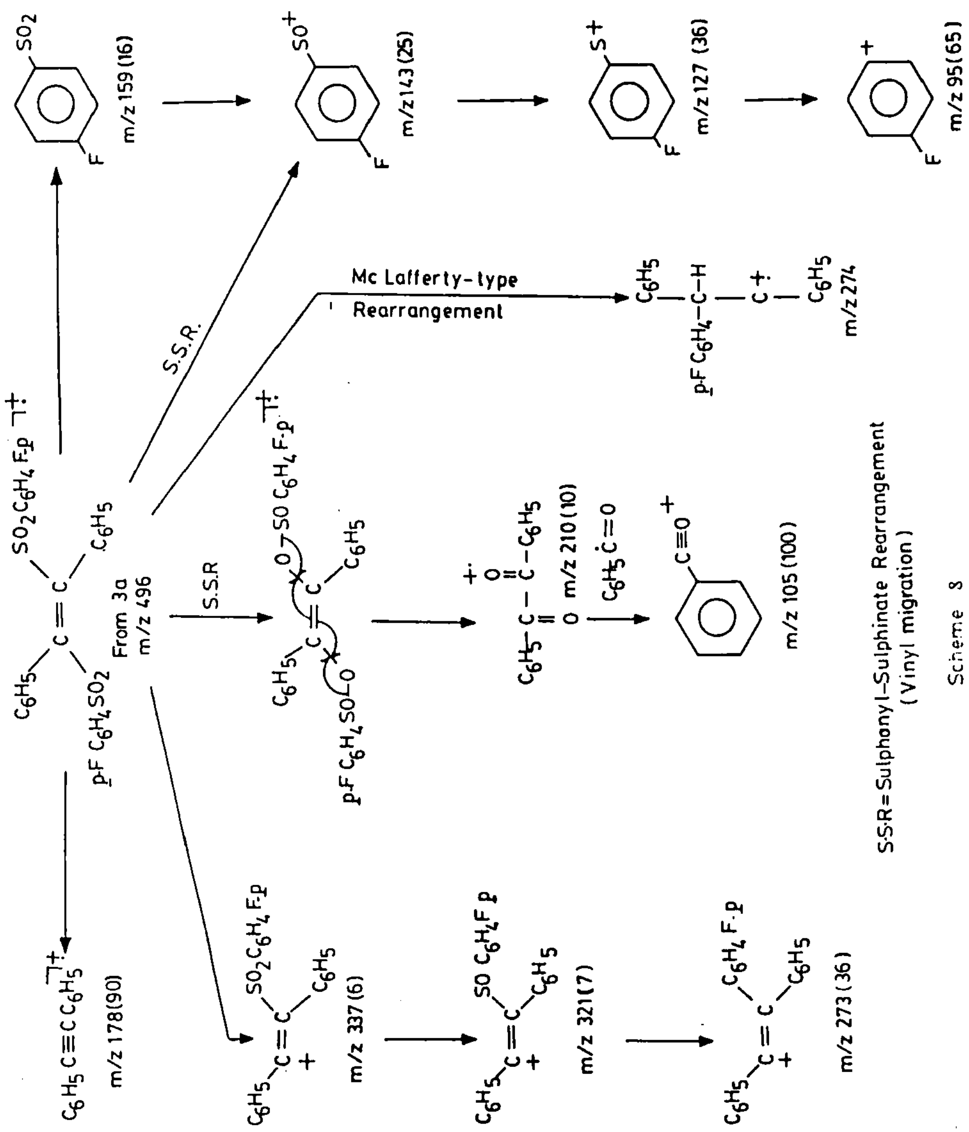
Scheme 6



Scheme 7

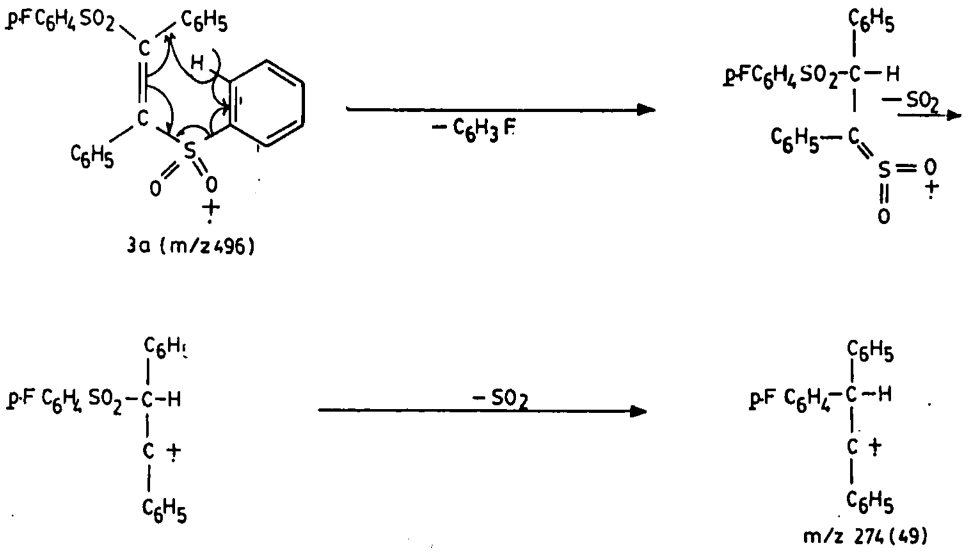
8 and 9. Major fragments of **2a** and **3a** with their relative intensities are presented in Schemes 5 and 8 respectively.

The fragmentation features of 1,1-bis-sulphide **8** (Scheme 10) and 1,1-bis-sulphone **9** (Scheme 11) were almost similar to those of their (*E*)- and (*Z*)-isomeric counterparts. **2a**, **b** and **3a**, **b** respectively. The M^+ ion peaks were absent in both compounds and base peaks were constituted by the diphenylacetylene radical ion.

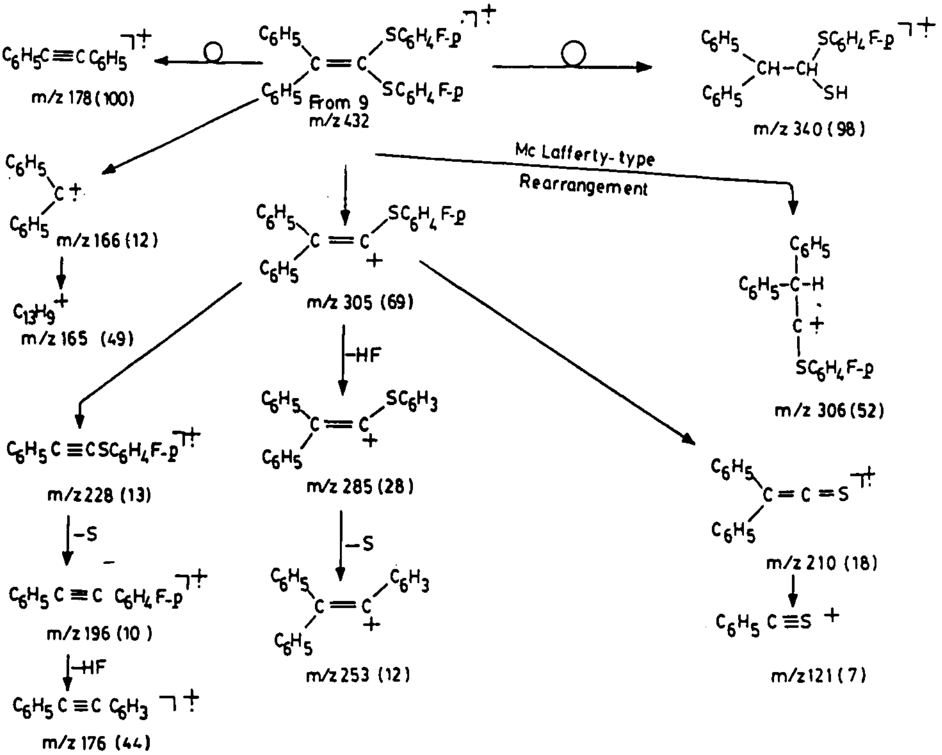


S·S·R = Sulphonyl–Sulphinate Rearrangement
(Vinyl migration)

Scheme 3

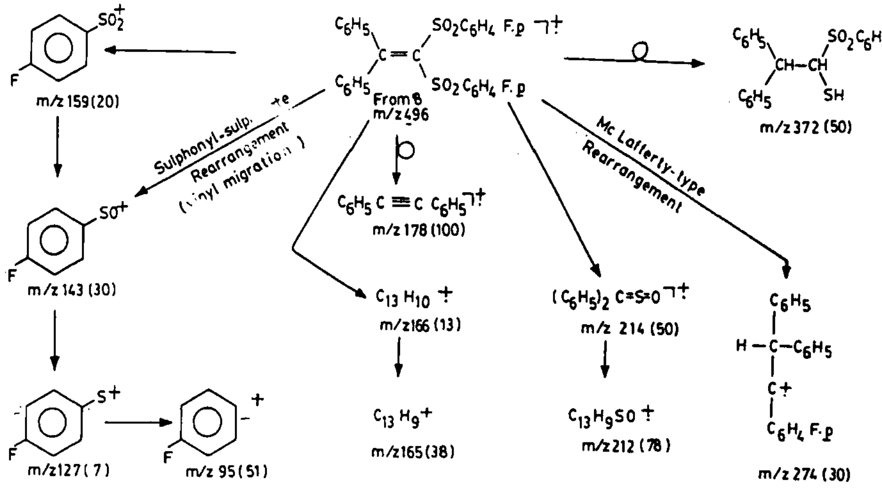


Scheme 9



Scheme 10

A peculiar feature observed was the presence of abundant peaks at m/z 340 in 1,1-bis-sulphide and 372 in 1,1-bis-sulphone which are attributed to the probable ions shown in Schemes 10 and 11 respectively.



Scheme 11

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer Infrared Spectrophotometer model 983 G as KBr pellets and ^{1}H NMR at 60 MHz with a Hitachi R-600 NMR spectrometer. *p*-Fluorobenzenenesulphenyl chloride was prepared by adopting a procedure similar to the preparation of *p*-toluenesulphenyl chloride.[20] The characterization data of all newly prepared compounds are presented in Table 1.

Potassium p-fluorobenzenethiolate. To a solution of 3.2 g (0.025 mol) of *p*-fluorobenzenethiol in 150 ml of dry toluene, 0.975 g (0.025 g atom) of freshly cut potassium metal was added. The mixture was heated under reflux for 5 hr, when white powdered material separated. The reaction mixture was cooled and the solid separated was filtered and washed with dry toluene to free it from thiol. The salt thus collected was dried in a vacuum desiccator.

1,1-Dichloro-2,2-bis(phenyl)ethylene (7). A reaction mixture of 1,1,1-trichloro-2,2-bis(phenyl)ethane[21] (10 g, 0.07 mol), KOH (11 g) and methanol (500 ml) was refluxed for 10 hr, cooled to room temperature and poured onto crushed ice (800.0 g). The crystalline solid separated was filtered to yield 15.5 g (89.3%) of **7** and it was recrystallised from methanol, m.p. 79–80° (l it.[22] m.p. 79–80°).

(E)- And (Z)-1-p-fluorophenylsulphenylstilbenes (1a and 1b). Diphenylacetylene (8.9 g, 0.05 mol) in *n*-heptane (250 ml) was treated with *p*-fluorobenzenethiol (6.4 g, 0.05 mol) and the reaction mixture was heated under reflux for 10 hr and left overnight at room temperature. The solution was washed repeatedly with 2% NaOH solution till free from thiol and dried (anhyd $CaCl_2$). The solution was decanted and solvent removed under reduced pressure. The syrupy liquid obtained was triturated with methanol when the material got solidified. The solid was purified by recrystallisation from methanol to give an analytical sample of **1b**.

The mother liquor obtained after separating the crystals of **1b** was concentrated to give another crop of **1b**. Then the solvent was evaporated and the residue obtained was recrystallised from aqueous methanol to give a pure sample of **1a**.

(E)- and (Z)-1,2-bis(p-fluorophenylsulphenyl)stilbenes (2a and 2b). To a solution of **1a** or **1b** (7.655 g, 0.025 mol) in gl. acetic acid (75 ml), a solution of *p*-fluorobenzenesulphenyl chloride in gl. acetic acid (25 ml) was added dropwise, while stirring. Addition took about 30 min, and stirring was continued for 10 hr. The solid separated was filtered and recrystallised from methanol to give an analytical sample of **2a**.

The filtrate after separating **2a**, was concentrated, when a solid material was separated. It was recrystallised from methanol to afford light yellow needles of **2b**.

The compound **2a** was also prepared from benzoin and *p*-fluorobenzenethiol following the procedure of Benati et al.[3] used in the preparation of *trans*-1,2-bis(*p*-bromophenylsulphenyl)stilbene and found to be identical (m.p. and m.m.p.) with **2a** prepared by the above method.

(E)-1,2-Bis(p-fluorophenylsulphonyl)stilbene (3a). A boiling solution of **2a** (2.16 g, 0.005 mol) in acetic acid (50 ml) was treated with 30% H_2O_2 (20 ml). The reaction mixture was refluxed for 1 hr and cooled. The solid **3a** separated was collected and purified by recrystallisation from gl. acetic acid.

Compound **3a** was also obtained from **6a** in a similar manner.

(Z)-1,2-Bis(p-fluorophenylsulphonyl)stilbene (3b). A solution of **2b** (2.16 g, 0.005 mol) in gl. acetic acid (50 ml) was just warmed and then treated with 30% H_2O_2 (5 ml). The reaction mixture was left overnight and poured onto 200 g of crushed ice. The colourless solid separated was collected and recrystallised from gl. acetic acid to give **3b**.

Similarly, **6b**, on oxidation gave **3b**.

(E)- And (Z)-1-bromo-2-p-fluorophenylsulphenylstilbenes (4a and 4b). A solution of **1a** or **1b** (3.06 g, 0.01 mol) in gl. acetic acid (75 ml) was stirred and a solution of bromine (1.6 g, 0.01 mol) in gl. acetic acid (20 ml) was added dropwise. After addition, stirring was continued for 1 hr. The solid separated was filtered and purified by recrystallisation from methanol to give **4b**.

The filtrate after separating **4b**, on evaporation of the solvent yielded crude compound **4a**. It was recrystallised from 95% ethanol.

(E)-1-Bromo-2-p-fluorophenylsulphonylstilbene (5a). A boiling solution of 0.8 g (0.0021 mol) of **4a** in 25 ml of gl. acetic acid was treated with 10 ml of 30% H_2O_2 and refluxed for 1 hr. The solid **5a** separated on cooling was filtered and recrystallised from gl. acetic acid.

Similarly, **5b** was prepared from **4b**.

(E)-1-p-Fluorophenylthio-2-p'-fluorophenylsulphonylstilbene (6a). About 0.15 g (0.0012 mol) of p-fluorobenzenethiol was added to an ethanolic solution of sodium ethoxide prepared from 0.027 g (0.0012 g atom) of sodium and 10 ml of abs. ethanol. The mixture was then added to a solution of 0.5 g (0.0012 mol) of **5a** in 40 ml of abs. ethanol. The reaction mixture was refluxed for 6 hr. The product **6a** separated on cooling was collected and purified by recrystallisation from 95% ethanol.

Similarly, from **5b**, the (*Z*)-isomer **6b** was obtained.

1,1-Bis(p-fluorophenylsulphenyl)-2,2-bis(phenyl)ethylene (8). To a well stirred and boiling solution of 2.48 g (0.01 mol) of **7** in 150 ml of dry DMF, a solution of 3.32 g (0.02 mol) of potassium salt of p-fluorobenzenethiol in 25 ml of dry DMF was added dropwise. Addition took about 30 min and heating was continued for 10 hr. The contents were cooled and poured into 200 ml of ice cold water. The solid **8** separated was filtered and recrystallised from 95% ethanol.

1,1-Bis(p-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylene (9). A boiling solution of 1.0 g (0.0025 mol) of **8** in 25 ml of gl. acetic acid was treated with 15 ml of 30% H_2O_2. The solution was refluxed for 1 hr and cooled. The solid **9** separated was filtered and recrystallised from methanol.

Oxidation of 9 with chromic acid. A mixture containing 1.0 g of **9**, 5.0 g of chromic acid and 30 ml of acetic acid was refluxed for 10 hr and poured into 250 ml of ice cold water. The solid separated was filtered, washed with water and recrystallised from pet. ether (40–60°), m.p. 46–47°. There was no depression in the melting point of this compound on admixture with benzophenone.

Isomerisation of 2b to 2a. Compound **2b** (0.15 g) was heated at 110° for 5 min. The melt was cooled and recrystallised from methanol to give colourless needles. It was found to be identical with **2a** from its m.p.and m.m.p.

Isomerisation of 3b to 3a. A sample of **3b** (0.25 g) was heated above its m.p. and heating was continued for 5 min and cooled. On recrystallisation from acetic acid, yielded colourless needles of **3a**.

Isomerisation of 4a to 4b. A solution of **4a** (0.5 g) in 250 ml of benzene was irradiated with UV light for 15 hr. The residue obtained on evaporation of the solvent was subjected to fractional crystallisation from gl. acetic acid. Light yellow needles, (0.24 g, 48.0%) obtained did not show any depression in m.p. (135–136°C) on admixture with an authentic sample of **4b**.

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