CHAPTER III

EXPERIMENTAL
Section (i)

All melting points were determined on Mel-Temp apparatus, Laboratory devices, Cambridge, Mass, USA and are uncorrected.

**Ultraviolet Absorption Measurements.** The ultraviolet absorption spectra were determined with a Cary Model 2390 Ultraviolet spectrophotometer. The solvent used was ethanol and it was purified by distillation after treatment with lead acetate and sodium hydroxide.

**Infrared Absorption Measurements.** The infrared absorption measurements were measured by means of a Perkin-Elmer Infrared spectrophotometer Model 983G as KBr pellets and as nujol mulls.

**Nuclear Magnetic Resonance (H) Spectra.** NMR spectra at 60 MHz were recorded with a Hitachi R-600 High resolution NMR spectrometer. Tetramethyl silane is used as an internal standard.

**Mass Spectrometry.** Mass spectral recordings were obtained from Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, India.

**Sources and purification of thiols**

The following thiols were obtained from M/s Aldrich Chemical Company, Inc., Wisconsin, U.S.A. and were used without further purification.

- p-FluorothioephenoI B.P. 54° C.
- p-ChlorothioephenoI M.P. 49-51° C.
- p-MethoxythioephenoI B.P. 100-103° C.
Tolan (Diphenylacetylene)

It is prepared according to the procedure of Smith and Falkof.\(^1\)

Into a two-litre three-necked round-bottomed flask fitted with a reflux condenser, a mechanical stirrer and a dropping funnel, a solution of 90.0 g (0.5 mole) of trans-stilbene in 1500 ml of ether was taken and 27.6 ml (86.4 g, 0.54 mole) of bromine was added in a course of ten minutes. After stirring the reaction mixture for 1 hour, the stilbene dibromide separated, was filtered and washed with ether, yield 120.0 g, m.p. 234-237° C (literature\(^1\), m.p. 235-237° C).

About 180.0 g of potassium hydroxide and 300 ml of absolute ethanol were introduced into a one-litre round-bottomed flask fitted with a reflux condenser, protected with a calcium chloride guard tube. The contents of the flask were heated in an oil bath at 130-140° C for 3 hours, when most of the potassium hydroxide dissolved. The solution was cooled somewhat and stilbene dibromide was added in several portions. The mixture was refluxed for 24 hours and cooled. The product separated was filtered, washed with water and dried over calcium chloride in a vacuum desiccator for 20 hours. Recrystallisation of the crude product from 95% ethanol gave about 60.0 g of colourless needles of tolan melting at 60-61° C (literature\(^1\), m.p. 60-61° C).

\textit{p}-Fluorobenzenesulphenyl chloride.

Dry chlorine gas was passed for 4 hours into 200 ml of anhydrous carbon tetrachloride contained in a 500 ml three-necked round-
bottomed flask equipped with a glycerine-sealed stirrer, dropping funnel and a gas inlet tube. The dropping funnel was protected with a calcium chloride guard tube. The gas inlet tube was replaced by a calcium chloride guard tube and the reaction vessel was cooled externally with ice water and the contents were protected from light by covering the flask with a black cloth.

To the saturated solution of chlorine two crystals of iodine were added to initiate the reaction. The solution was stirred and a solution of 3.84 g (0.03 mole) of p-fluorothiophenol in 10 ml of anhydrous carbon tetrachloride was added dropwise during a period of 20 minutes. After an additional 60 minutes' stirring, the solvent and excess of chlorine were rapidly removed under reduced pressure. The crude p-fluorobenzenesulphenyl chloride obtained (4.1 g, 84.4%) was used as such without any further purification.

**p-Chlorobenzenesulphenyl chloride**

A 500 ml three-necked round-bottomed flask was equipped with a glycerine-sealed stirrer, a dropping funnel guarded with a calcium chloride tube and a gas inlet tube. About 200 ml of anhydrous carbon tetrachloride was introduced into the flask and saturated with dry chlorine gas by passing chlorine for 4 hours into it. The gas inlet was replaced by a calcium chloride guard tube and the reaction vessel was cooled externally with ice water and the vessel was covered with a black cloth.

The stirrer was started and two crystals of iodine were added to the saturated solution of chlorine to initiate the reaction. Then a solution of 4.32 g (0.03 mole) of p-chlorothiophenol in 25 ml of anhy-
drous carbon tetrachloride was added dropwise over a period of 30 minutes. After stirring the solution for 60 minutes, the solvent and the excess of chlorine were removed under reduced pressure. The yield of the crude p-chlorobenzenesulphenyl chloride was 4.58 g (85.8%) and used without further purification.

**p-Methoxybenzenesulphenyl chloride**

Dry chlorine gas was passed for 4 hours into 200 ml of anhydrous carbon tetrachloride contained in a 500 ml three-necked flask fitted with a glycerine sealed stirrer, dropping funnel guarded with a calcium chloride tube and a gas inlet tube. The gas inlet tube was replaced by a calcium chloride guard tube and the reaction vessel was cooled in ice water. The flask was covered with a black cloth.

Two crystals of iodine were added and the stirrer was set in motion. To the well stirred solution, a solution of 4.2 g (0.03 mole) of p-methoxythiophenol in 30 ml of anhydrous carbon tetrachloride was added over a period of 60 minutes. After an additional 60 minutes' stirring, the solvent and excess of chlorine were removed under reduced pressure. The crude p-methoxybenzenesulphenyl chloride obtained (4.35 g, 83.3%) was used without further purification.

**Dry dimethylformamide**

Dimethylformamide AR grade (500 ml) was taken in a one-litre round-bottomed flask fitted with a reflux condenser and guarded with a calcium chloride drying tube. About 250 g of freshly heated
quick lime was introduced into the flask, refluxed for 6 hours, left overnight and distilled under vacuum, rejecting the first and last 50 ml portions of dimethylformamide.

**Preparation of Potassium salts of Thiols**

*Potassium p-fluorobenzenethiolate.* In a 250 ml round-bottomed flask fitted with a reflux condenser, guarded with a calcium chloride drying tube, 150 ml of dry toluene and 3.2 g (0.025 mole) of p-fluoro thiophenol were taken. To this solution 0.975 g (0.025 g atom) of freshly cut potassium metal was added. The mixture was heated under reflux for 5 hours, when, white powdered material separated out. The mixture was allowed to cool, filtered and washed with dry toluene to free from thiol. The potassium p-fluorobenzenethiolate thus collected was dried in vacuum desiccator.

*Potassium p-chlorobenzenethiolate.* About 3.6 g (0.025 mole) of p-chlorothiophenol and 150 ml of dry toluene were taken in a 250 ml of round-bottomed flask fitted with a reflux condenser, guarded with a calcium chloride drying tube. Potassium metal (0.975 g, 0.025 g atom) was added and heated under reflux for 6 hours. During refluxion white powdered salt was separated. The contents of the flask were cooled, filtered and was washed with dry toluene. The potassium p-chlorobenzenethiolate thus obtained was dried in a vacuum desiccator.
Potassium p-methoxybenzenethiolate.- p-Methoxythiophenol (3.5 g, 0.025 mole) was dissolved in dry toluene (150 ml) and taken in a 250 ml round-bottomed flask fitted with a reflux condenser guarded with calcium chloride drying tube. To the above solution, freshly cut potassium metal (0.975 g, 0.025 g atom) was added and the mixture was refluxed for 5 hours. The contents of the flask were cooled, and the product was filtered and washed with dry toluene. The potassium salt of p-methoxythiophenol was dried in a vacuum desiccator.

Preparation of 1,1-dichloro-2,2-bis(phenyl)ethylene

(a) Preparation of 1,1,1-trichloro-2,2-bis(phenyl)ethane.- This compound was prepared by Fritsch and Feldmann\(^2\) by a different procedure other than what is described here.

Chloral hydrate (16.5 g, 0.1 mole) and AR benzene (15.4 g, 0.2 mole) were taken in a 250 ml three-necked round-bottomed flask equipped with a thermometer, glycerine sealed stirrer and a calcium chloride guard tube. To the reaction mixture, 100 ml of concentrated sulphuric acid was added slowly and the mixture was kept well stirred for one hour. During this period the temperature rose to about 50° C and some granular 1,1,1-trichloro-2,2-bis(phenyl)ethane started separating out. The mixture was stirred for another one hour in order to ensure the completion of the reaction. The reaction mixture was poured into 2 litres of 2:1 mixture of ice and water while stirring. The precipitated sticky solid was filtered, washed thoroughly with cold
water. The occluded acid was removed by transferring the product into a beaker containing 500 ml of boiling water and stirred well. This effected the compound to melt. The aqueous layer was decanted and the washings were repeated with two further 500 ml portions of water. To the third washing, added a little sodium bicarbonate and stirred until the mixture was neutral to litmus. The solid was filtered at the pump and dried upon the filter paper in the air at 50-60° C. The crude 1,1,1-trichloro-2,2-bis(phenyl)ethane (23.0 g, 80.9%), melted at 58-60° C, was recrystallised from methanol, m.p. 63-64° C (literature², m.p. 64° C).

(b) Dehydrochlorination of 1,1,1-trichloro-2,2-bis(phenyl)ethane to 1,1-dichloro-2,2-bis(phenyl)ethylene.- About 10.0 g (0.07 mole) of 1,1,1-trichloro-2,2-bis(phenyl)ethane was introduced into a solution of 11.0 g of potassium hydroxide dissolved in 500 ml of methanol contained in a one-litre round-bottomed flask fitted with a reflux condenser. The reaction mixture was refluxed for 10 hours, cooled to room temperature and poured onto 800.0 g of crushed ice. The crystalline solid separated was filtered off and washed with water and dried to yield 15.5 g (89.3%) of 1,1-dichloro-2,2-bis(phenyl)ethylene. It was recrystallised from methanol to give colourless needles, m.p. 79-80° C (literature³, m.p. 79-80° C).
Section (ii)

Preparation of (E)- and (Z)-l-p-fluorophenylthiostilbenes

In a 500 ml round-bottomed flask fitted with a reflux condenser a solution of tolan (8.9 g, 0.05 mole) dissolved in 250 ml of n-heptane was taken. The solution was heated to boiling and p-fluoro-thiophenol (6.4 g, 0.05 mole) was added at once. The reaction mixture was heated under reflux for 10 hours and left overnight at room temperature. The contents of the flask were transferred to a separating funnel and washed repeatedly with 2% NaOH solution till free from thiol. Finally, it was washed with water and dried over anhydrous calcium chloride. The n-heptane solution was decanted and the solvent was removed under reduced pressure. The syrupy liquid obtained after removing the solvent was triturated with methanol, when the material got solidified. The yield of the crude product was 13.70 g (89.6%), m.p. 92-95° C. Recrystallisation of the product from methanol gave colourless crystals of (E)-l-p-fluorophenylthiostilbene, m.p. 97-98° C.

Anal. calcd. for C_{20}H_{15}FS: C, 78.40; H, 4.94. Found: C, 78.56; H, 5.07.

$\lambda_{\text{ethanol}}$ max 306 (ε 13,910), 262 (17,258), 205 (25,102); $\lambda_{\text{KBr}}$ max 437, 480, 498, 540, 572, 615, 680, 750, 813, 873, 904, 930, 1005, 1078 s(S-aryl), 1178, 1210, 1392, 1440, 1480, 1583, 1628 w(C=C) and 3065 cm$^{-1}$; NMR(CDCl$_3$): δ 6.81 (s, 1H, vinyl H), 7.28 (m, 10H, Ar-H), 7.63 (m, 4H, F-Ar-H); MS, m/z (% int): 306 (61), 305 (2), 273 (27), 252 (2),
185 (6), 179 (84), 178 (100), 176 (18), 152 (16), 121 (47), 102 (3), 89 (3), 77 (10), 76 (7) and 63 (4).

The filtrate obtained after filtering the crystals of (E)-1-p-fluorophenylthiostilbene was concentrated when a crop of (E)-1-p-fluorophenylthiostilbene was obtained. After filtering the crystals, the solvent was evaporated and the residue obtained was recrystallised, when the crystals of (Z)-1-p-fluorophenylthiostilbene (yield 0.3 g, 7.2%) was obtained. It was recrystallised from aqueous methanol, m.p. 67-68°C.

Anal. calcd. for C_{20}H_{15}FS: C, 78.40; H, 4.94. Found: C, 78.60; H, 5.12.

Preparation of (E)- and (Z)-1-p-chlorophenylthiostilbenes

Tolan (8.9 g, 0.05 mole) was taken in a 500 ml round-bottomed flask fitted with a reflux condenser and dissolved in 250 ml of n-heptane. The solution was heated to boiling and p-chlorothiophenol (7.2 g, 0.05 mole) was added. The reaction mixture was heated for half-an-hour at the boiling temperature and left overnight at room
The reaction mixture was transferred to a separating funnel and washed with 2% sodium hydroxide solution repeatedly till free from thiol and finally washed with water. The heptane layer was collected and dried over anhydrous calcium chloride. The solution was decanted and solvent removed to get a syrupy liquid which on treatment with methanol gave a solid material. The yield of the crude product was 14.7 g (91.3%) and melted at 70-75° C. Recrystallisation of the product from methanol gave (E)-1-p-chlorophenylthiostilbene melting at 77-78° C.

Anal. calcd. for \( \text{C}_{20}\text{H}_{15}\text{ClS} \): C, 74.40; H, 4.68. Found: C, 74.67; H, 4.83.

\( \lambda_{\text{ethanol}} \) max 308 (c 12,490), 204 (44,030); \( \nu_{\text{Nujol}} \) max 490, 508, 518, 551, 591, 694, 763, 813, 870, 913, 939, 1009, 1031, 1077, 1093 s(S-aryl), 1101, 1398, 1473, 1490, 1597, 1672 w(C=C), 2330, 3062 and 3190 cm\(^{-1}\); NMR(CDCl\(_3\)): \( \delta \) 7.09 (s, 1H, vinyl H), 7.25 (m, 10H, Ar-H), 7.63 (m, 4H, Cl-Ar-H).

The filtrate obtained after separating the first crop of the (E)-1-p-chlorophenylthiostilbene was concentrated when second crop of the (E)-isomer was separated. The filtrate after separation of the crystals was evaporated completely and the residue obtained was recrystallised from aqueous methanol to give 1.3 g (8.1%) of (Z)-1-p-chlorophenylthiostilbene, m.p. 61-62° C.

Anal. calcd. for \( \text{C}_{20}\text{H}_{15}\text{ClS} \): C, 74.40; H, 4.68. Found: C, 74.40; H, 4.75.
Preparation of \( \text{(E)}-1\)-p-methoxyphenylthiostilbene

A solution of tolan (8.9 g, 0.05 mole) in n-heptane (250 ml) was taken in a 500 ml round-bottomed flask fitted with a reflux condenser. It was heated to boiling, \( p\)-methoxythiophenol (7.0 g, 0.05 mole) was added in one lot and refluxed for 15 hours. The mixture was washed with 2% sodium hydroxide solution repeatedly and finally with water till free from thiol. The heptane layer was collected, dried over anhydrous calcium chloride, decanted and evaporated off the solvent. The residue left over was distilled under reduced pressure. The distillate collected at 114-117° C/3 mm, yielded 1.0 g of unreacted diphenylacetylene and the residue amounted to 12.0 g (75.5%) of viscous oil. This oil was mixed with 20 ml of petroleum ether (40-60°) and cooled in a refrigerator, when colourless crystals of \( \text{(E)}-1\)-p-methoxyphenylthiostilbene was obtained. Recrystallisation of the product from methanol yielded colourless crystals, m.p. 46-47° C.

Anal. calcd. for \( \text{C}_{21}\text{H}_{18}\text{OS} \): C, 79.21; H, 5.70; Found: C, 79.00; H, 5.91.

\[ \lambda_{\text{ethanol}}^{\text{max}} = 311 \ \text{(e 14,351)}, 259 \ (26,067); \ \nu_{\text{KBr}}^{\text{max}} = 510, 532, 584, 599, 620, 637, 649, 680, 697, 720, 750, 759, 782, 793, 810, \]
845, 850, 868, 882, 890, 901, 920, 1037, 1082 m(S-aryl), 1180, 1253, 1287, 1299, 1387, 1401, 1457, 1590, 1618 w(C=C), 2332, 2839 and 3054 cm⁻¹.

Section (iii)

Preparation of (E)- and (Z)-1,2-bis(p-fluorophenylthio)stilbenes

A 250 ml two-necked flask was fitted with a calcium chloride tube, a dropping funnel guarded with a drying tube and a magnetic stirrer. A solution of 7.65 g (0.025 mole) of (E)-1-p-fluorophenylthiostilbene in 75 ml of glacial acetic acid (Analytical grade) was introduced into it. The stirrer was set in motion and a solution of 4.05 g (0.025 mole) of p-fluorobenzenesulphonyl chloride in 25 ml of glacial acetic acid (Analytical grade) was added dropwise. The addition took about 30 minutes and stirring was continued for 10 hours. During stirring, decolourisation of the solution was observed and some solid material got separated. It was collected by filtration. The yield of the crude product was 2.3 g (21.3%). Recrystallisation from methanol gave (E)-1,2-bis(p-fluorophenylthio)stilbene as colourless needles, m.p. 136-137° C.

Anal. calcd. for C26H18F2S2: C 72.20; H, 4.19; S, 14.82.
Found: C, 72.47; H, 4.42; S, 14.61.

λ max ethanol 312 (6 9,323), 244 (14,560), 205 (48,161); λ max KBr 306, 314, 352, 377, 397, 416, 441, 512, 524, 590, 632, 699, 746, 797, 814, 829, 850, 860, 921, 958, 1010, 1030, 1088 m(S-aryl), 1180, 1220, 1261, 1291, 1396, 1443, 1487, 1588, 1638 w(C=C), 1764, 1887, 1973,
2330, 2924, 3060 and 3451 cm⁻¹; MS, m/z (% int): 434 (10), 433 (5), 432 (36), 305 (48), 285 (11), 284 (20), 273 (8), 272 (33), 252 (9), 228 (15), 210 (40), 196 (10), 178 (100), 176 (47), 165 (13), 152 (26), 127 (30), 126 (11), 121 (10), 102 (5), 95 (4), 89 (6), 83 (59), 77 (15), 63 (10) and 51 (19).

The filtrate from the above reaction mixture after separating the (E)-1,2-bis(p-fluorophenylthio)stilbene was concentrated on a water bath when a solid material was separated. This was collected on a Buchner and weighed 4.2 g (38.9%). It was recrystallised from methanol to give light yellow crystals of (Z)-1,2-bis(p-fluorophenylthio)stilbene, m.p. 87-88° C.

Anal. calcd. for C₂₆H₁₈F₂S₂: C, 72.20; H, 4.19; S, 14.82. Found: C, 72.10; H, 4.45; S, 14.64.

λ max ethanol 310 (¢ 8,646), 238 (14,523), 201 (46,176); λ max KBr 315
345, 367, 389, 399, 413, 426, 458, 470, 512, 562, 620, 633, 694, 736,
763, 812, 829, 862, 910, 933, 979, 1044, 1037, 1076, 1088m(S-aryl),
1175, 1187, 1226, 1276, 1292, 1397, 1443, 1488, 1535, 1637w(C=C),
1888, 2323, 3076 and 3453 cm⁻¹; MS, m/z (% int): 434 (10), 433 (26),
432 (100), 305 (60), 284 (14), 273 (3), 272 (18), 252 (4), 228 (12),
210 (22), 210 (22), 196 (4), 178 (59), 176 (12), 165 (7), 152 (10),
127 (10), 121 (5), 102 (2), 95 (2), 89 (2), 83 (23), 77 (7), 63 (3) and
51 (5).
Preparation of (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene

Into a 100 ml round-bottomed flask fitted with a reflux condenser, a solution of 2.16 g (0.005 mole) of (E)-1,2-bis(p-fluorophenylthio)stilbene dissolved in 50 ml of glacial acetic acid was taken. This was heated to boiling and 20 ml of 30% hydrogen peroxide was added. The solution was then gently refluxed for 1 hour and cooled. The solid separated was collected by filtration to yield 2.0 g (80.6%) of (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene. Recrystallisation of the product from glacial acetic acid gave an analytical sample of (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene, m.p. 267-268° C.

Anal. calcd. for C_{26}H_{18}F_{2}O_{4}S_{2}: C, 62.89; H, 3.65; S, 12.91.
Found: C, 63.10; H, 3.86; S, 12.94.

\(\lambda_{\text{max}}\) ethanol 245 (6 21,351), 225 (27,523), 202 (42,826); \(\lambda_{\text{max}}\) KBr 198, 343, 398, 452, 501, 526, 548, 570, 598, 656, 708, 792, 818, 834, 849, 1011, 1030, 1055, 1081s(S-aryl), 1148s(SO_{2}), 1163, 1233, 1292, 1332s(SO_{2}), 1403, 1445, 1490, 1590, 1636w(C=C), 1918, 2358, 3071 and 3437 cm\(^{-1}\); MS, \(m/z\) (% int): 337 (4), 321 (5), 305 (2), 274 (49), 273 (36), 252 (4), 178 (90), 176 (28), 166 (8), 165 (15), 159 (16), 152 (28), 143 (25), 127 (36), 126 (12), 105 (100), 102 (5), 95 (65), 89 (6), 83 (7), 77 (12), 76 (9), 75 (23), 64 (4), 63 (5) and 51 (6).

Preparation of (Z)-1,2-bis(p-fluorophenylsulphonyl)stilbene

A solution of 2.16 g (0.005 mole) of (Z)-1,2-bis(p-fluorophenylthio)stilbene in 50 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a Leibig condenser. The
solution was heated to boiling, treated with 15 ml of 30% hydrogen peroxide, left overnight and poured onto 200.0 g of crushed ice. The colourless solid separated was collected by filtration. The crude (Z)-1,2-bis(p-fluorophenylsulphonyl)stilbene weighed 2.0 g (80.9%) and melted at 163-165° C. Recrystallisation of the product from glacial acetic acid gave an analytical sample, m.p. 165-166° C.

Anal. calcd. for $C_{26}H_{18}F_2O_4S_2$: C, 62.89; H, 3.65; S, 12.91. Found: C, 62.99; H, 3.89; S, 12.82.

Preparation of (E)- and (Z)-1,2-bis(p-chlorophenylthio)stilbenes

A 250 ml two-necked flask was equipped with a calcium chloride guard tube, a dropping funnel protected with a calcium chloride tube and a magnetic stirrer. A solution of 8.1 g (0.025 mole) of (E)-1-p-chlorophenylthiostilbene in 75 ml of glacial acetic acid was introduced into the flask. The solution was stirred and a solution of (4.5 g, 0.025 mole) of p-chlorophenylsulphenyl chloride in 25 ml of glacial acetic acid was added dropwise during a period of 40 minutes.
Decolourisation of the solution was observed and stirring was continued for 10 hours at lab. temperature. The solid formed was filtered to yield 1.8 g (15.5%) of (E)-1,2-bis(p-chlorophenylthio)stilbene. It was purified by recrystallisation from methanol, m.p. 186-187° C.

Anal. calcd. for $C_{26}H_{18}Cl_2S_2$: C, 67.10; H, 3.90; S, 13.78.
Found: C, 66.82; H, 4.00; S, 13.95.

$\lambda_{\text{max}}$ ethanol 313 (ε 10,002), 245 (14,437), 205 (49,290); $\lambda_{\text{max}}$ KBr 199, 205, 389, 422, 494, 524, 594, 701, 742, 748, 795, 818, 926, 1012, 1030, 1089 s(S-aryl), 1159, 1265, 1360, 1387, 1442, 1474, 1489, 1571, 1636 s(C=C), 1902 and 2330 cm$^{-1}$.

The filtrate obtained from the above reaction mixture after separating the (E)-1,2-bis(p-chlorophenylthio)stilbene was concentrated on a water bath when the crude (Z)-1,2-bis(p-chlorophenylthio)stilbene was obtained. It was collected by filtration to yield 3.2 g (27.5%) of the product which was recrystallised from methanol, m.p. 136-137° C.

Anal. calcd. for $C_{26}H_{18}Cl_2S_2$: C, 67.10; H, 3.90; S, 13.78.
Found: C, 67.27; H, 4.13; S, 13.91.

$\lambda_{\text{max}}$ ethanol 310 (ε 9,364), 238 (13,232), 202 (48,343); $\lambda_{\text{max}}$ KBr 316, 353, 468, 488, 507, 563, 703, 746, 753, 823, 830, 953, 1010, 1049, 1075 s(S-aryl), 1177, 1283, 1323, 1390, 1443, 1472, 1564, 1646 s(C=C), 1913, 2332, 3087 and 3442 cm$^{-1}$.

**Preparation of (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene**

To a refluxing solution of 2.32 g (0.005 mole) of (E)-1,2-
bis(p-chlorophenylthio)stilbene in 50 ml of glacial acetic acid contained in a 100 ml round-bottomed flask fitted with a reflux condenser, 15 ml of 30% hydrogen peroxide was added. The solution was heated under reflux for 1 hour and allowed to cool. The solid separated was collected by filtration to yield 2.2 g (83.3%) of the product. Recrystallisation from glacial acetic acid gave colourless needle shaped crystals of (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene, m.p. 300-301° C.

Anal. calcd. for C$_{26}$H$_{18}$Cl$_2$O$_4$S$_2$: C, 58.98; H, 3.43; S, 12.12. Found: C, 58.87; H, 3.64; S, 12.28.

$\lambda_{\text{max}}$ ethanol 247 (ε 23,167), 226 (26,467), 210 (43,658); $\gamma$ KBr 197, 201, 270, 316, 353, 468, 486, 507, 563, 607, 709, 753, 823, 830, 953, 1009, 1073, 1092 s(S-aryl), 1146 s(SO$_2$), 1177, 1283, 1323 s(SO$_2$), 1390, 1472, 1569, 1647 w(C=C), 1913, 2327, 2357, 3087 and 3457 cm$^{-1}$.

Preparation of (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene

(Z)-1,2-Bis(p-chlorophenylthio)stilbene (2.32 g, 0.005 mole) was dissolved in glacial acetic acid (50 ml) and taken in a 100 ml round-bottomed flask fitted with a reflux condenser. To this solution, 15 ml of 30% hydrogen peroxide was added. The solution was just heated to boiling and left overnight at room temperature. The solution was then poured onto 200.0 g of crushed ice and the solid separated was collected by filtration. Recrystallisation of the product from glacial acetic acid gave 2.3 g (87.7%) of (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene as fine colourless needles, m.p. 204-205° C.

Anal. calcd. for C$_{26}$H$_{18}$Cl$_2$O$_4$S$_2$: C, 58.98; H, 3.43; S, 12.12. Found: C, 59.18; H, 3.61; S, 12.31.
Preparation of (E)- and (Z)-1,2-bis(p-methoxyphenylthio)stilbenes

Into a 250 ml two-necked flask fitted with a dropping funnel protected with a calcium chloride guard tube, a drying tube and a magnetic stirrer, 7.95 g (0.025 mole) of (E)-1-p-methoxyphenylthio-stilbene and 75 ml of glacial acetic acid (AR grade) were introduced. The stirrer was started and a solution of 4.35 g (0.025 mole) of p-methoxybenzenesulphonyl chloride in 25 ml of glacial acetic acid was added dropwise. Addition took about 30 minutes and stirring was continued for 10 hours, during which period a solid material was separated. It was collected by filtration to yield, 1.9 g (16.7%) of the product. The crude product was recrystallised from methanol to give an analytical sample of (E)-1,2-bis(p-methoxyphenylthio)stilbene, m.p. 197-198° C.

Anal. calcd. for C_{28}H_{24}O_{2}S_{2}: C, 73.65; H, 5.30; S, 14.04.
Found: C, 73.83; H, 5.13; S, 13.93.

\[ \lambda_{\text{max}}^{\text{ethanol}} = 240 (\epsilon 19,486), 226 (25,956), 214 (43,176); \]
\[ \nu_{\text{max}}^{\text{KBr}} = 193, 205, 316, 394, 403, 467, 494, 524, 564, 582, 594, 610, 644, 662, 677, 700, 725, 737, 756, 799, 820, 842, 918, 962, 1012, 1032, 1053, 1086s(S-aryl), 1150s(SO_2), 1175, 1244, 1286, 1292, 1324s(SO_2), 1392, 1443, 1471, 1484, 1571, 1638w(C=O), 1761, 1908, 1960, 2325, 2927, \\
\text{and } 3067 \text{ cm}^{-1}. \]
The mother liquor obtained after filtering the (E)-isomer was diluted with water, when crude (Z)-1,2-bis(p-methoxyphenylthio)-stilbene precipitated out. It weighed 3.5 g (30.7%) and melted at 179-181° C. It was recrystallised from 95% ethanol to give colourless crystals melting at 182-183° C.

Anal. calcd. for C_{28}H_{24}O_{2}S_{2}: C, 73.65; H, 5.30; S, 13.93. Found: C, 73.85; H, 5.18; S, 13.98.

Preparation of (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene

To a boiling solution of 2.23 g (0.005 mole) of (E)-1,2-bis(p-methoxyphenylthio)stilbene in 40 ml of glacial acetic acid contained in a 100 ml round-bottomed flask fitted with a reflux condenser, 10 ml of 30% hydrogen peroxide was added. The solution was heated under reflux for 1 hour. It was allowed to cool and the solid separated was collected by filtration to yield 2.1 g (80.8%) of (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene. Recrystallisation from glacial acetic acid gave colourless needles, m.p. 227-228° C.
Anal. calcd. for C$_{28}$H$_{24}$O$_6$S$_2$: C, 64.59; H, 4.65; S, 12.32.

Found: C, 64.81; H, 4.52; S, 12.26.

$\lambda_{\text{ethanol}}$ max 249 (ε 25,557), 229 (28,374), 203 (45,002); $\nu_{\text{KBr}}$ max 191, 344, 449, 478, 518, 551, 574, 594, 606, 626, 659, 695, 719, 789, 807, 830, 915, 1015, 1084s(S-aryl), 1147s(SO$_2$), 1190, 1259, 1281, 1302, 1332s(SO$_2$), 1415, 1444, 1466, 1495, 1593, 1757, 1894, 2847, 2951, 3022, 3062 and 3439 cm$^{-1}$.

Preparation of (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene

Into a 100 ml conical flask about 2.28 g (0.005 mole) of (Z)-1,2-bis(p-methoxyphenylthio)stilbene was taken and dissolved in 40 ml of glacial acetic acid. To this solution, 10 ml of 30% hydrogen peroxide was added, the conical flask was corked tightly and left overnight at room temperature. It was poured onto 200.0 g of crushing ice. The solid separated was collected on the Buchner and recrystallised from glacial acetic acid to yield 2.2 g (84.6%) of (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene as colourless crystals, m.p. 165-166° C.

Anal. calcd. for C$_{28}$H$_{24}$O$_6$S$_2$: C, 64.59; H, 4.65; S, 12.32.

Found: C, 64.87; H, 4.57; S, 12.21.

$\lambda_{\text{ethanol}}$ max 245 (ε 21,964); 228 (28,220), 210 (45,945);

$\nu_{\text{KBr}}$ max 338, 448, 475, 512, 536, 559, 574, 594, 607, 627, 655, 665, 696, 718, 760, 813, 834, 964, 1018, 1085m(S-aryl), 1151s(SO$_2$), 1186, 1263, 1372s(SO$_2$), 1414, 1443, 1461, 1495, 1591, 2325, 2848, 2928, 3057 and 3451 cm$^{-1}$.
Preparation of (E)- and (Z)-1-bromo-2-p-fluorophenylthiostilbenes from (E)-1-p-fluorophenylthiostilbene

About 3.06 g (0.01 mole) of (E)-1-fluorophenylthiostilbene and 75 ml of glacial acetic acid were taken in a 250 ml conical flask fitted with a magnetic stirrer. The stirrer was started and a solution of 1.6 g (0.01 mole) of bromine in 20 ml of acetic acid was added dropwise. During addition decolourisation was observed with immediate precipitation. The addition took about 20 minutes and stirring was continued for 1 hour. The solid obtained was filtered to yield 2.1 g (54.5%) of crude (Z)-1-bromo-2-p-fluorophenylthiostilbene, m.p. 133-135° C. It was then purified by recrystallisation from methanol to give an analytical sample, m.p. 135-136° C.

Anal. calcd. for C_{20}H_{14}FBrS: C, 62.34; H, 3.66. Found: C, 62.61; H, 3.52.

$\lambda_{max}^{\text{ethanol}}$ 318 (6 7,824), 264 (14,921), 224 (25,642), 201 (40,829);
$\nu_{max}^{\text{KBr}}$ 495, 585, 688, 730, 814, 950, 1002, 1068s(S-aryl), 1180, 1215, 1390, 1438, 1480, 1562, 1583, 1629w(C=C); 1830 and 3070 cm$^{-1}$.

The filtrate from the above reaction mixture after separating the (Z)-1-bromo-2-p-fluorophenylthiostilbene on evaporation of the solvent yielded 1.2 g (31.25%) of crude (E)-1-bromo-2-p-fluorophenylthiostilbene. It was recrystallised from ethanol to give long needle shaped crystals, m.p. 110-111° C.
Anal. calcd. for C_{20}H_{14}BrS: C, 62.34; H, 3.66. Found: C, 62.55; H, 3.79.

$\lambda_{\text{ethanol}}^\text{max}$ 320 (ε 7,944), 265 (10,562), 223 (25,824), 203 (41,184);

$\gamma_{\text{KBr}}^\text{max}$ 505, 585, 684, 712, 819, 950, 1006, 1038, 1070 (S-aryl), 1180, 1225, 1290, 1395, 1445, 1485, 1582, 1628 (C=C) and 3072 cm$^{-1}$.

Preparation of (E)- and (Z)-1-bromo-2-p-fluorophenylthiostilbenes from (Z)-1-p-fluorophenylthiostilbene

Into a 100 ml conical flask fitted with a magnetic stirrer, a solution of 0.5 g (0.0016 mole) of (Z)-1-p-fluorophenylthiostilbene in 20 ml of glacial acetic acid was taken. While stirring the solution, a solution of 0.256 g (0.0016 mole) of bromine in 5 ml of acetic acid was added dropwise. During addition, decolourisation was observed with immediate precipitation. The addition took about 5 minutes and stirring was continued for an additional half-an-hour. The product separated was filtered to yield 0.3 g (48.7%) of crude (Z)-1-bromo-2-p-fluorophenylthiostilbene. It was then recrystallised from methanol to give light yellow needles, m.p. 135-136°C. It did not show any depression in the melting point on admixture with an authentic sample of (Z)-1-bromo-2-p-fluorophenylthiostilbene.

The filtrate from the above reaction mixture, after separating the (Z)-1-bromo-2-p-fluorophenylthiostilbene, on evaporation of the solvent yielded 0.207 g (33.6%) of crude (E)-1-bromo-2-p-fluorophenylthiostilbene. It was recrystallised from 95% ethanol to give an analytical sample, m.p. 110-111°C. No depression in melting point of this
compound was observed on admixture with an authentic sample of (E)-1-bromo-2-p-fluorophenylthiostilbene.

**Oxidation of (E)-1-bromo-2-p-fluorophenylthiostilbene to (E)-1-bromo-2-p-fluorophenylsulphonylstilbene**

About 0.8 g (0.0021 mole) of (E)-1-bromo-2-p-fluorophenylthiostilbene was taken in a 100 ml round-bottomed flask fitted with a reflux condenser and then dissolved in 25 ml of glacial acetic acid. The solution was heated to boiling and treated with 10 ml of 30% hydrogen peroxide. The reaction mixture was refluxed for 1 hour. The solid separated on cooling was filtered and recrystallised from glacial acetic acid to yield 0.751 g (85.8%) of (E)-1-bromo-2-p-fluorophenylsulphonylstilbene as colourless crystals, m.p. 134-135°C.

Anal. calcd. for C_{20}H_{14}FBrO_{2}S: C, 57.56; H, 3.38. Found: C, 57.76; H, 3.69.

\[\lambda_{\text{max}}^{\text{ethanol}}: 264 (\epsilon 15,456), 209 (40,637); \gamma^{\text{Nujol}}_{\text{max}}: 416, 465, 494, 515, 545, 560, 613, 641, 653, 662, 700, 730, 767, 794, 834, 964, 1011, 1031, 1065, 1090s(S-aryl), 1149s(SO_{2}), 1229, 1290, 1322s(SO_{2}), 1360, 1404, 1442, 1499, 1590, 1630w(C=C), 2309, 2926 and 2980 cm^{-1}.\]

**Conversion of (E)-1-bromo-2-p-fluorophenylsulphonylstilbene to (E)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstilbene**

About 0.15 g (0.0012 mole) of p-fluorothiophenol was added to an ethanolic solution of sodium ethoxide prepared from 0.028 g (0.0012 g atom) of sodium metal and 10 ml of absolute ethanol. This solution was then added to a hot solution of 0.5 g (0.0012 mole) of
(E)-1-bromo-2-p-fluorophenylsulphonylstilbene in 40 ml of absolute ethanol and taken in 100 ml round-bottomed flask fitted with a reflux condenser. The reflux condenser was protected by a calcium chloride guard tube. The mixture was boiled at reflux temperature for 6 hours. The product separated on cooling was collected by filtration, yield 0.4 g (72.2%). This was recrystallised from 95% ethanol to give colourless crystals of (E)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstilbene, m.p. 179-180° C.

Anal. calcd. for C_{26}H_{18}F_{2}O_{2}S_{2}: C, 67.22; H, 3.91. Found: C, 67.47; H, 4.17.

\[ \chi_{\text{ethanol}}^{\text{max}} \] 290 (ε 13,821), 206 (40,890); \[ \nu_{\text{KBr}}^{\text{max}} \] 480, 505, 538, 560, 645, 678, 742, 822, 975, 1005, 1078s(S-aryl), 1146s(SO_{2}), 1228, 1280, 1290, 1312s(SO_{2}), 1398, 1440, 1435, 1552, 1583 and 3040 cm\(^{-1}\).

Oxidation of (E)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstilbene to (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene

A solution of 0.2 g (0.0043 mole) of (E)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstilbene in 30 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling, 10 ml of 30% hydrogen peroxide was added and refluxed for 1 hour. The solid separated on cooling was collected by filtration to yield 0.2 g (94.3%) of (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene. It was recrystallised from 95% ethanol to give colourless crystals, m.p. 267-268° C. No depression in the mixed melting of this compound was observed on admixture with (E)-1,2-bis-(p-fluorophenylsulphonyl)stilbene.
Anal. calcd. for C_{26}H_{18}F_{2}O_{4}S_{2}: C, 62.89; H, 3.65; S, 12.91. Found: C, 62.81; H, 3.42; S, 12.79.

**Oxidation of (Z)-1-bromo-2-p-fluorophenylthiostilbene to (Z)-1-bromo-2-p-fluorophenylsulphonylstilbene**

A solution of 1.536 g (0.004 mole) of (Z)-1-bromo-2-p-fluorophenylthiostilbene in 40 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 10 ml of 30% hydrogen peroxide was added. The solution was refluxed for 1 hour and the solid separated on cooling was filtered to yield 1.51 g (84.26%) of (Z)-1-bromo-2-p-fluorophenylsulphonylstilbene. Recrystallisation from glacial acetic acid gave colourless crystals, m.p. 168-169° C.

Anal. calcd. for C_{20}H_{14}FBrO_{2}S: C, 57.56; H, 3.38. Found: C, 57.23; H, 3.53.

\[ \lambda_{\text{max}} \text{ ethanol} = 260 (E 14,000), 206 (42,924); \quad \gamma_{\text{max}} \text{ Nujol} = 477, 494, 512, 522, 544, 569, 611, 657, 663, 707, 739, 790, 835, 962, 1012, 1030, 1075(\text{S-aryl}), 1140(\text{SO}_2), 1161, 1232, 1290, 1320(\text{SO}_2), 1376, 1461, 1569, 1710, 2331, 2727, 2862 and 2943 cm^{-1}. \]

**Conversion of (Z)-1-bromo-2-p-fluorophenylsulphonylstilbene to (Z)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstilbene**

Into a 100 ml round-bottomed flask, a solution of 1.12 g (0.0025 mole) of (Z)-1-bromo-2-p-chlorophenylthiostilbene in 25 ml of absolute ethanol was taken. The flask was fitted with a reflux conden-
ser guarded with a calcium chloride tube. Then a solution of sodium
p-fluorobenzene thiolate prepared separately by dissolving 0.058 g
(0.0025 g atom) of sodium, 0.32 g (0.0025 mole) of p-fluorothio-
phenol in 10 ml of absolute ethanol, was added. The reaction
mixture was refluxed for 6 hours and the product separated on cooling
was collected on a Buchner. The yield of the crude (Z)-1-p-fluoro-
phenylthio-2-p'-fluorophenylsulphonylstilbene was 0.92 g (74.8%). Re-
crystallisation of the product from 95% ethanol gave colourless needles,
melting at 183-184° C.

Anal. calcd. for C_{26}H_{18}F_2O_2S_2: C, 67.22; H, 3.91. Found:
C, 67.52; H, 3.80.

\[ \lambda_{\text{max}} \text{ ethanol} \quad 288 (\epsilon 11,289), 205 (42,328); \]
\[ \nu_{\text{max}} \text{ Nujol} \quad 491, 503, 549, 572, 614, 637, 657, 666, 699, 710, 750, 790, 816, 830, 841, 854,
901, 1013, 1025, 1082 s(S-aryl), 1098, 1150 s(SO_2), 1190, 1233, 1265,
1295, 1317 s(SO_2), 1376, 1459, 1490, 1555, 1591, 1737, 1995, 2365,
2725, 2866, 2937, 2945 and 2962 cm\(^{-1}\).

Oxidation of (Z)-1-p-fluorophenylthio-2-p'-fluorophenylsulphonylstil-
bene to (Z)-1,2-bis(p-fluorophenylsulphonylstilbene

A solution of 0.494 g (0.001 mole) of (Z)-1-p-fluorophenylthio-
2-p'-fluorophenylsulphonylstilbene in glacial acetic acid (25 ml) was
taken in a 100 ml round-bottomed flask fitted with a reflux condenser.
The solution was then heated to boiling and treated with 10 ml of
30% hydrogen peroxide, boiled for one minute and left overnight at
room temperature. The product separated was collected by filtration.
The crude (Z)-1,2-bis(p-fluorophenylsulphonylstilbene, weighed 0.45 g.
It was recrystallised from glacial acetic acid to give an analytical sample, m.p. 165-166° C. No depression in melting point of this compound was observed on admixture with (Z)-1,2-bis(p-fluorophenylsulphonyl)stilbene.

Anal. calcd. for C_{26}H_{18}F_{2}O_{4}S_{2}: C, 62.89; H, 3.65; S, 12.91. Found: C, 62.69; H, 3.39; S, 12.80.

Preparation of (E)- and (Z)-1-bromo-2-p-chlorophenylthiostilbenes from (E)-1-p-chlorophenylthiostilbene

About 3.22 g (0.01 mole) of (E)-1-p-chlorophenylthiostilbene was taken in a 250 ml conical flask and dissolved in 75 ml of glacial acetic acid. The solution was kept stirring with a magnetic stirrer and 1.6 g (0.01 mole) of bromine dissolved in 20 ml of acetic acid was added drop-wise. During addition, decolourisation was observed with immediate precipitation. The addition took about 20 minutes and stirring was continued for one hour. The solid separated was filtered to yield 2.3 g (57.4%) of (Z)-1-bromo-2-p-chlorophenylthiostilbene. It was purified by recrystallisation from methanol, m.p. 171-172° C.


\[ \text{\lambda}_{\text{max}}^{\text{ethanol}} \quad 322 (\leq 6,998), \ 268 (15,081), \ 227 (26,000), \ 202 (40,111); \]
\[ \gamma_{\text{max}}^{\text{KBr}} \quad 460, \ 511, \ 626, \ 630, \ 664, \ 702, \ 710, \ 728, \ 745, \ 790, \ 817, \ 820, \ 923, \ 935, \ 1004, \ 1030, \ 1080 \text{m(S-aryl)}, \ 1175, \ 1185, \ 1200, \ 1242, \ 1298, \ 1390, \ 1480, \ 1495, \ 1576, \ 1602, \ 1897, \ 1950 \text{ and } 3070 \text{ cm}^{-1}. \]
The filtrate from the above reaction mixture, after separating the (Z)-1-bromo-2-p-chlorophenylthiostilbene on evaporation yielded 1.3 g (32.4%) of crude (E)-1-bromo-2-p-chlorophenylthiostilbene. It was recrystallised from ethanol, m.p. 109-110° C.


λ (ethanol) max 323 (ε 10,555), 269 (14,223), 227 (26,432), 202 (44,463);

λ (KBr) max 446, 496, 517, 609, 615, 697, 715, 785, 847, 910, 979, 1000, 1027, 1078 (S-aryl), 1193, 1232, 1269, 1398, 1407, 1427, 1466, 1477, 1531, 1580, 1605, 1855, 1927, 2325 and 3013 cm⁻¹.

Preparation of (E)- and (Z)-1-bromo-2-p-chlorophenylthiostilbenes from (Z)-1-p-chlorophenylthiostilbene

About 1.0 g (0.003 mole) (Z)-1-p-chlorophenylthiostilbene was taken into a 100 ml conical flask and dissolved in 30 ml of glacial acetic acid. The solution was stirred with a magnetic stirrer and a solution of 0.480 g (0.003 mole) of bromine in 10 ml of glacial acetic acid was added dropwise. During addition decolourisation was observed with immediate precipitation. The addition took about 5 minutes and stirring was continued for an additional half an hour. The solid obtained was filtered to yield 0.624 g (51.8%) of the crude product. It was purified by recrystallisation from methanol to give light yellow needle shaped crystals of (Z)-1-bromo-2-p-chlorophenylthiostilbene, m.p. 171-172° C. It did not show any depression in the melting point
on admixture with an authentic sample of \((Z)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene.

The filtrate from the above reaction mixture after separating the \((Z)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene, on evaporation yielded 0.421 (34.9\%) of crude \((E)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene. It was then recrystallised from 95\% ethanol to give an analytical sample of \((E)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene, m.p. 109-110\° C. No depression in melting point of this compound was observed on admixture with an authentic sample of \((E)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene.

**Oxidation of \((E)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene to \((E)\)-1-bromo-2-\(p\)-chlorophenylsulphonylstilbene**

Into a 100 ml round-bottomed flask fitted with a reflux condenser, a solution of 1.0 g (0.0025 mole) of \((E)\)-1-bromo-2-\(p\)-chlorophenylthiostilbene in 30 ml of acetic acid was taken. The reaction mixture was heated to boiling and 10 ml of 30\% hydrogen peroxide was added. The solution was refluxed for one hour and cooled. The solid separated on cooling was collected on a Buchner to yield 0.95 g (87.9\%) of \((E)\)-1-bromo-2-\(p\)-chlorophenylsulphonylstilbene. It was recrystallised from ethanol to give an analytical sample, m.p. 174-175\° C.

Anal. calcd. for \(C_{20}H_{14}ClBrO_2S\): C, 55.47; H, 3.23. Found: C, 55.61; H, 3.09.
Conversion of \((E)-1\text{-bromo-2-}p\text{-chlorophenylsulphonylstilbene}\) to \((E)-1\text{-p-chlorophenylthio-2-}p\text{-chlorophenylsulphonylstilbene}\)

A solution of 0.7 g (0.0016 mole) of \((E)-1\text{-bromo-2-}p\text{-chlorophenylsulphonylstilbene}\) in 25 ml of absolute ethanol was taken in 100 ml round-bottomed flask fitted with a reflux condenser guarded with a calcium chloride guard tube. To this solution was added a solution of sodium \(p\text{-chlorobenzenethiolate}\) prepared separately by dissolving 0.037 g (0.001 g atom) of sodium in 10 ml of absolute ethanol and adding 0.23 g (0.0016 mole) of \(p\text{-chlorothiophenol}\). The reaction mixture was refluxed for 8 hours. The product separated on cooling was collected by filtration to yield 0.52 g (65.6%) of \((E)-1\text{-p-chlorophenylthio-2-}p\text{-chlorophenylsulphonylstilbene}\). The crude product was recrystallised from methanol to give an analytical sample, m.p. 205-206\(^\circ\) C.

Anal. calcd. for \(C_{26}H_{18}Cl_2O_2S_2\cdot C\): C, 62.91; H, 3.62. Found: C, 62.47; H, 3.76.

\[\lambda_{\text{ethanol}}\] 291 (ε 15,005), 205 (41,642); \[\nu_{\text{KBr}}\] max 428, 478, 560, 612, 627, 675, 700, 712, 736, 750, 812, 820, 825, 856, 870, 1027, 1030, 1082 s(\(S\text{-aryl}\)), 1137 s(\(SO_2\)), 1180, 1190, 1250, 1290, 1335 s(\(SO_2\)), 1390, 1460, 1487, 1590, 1607 w(\(C=C\)), 1900, 3062 and 3070 cm\(^{-1}\).
Oxidation of (E)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonyl stilbene to (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene

A solution of 0.255 g (0.0005 mole) of (E)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonyl stilbene in 25 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. It was heated to boil and 10 ml of 30% hydrogen peroxide was added. The reaction mixture was refluxed for one hour. The colourless crystals separated on cooling were collected by filtration to yield 0.223 g (84.5%) of (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene. An analytical sample melting at 300-301° C was obtained by recrystallisation of the product from glacial acetic acid. There was no depression in melting point on admixture of this compound with (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene prepared in earlier method.

Anal. calcd. for C_{26}H_{18}Cl_{18}O_{14}S_{2}: C, 58.98; H, 3.43.
Found: C, 58.76; H, 3.23.

Oxidation of (Z)-1-bromo-2-p-chlorophenylthiostilbene to (Z)-1-bromo-2-p-chlorophenylsulphonyl stilbene

To a boiling solution of 2.0 g (0.005 mole) of (Z)-1-bromo-2-p-chlorophenylthiostilbene dissolved in 30 ml of acetic acid and taken in a 250 ml round-bottomed flask fitted with a reflux condenser, 10 ml of 30% hydrogen peroxide was added. The solution was refluxed for one hour. The product separated on cooling was collected by filtration to yield 1.8 g (83.3%) of (Z)-1-bromo-2-p-chlorophenylsulphonyl stilbene. Recrystallisation of the product from methanol gave an analytical sample, m.p. 136-137° C.
Anal. calcd. for $C_{20}H_{14}ClBrO_2S$: C, 55.43; H, 3.23. Found: C, 55.63; H, 3.27.

$\lambda_{\text{ethanol}}$max 269 (ε 15,547), 210 (38,983); $\nu_{\text{KBr}}$max 450, 481, 525, 560, 610, 647, 697, 763, 780, 827, 837, 847, 920, 965, 1030, 1080, 1092s(S-aryl), 1132s(SO$_2$), 1190, 1290, 1317s(SO$_2$), 1457, 1497, 1582, 1680w(C=C), 1767 and 3034 cm$^{-1}$.

Conversion of (Z)-1-bromo-2-p-chlorophenyl sulphonylstilbene to (Z)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonylstilbene

Into a 100 ml round-bottomed flask fitted with a reflux condenser and guarded with calcium chloride tube, a solution of 1.5 g (0.0034 mole) of (Z)-1-bromo-2-p-chlorophenylsulphonylstilbene in 25 ml absolute ethanol was taken. To this solution was added a solution of sodium p-chlorophenythiolate prepared separately by dissolving 0.078 g of sodium (0.0034 g atom) in 25 ml of absolute ethanol and adding 0.49 g (0.0034 mole) of p-chlorothiophenol. The solution was heated under reflux for 7 hours and cooled. The solid separated was collected by filtration to yield 1.25 g (73.96%) of (Z)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonylstilbene. The crude product was recrystallised from ethanol, to give an analytical sample, m.p. 159-160° C.

Anal. calcd. for $C_{26}H_{18}Cl_2O_2S_2$: C, 62.91; H, 3.62. Found: C, 62.58; H, 3.71.

$\lambda_{\text{ethanol}}$max 289 (ε 12,542), 205 (45,024); $\nu_{\text{KBr}}$max 458, 479, 492, 602, 612, 617, 678, 698, 712, 750, 780, 812, 825, 836, 876, 973, 975,
Oxidation of (Z)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonylstilbene to (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene

In a 100 ml round-bottomed flask, 1.0 g (0.002 mole) of (Z)-1-p-chlorophenylthio-2-p'-chlorophenylsulphonylstilbene and 25 ml of glacial acetic acid were taken. The flask was fitted with a reflux condenser. The contents of the flask were heated to boil and treated with 10 ml of 30% hydrogen peroxide. The resultant solution was left overnight and the product separated was collected by filtration to yield 0.820 g (78.1%) of (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene. The crude product was recrystallised from glacial acetic acid to give an analytical sample, m.p. 204-205°C. No depression in melting point of this compound was observed on admixture with (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene prepared earlier.

Anal. calcd. for C_{26}H_{18}Cl_{2}O_{4}S_{2}: C, 58.98; H, 3.43. Found: C, 58.69; H, 3.40.

Preparation of (E)- and (Z)-1-bromo-2-p-methoxyphenylthiostilbenes from (E)-1-p-methoxyphenylthiostilbene

A solution cf 3.17 g (0.01 mole) of (E)-1-p-methoxyphenyl- thiostilbene in 70 ml of glacial acetic acid was taken in a 250 ml conical flask fitted with a magnetic stirrer. To the well stirred solution, 1.6 g (0.01 mole) of bromine in 20 ml of acetic acid was added during a period of 20 minutes. Decolourisation with immediate precipitation was observed during addition. After the addition of bromine,
stirring was continued for 1 hour. The solid separated was filtered to yield 1.9 g (47.8%) of (Z)-1-bromo-2-p-methoxyphenylthiostilbene. It was then purified by recrystallisation from 95% ethanol, m.p. 185-186° C.

Anal. calcd. for C₂₁H₁₇BrO₂S: C, 63.46; H, 4.31. Found: C, 63.65; H, 4.44.

λ_max (ε) ethanol 321 (8,625), 265 (10,329), 230 (28,556), 204 (42,118); ν_max KBr 548, 595, 675, 765, 824, 1020, 1063s(S-aryl), 1170, 1242, 1263, 1440, 1485, 1584, 2320, 2445 and 3060 cm⁻¹.

The filtrate obtained after filtering off the (Z)-1-bromo-2-p-methoxyphenylthiostilbene on dilution with water gave a solid material. It was collected by filtration to yield 1.3 g (32.7%) of (E)-1-bromo-2-p-methoxyphenylthiostilbene. It was recrystallised from 95% ethanol, to give an analytical sample, m.p. 194-195° C.

Anal. calcd. for C₂₁H₁₇BrO₂S: C, 63.46; H, 4.31. Found: C, 63.37; H, 4.57.

λ_max (ε) ethanol 324 (9,056), 272 (11,821), 204 (40,056); ν_max KBr 415, 550, 608, 663, 688, 825, 1020, 1065s(S-aryl), 1248, 1440, 1483, 1578, 2325, 2441 and 3062 cm⁻¹.

Oxidation of (E)-1-bromo-2-p-methoxyphenylthiostilbene to (E)-1-bromo-2-p-methoxyphenylsulphonylstilbene

In a 100 ml round-bottomed flask fitted with a reflux condenser, a solution of 0.715 g (0.0018 mole) of (E)-1-bromo-2-p-methoxy-
phenylthiostilbene in 30 ml of acetic acid was taken. The contents of the flask were heated to boiling and treated with 10 ml of 30% hydrogen peroxide. The reaction mixture was refluxed for 1 hour and the product separated on cooling was filtered to yield 0.652 g (84.5%) of \((E)-1\text{-bromo-2-p-methoxyphenylsulphonylstilbene}\). Recrystallisation of the product from glacial acetic acid gave an analytical sample, m.p. 155-156° C.


Conversion of \((E)-1\text{-bromo-2-p-methoxyphenylsulphonylstilbene}\) to \((E)-1\text{-p-methoxyphenylthio-2-p'-methoxyphenylsulphonylstilbene}\)

Into a 100 ml round-bottom flask fitted with a reflux condenser, 0.429 g (0.001 mole) of \((E)-1\text{-bromo-2-p-methoxyphenylsulphonylstilbene}\) and 30 ml of absolute ethanol were introduced and heated to boiling. A solution of sodium p-methoxybenzenethiolate prepared separately from 0.14 g (0.001 mole) of p-methoxythiophenol, 0.23 g (0.001 g atom) of sodium and 10 ml of absolute ethanol was added. The reaction mixture was refluxed for 7 hours and the product separated on cooling was collected by filtration. The yield of \((E)-1\text{-p-methoxyphenylthio-2-p'-methoxyphenylsulphonylstilbene}\) was 0.346 g (70.9%).
It was recrystallised from 95% ethanol to give an analytical sample, m.p. 218-219° C.

Anal. calcd. for C_{28}H_{24}O_{4}S_{2}: C, 68.83; H, 4.05. Found: C, 69.03; H, 4.98.

\begin{align*}
\lambda_{\text{max}}^\text{ethanol} & = 293 (\varepsilon 14,056), 207 (39,434); \\
\lambda_{\text{max}}^\text{KBr} & = 540, 648, 685, 798, 1005, 1077s(S-aryl), 1135s(SO_2), 1178, 1255, 1320s(SO_2), 1440, 1488, 1587, 2510, 2648, 2880, 2985 and 3180 \text{ cm}^{-1}.
\end{align*}

Oxidation of (E)-1-p-methoxyphenylthio-2-p'-methoxyphenylsulphonyl-stilbene to (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene

A solution of 0.22 g (0.00045 mole) of (E)-1-p-methoxyphenylthio-2-p'-methoxyphenylsulphonyl-stilbene in 30 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 5 ml of 30% hydrogen peroxide was added and refluxed for 1 hour. It was allowed to cool and the solid separated was collected by filtration to yield 0.21 g (89.7%) of the product. Recrystallisation from glacial acetic acid gave colourless needles of (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene, m.p. 227-228° C. The melting point of this compound was same as (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene prepared earlier.

Anal. calcd. for C_{28}H_{24}O_{4}S_{2}: C, 64.59; H, 4.65. Found: C, 64.31; H, 4.36.
Oxidation of (Z)-1-bromo-2-p-methoxyphenylthiostilbene to (Z)-1-bromo-2-p-methoxyphenylsulphonylstilbene

About 1.3 g (0.0032 mole) of (Z)-1-bromo-2-p-methoxyphenylthiostilbene was dissolved in 45 ml of glacial acetic acid and taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and treated with 10 ml of 30% hydrogen peroxide. The mixture was heated under reflux for 1 hour and cooled. The solid separated was collected by filtration to yield 1.25 g (91.9%) of (Z)-1-bromo-2-p-methoxyphenylsulphonylstilbene. Recrystallisation from glacial acetic acid afforded an analytical sample as colourless needles, m.p. 222-223°C.

Anal. calcld. for C_{21}H_{17}BrO_{3}S: C, 58.74; H, 3.99. Found: C, 58.94; H, 3.78.

\( \lambda_{\text{max}} \) \( \text{ethanol} \) 273 ( \( \epsilon \) 15,992), 207 (39,085); \( \psi_{\text{KBr}} \) 483, 552, 664, 685, 718, 833, 912, 1022, 1068 m(S-aryl), 1150s(SO_2), 1238, 1267, 1315s(SO_2), 1440, 1485, 1593, 2328, 2561 and 3075 cm\(^{-1}\).

Conversion of (Z)-1-bromo-2-p-methoxyphenylsulphonylstilbene to (Z)-1-p-methoxyphenylthio-2-p'-methoxyphenylsulphonylstilbene

In a 100 ml round-bottomed flask fitted with a reflux condenser guarded with a calcium chloride tube, a solution of (Z)-1-bromo-2-p-methoxyphenylsulphonylstilbene (0.858 g, 0.002 mole), dissolved in absolute ethanol (40 ml) was taken. A solution of sodium salt of p-methoxythiophenol prepared separately from 0.280 g (0.002 mole), p-methoxythiophenol, sodium (0.046 g, 0.002 g atom) in absolute
ethanol (10 ml) was added at once. The reaction mixture was refluxed for 6 hours and allowed to cool. The solid separated was filtered to yield 0.84 g (86.1%) of the product. It was recrystallised from 95% ethanol to give colourless needles of \((Z)-1-\text{p-methoxyphenylthio-2-p'-methoxyphenylsulphonyl} \text{stilbene, m.p. 216-217° C.}\)

Anal. calcd. for \(C_{28}H_{24}O_4S_2\): C, 68.83; H, 4.95. Found: C, 68.99; H, 4.82.

\(\lambda_{\text{max}}^{\text{ethanol}} 286 (\varepsilon 11,388), 206 (40,191); \beta_{\text{KBr}} \text{max} 543, 645, 670, 750, 798, 1005, 1084s(S\text{-aryl}), 1143s(SO_2), 1180, 1298, 1310s(SO_2), 1348, 1460, 1498, 1510, 2613, 2598, 2650, 2890, 2923, 2989 and 3182 cm\(^{-1}\).\)

Oxidation of \((Z)-1-\text{p-methoxyphenylthio-2-p'-methoxyphenylsulphonyl} \text{stilbene to (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene}\

A solution of 0.585 g (0.0012 mole) of \((Z)-1-\text{p-methoxyphenylthio-2-p'-methoxyphenylsulphonyl} \text{stilbene in 30 ml of glacial acetic acid was taken in a 100 ml conical flask and heated to boiling. About 10 ml of 30\% hydrogen peroxide was added, left aside for 1 hour, and then poured over 200.0 g of crushed ice. The solid separated was filtered to give 0.51 g (81.7\%) of \((Z)-1,2\text{-bis(p-methoxyphenylsulphonyl)stilbene. It was recrystallised from 95\% ethanol to give colourless crystals, m.p. 165-166° C. It showed no depression in melting point on admixture with (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene prepared in earlier method.}\n
Anal. calcd. for \(C_{28}H_{24}O_4S_2\): C, 64.59; H, 4.65. Found: C, 64.40, H, 4.39.
(E)-1,2-Bis(p-fluorophenylthio)stilbene

Into a 250 ml two-necked flask fitted with a gas inlet tube, a reflux condenser protected with a calcium chloride drying tube and a magnetic stirrer, a solution of 4.0 g of benzoin in 75 ml of glacial acetic acid was introduced. The stirrer was set in motion. To the well stirred solution, 7.6 g of p-fluorothiophenol was added at once and then saturated with dry hydrogen chloride gas for 2 hours. About 10.0 g of pulverised anhydrous zinc chloride was added to the reaction mixture and the passage of hydrogen chloride gas and stirring was continued for an additional 30 minutes. The reaction mixture was left in a refrigerator for 2 days, when colourless crystals separated out. The crystals were filtered, and washed with cold 95% ethanol followed by light petroleum ether (b.p. 40-60°) to yield 0.65 g of the product melting at 134-136° C. Recrystallisation from methanol produced colourless needles, m.p. 136-137° C. No depression in melting point of this compound was observed on admixture with (E)-1,2-bis(p-fluorophenylthio)stilbene prepared earlier.

Anal. calcd. for: C_{26}H_{16}F_{2}S_{2}: C, 72.70; H, 4.19. Found: C, 72.03; H, 4.02.

Oxidation of (E)-1,2-bis(p-fluorophenylthio)stilbene to (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene

In a 100 ml round-bottomed flask fitted with a reflux condenser, 0.2 g (0.00046 mole) of (E)-1,2-bis(p-fluorophenylthio)stilbene and
25 ml of glacial acetic acid were placed. The contents of the flask were heated to boiling and 5 ml of 30% hydrogen peroxide was added. The reaction mixture was gently heated under reflux for 1 hour and then allowed to cool. The (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene separated was collected by filtration. The yield was 0.178 g (79.6%). It was recrystallised from methanol. It melted at 267-268° C. The melting point of this compound was not depressed on admixture with (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene prepared earlier.

(E)-1,2-Bis(p-chlorophenylthio)stilbene

About 4.0 g of benzoin was dissolved in 75 ml of glacial acetic acid and taken in 250 ml two-necked flask fitted with a glass inlet tube and a reflux condenser guarded with a calcium chloride drying tube. The solution was stirred with a magnetic stirrer and 8.6 g of p-chlorothiophenol was added. The reaction mixture was saturated with dry hydrogen chloride gas for 2 hours, while continuing the stirring. Pulverised anhydrous zinc chloride (10.0 g) was introduced into the flask and the passage of hydrogen chloride gas and stirring was continued for an additional 30 minutes. The reaction mixture was kept in a refrigerator for 2 days when colourless crystals separated out. The crystals were filtered and washed with cold ethanol followed by light petroleum ether (b.p. 40-60°). The crude (E)-1,2-bis(p-chlorophenylthio)stilbene weighed 0.7 g and recrystallised from 95% ethanol, m.p. 186-187° C. Melting point of this compound was not depressed on admixture with (E)-1,2-bis(p-chlorophenylthio)stilbene prepared by a different route.
Anal. calcd. for C_{26}H_{18}Cl_{2}S_{2}: C, 67.10; H, 3.90. Found: C, 66.83; H, 3.71.

Oxidation of (E)-1,2-bis(p-chlorophenylthio)stilbene to (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene

In a 100 ml round-bottomed flask fitted with a reflux condenser, a solution of 0.2 g (0.00043 mole) of (E)-1,2-bis(p-chlorophenylthio)stilbene in 25 ml of glacial acetic acid was taken. The solution was treated with 5 ml of 30% hydrogen peroxide and boiled under reflux for 1 hour. The solid separated on cooling was collected by filtration to yield 0.188 g (83.0%) of (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene. Recrystallisation of the product from acetic acid gave colourless crystals, m.p. 300-301° C. On admixture of this compound with (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene prepared earlier showed no depression in the melting point.

(E)-1,2-Bis(p-methoxyphenylthio)stilbene

A solution of 4.0 g of benzoin in 75 ml of glacial acetic acid was taken in a 250 ml two-necked flask fitted with a gas inlet tube and a reflux condenser protected with a calcium chloride tube. The solution was stirred with a magnetic stirrer and 8.4 g of p-methoxythiophenol was added. The reaction mixture was saturated with dry hydrogen chloride gas for 2 hours while continuing the stirring. About 10.0 g of pulverised anhydrous zinc chloride was added to the reaction mixture. The passage of hydrogen chloride gas and stirring was continued for an additional 30 minutes. The reaction mixture was left in
a refrigerator for 2 days. The colourless crystals separated were filtered and washed with cold 95% ethanol followed by light petroleum ether (b.p. 40-60°). The crude product weighing 0.710 g was recrystallised from 95% ethanol to give (E)-1,2-bis(p-methoxyphenylthio)-stilbene, m.p. 197-198° C. No depression in the melting point of this compound was observed on admixture with (E)-1,2-bis(p-methoxyphenylthio)stilbene, prepared earlier.

Anal. calcd. for C_{28}H_{24}O_{6}S_{2}: C, 64.59; H, 4.65. Found: C, 64.36; H, 4.61.

Oxidation of (E)-1,2-bis(p-methoxyphenylthio)stilbene to (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene

To a refluxing solution of 0.2 g (0.00044 mole) of (E)-1,2-bis(p-methoxyphenylthio)stilbene in 30 ml of glacial acetic acid contained in a 100 ml round-bottomed flask fitted with a reflux condenser, 10 ml of 30% hydrogen peroxide was added. The refluxion was continued for 1 hour and the colourless crystals separated on cooling were filtered to yield 0.183 g (80.5%) of the product. Recrystallisation from acetic acid gave an analytical sample of (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene, m.p. 227-228° C. On admixture of this compound with (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene prepared earlier showed no depression in the melting point.
Section (vi)

Preparation of 1,1-bis(p-fluorophenylthio)-2,2-bis(phenyl)ethylene

Into a 500 ml three-necked round-bottomed flask equipped with a mercury sealed stirrer, a dropping funnel and a reflux condenser guarded with a calcium chloride tube, 2.48 g (0.01 mole) of 1,1-dichloro-2,2-bis(phenyl)ethylene and 150 ml of dry dimethylformamide were taken. The solution was stirred and heated to boiling on a mantle. To the boiling solution, 3.32 g (0.02 mole) of potassium salt of p-fluorothiophenol in 25 ml of dry dimethylformamide was added over a period of 30 minutes. Heating and stirring was continued for 10 hours. The flask was cooled and the contents poured into 200 ml of ice-cold water. The solid separated was filtered to yield 2.1 g (48.6%) of 1,1-bis(p-fluorophenylthio)-2,2-bis(phenyl)ethylene and recrystallised from 95% ethanol, m.p. 86-87°C.

Anal. calcd. for C_{26}H_{18}F_{12}S: C, 72.20; H, 4.19; S, 14.82.

Found: C, 72.34; H, 4.42; S, 14.71.

$\lambda_{\text{max}}$ ethanol 264 (ε 19,263), 234 (28,321), 210 (49,692); $\gamma_{\text{max}}$ KBr 191, 203, 379, 411, 437, 459, 479, 506, 523, 610, 629, 639, 674, 694, 703, 749, 757, 814, 826, 850, 920, 965, 1012, 1033, 1073, 1093 m(S-aryl), 1231, 1293, 1397, 1442, 1488, 1590, 1759, 1887, 3066 and 3488 cm$^{-1}$;

MS, m/z (% int): 340 (98), 305 (69), 284 (21), 273 (8), 272 (40), 252 (8), 228 (13), 210 (18), 208 (13), 196 (10), 178 (100), 176 (44), 166 (10), 165 (49), 152 (23), 139 (24), 127 (10), 126 (8), 121 (7), 102 (3), 95 (8), 89 (10), 83 (28), 77 (26), 76 (8), 75 (25), 63 (18) and 51 (50).
Preparation of \(1,1\)-bis(p-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylen

To a boiling solution of 1.0 g (0.00233 mole) of \(1,1\)-bis(p-fluorophenylthio)-2,2-bis(phenyl)ethylenel taken in a 100 ml round-bottomed flask fitted with a reflux condenser, 10 ml of 30% hydrogen peroxide was added. The solution was refluxed for one hour and then allowed to cool. The solid separated was filtered to yield 0.94 g (81.3%) of \(1,1\)-bis(p-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylenel. It was recrystallised from methanol, m.p. 128-129° C.

Anal. calcd. for \(C_{26}H_{18}F_2O_2S_2\): C, 62.89; H, 3.65; S, 12.91.

Found: C, 63.17; H, 3.80; S, 12.79.

\(\lambda_{\text{max}}^{\text{ethanol}}\) 249 (\(\epsilon\) 17,241), 224 (26,003), 209 (48,432); \(\lambda_{\text{max}}^{\text{KBr}}\) 182, 397, 433, 456, 545, 569, 609, 639, 669, 684, 705, 749, 761, 810, 821, 836, 849, 919, 930, 975, 1000, 1010, 1032, 1087 m(S-aryl), 1097, 1136 s(SO\(_2\)), 1167, 1234, 1291, 1336 s(SO\(_2\)), 1404, 1444, 1490, 1590, 1903, 2330, 2358, 3062 and 3451 cm\(^{-1}\); MS, m/z (% int): 372 (50), 214 (50), 213 (76), 212 (78), 201 (55), 178 (100), 176 (70), 166 (13), 165 (38), 152 (43), 143 (30), 127 (7), 126 (14), 102 (8), 95 (51), 89 (7), 83 (5), 77 (83), 76 (14), 75 (38), 63 (11) and 51 (18).

Preparation of \(1,1\)-bis(p-chlorophenylthio)-2,2-bis(phenyl)ethylen

A 500 ml three-necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel and a mercury sealed stirrer. All the stands were protected by calcium chloride guard tubes. About 2.48 g (0.01 mole) of \(1,1\)-dichloro-2,2-bis(phenyl)ethylenel and 150 ml of dry dimethylformamide were introduced into the flask. The stirrer
was set in motion and the flask was heated on a mantle. To the boiling solution, 3.64 g (0.02 mole) of potassium p-chlorobenzenethiolate in 25 ml of dry dimethylformamide was added over a period of 30 minutes. Stirring and refluxion was continued for 10 hours. The contents of the flask were cooled to room temperature and poured into 200 ml of ice-cold water. The solid separated was filtered to yield 2.2 g (47.4%) of 1,1-bis(p-chlorophenylthio)-2,2-bis(phenyl)ethylene. Recrystallisation from methanol gave colourless crystals, m.p. 122-123°C.

Anal. calcd. for C_{26}H_{18}Cl_{2}S_{2}: C, 67.10; H, 3.90; S, 13.78. Found: C, 67.20; H, 4.20; S, 13.52.

Preparation of 1,1-bis(p-chlorophenylsulphonyl)-2,2-bis(phenyl)ethylene

A solution of 1.0 g (0.0022 mole) of 1,1-bis(p-chlorophenylthio)-2,2-bis(phenyl)ethylene in 30 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser.
The solution was heated to boiling, 10 ml of 30% hydrogen peroxide was added and refluxed for one hour. The 1,1-bis(p-chlorophenylsulphonyl)-2,2-bis(phenyl)ethylene separated on cooling was filtered and weighed 0.953 g (82.2%). It was recrystallised from methanol, m.p. 159-160° C.

Anal calcd. for C_{26}H_{18}Cl_{2}O_{4}S_{2}: C, 58.98; H, 3.43; S, 12.12. Found: 59.24; H, 3.58; S, 12.21.

\[
\text{\textit{\lambda}}_{\text{max}} \text{ ethanol} 248 (\epsilon 17,221), 229 (28,013), 208 (50,602); \text{\textit{\lambda}}_{\text{max}} \text{ KBr} 311, 344, 375, 409, 419, 431, 453, 469, 488, 511, 532, 563, 595, 620, 635, 658, 687, 705, 727, 749, 785, 797, 817, 850, 889, 913, 923, 946, 979, 1002, 1030, 1056, 1090 m (S-aryl), 1108, 1121, 1158 s (SO_{2}), 1176, 1214, 1225, 1238, 1281, 1296, 1334 s (SO_{2}), 1393, 1445, 1474, 1491, 1571, 1583, 1911, 2303, 3075 and 3451 cm^{-1}; \text{MS, m/z (int)}: 400 (3), 388 (39), 372 (5), 324 (5), 291 (4), 214 (27), 213 (48), 212 (62), 201 (24), 178 (100), 176 (41), 166 (9), 165 (13), 152 (18), 126 (7), 111 (8), 102 (3), 89 (6), 77 (6), 76 (8), 75 (9) and 63 (5).

\textit{Preparation of 1,1-bis(p-methoxyphenylthio)-2,2-bis(phenyl)ethylene}

A 500 ml three-necked round-bottom flask was fitted with a mercury sealed stirrer, a reflux condenser and a dropping funnel. All the exists were guarded with calcium chloride drying tubes. A solution of 1,1-dichloro-2,2-bis(phenyl)ethylene (2.48 g, 0.01 mole), in dry dimethylformamide (50 ml) was introduced into the flask. The stirrer was started and the solution heated to reflux temperature. Potassium
salt of $p$-methoxythiophenol (3.56 g, 0.02 mole) in dry dimethyl-formamide (20 ml) was added from the dropping funnel over a period of 20 minutes. The mixture was then refluxed for 10 hours while continuing the stirring. The flask was cooled and the contents were poured into 200 ml of ice cold water. The 1,1-bis($p$-methoxyphenyl-thio)-2,2-bis(phenyl)ethylene thus separated was filtered off. The yield was 2.3 g (50.4%). It was recrystallised from methanol to give colourless needles, m.p. 82-83°C.

Anal. calcd. for $C_{28}H_{24}O_2S_2$: C, 73.65; H, 5.30; S, 14.04. Found: C, 73.79; H, 5.39; S, 14.19.

Preparation of 1,1-bis($p$-methoxyphenylsulphonyl)-2,2-bis(phenyl)-ethylene

Into a 100 ml round-bottomed flask fitted with a reflux condenser, a solution of 1.0g (1.0021 mole) of 1,1-bis($p$-methoxyphenyl-thio)-2,2-bis(phenyl)ethylene in 25 ml of glacial acetic acid was taken. The solution was heated to boiling temperature and 10 ml of
30% hydrogen peroxide was added. The reaction mixture was heated under reflux for one hour. The solid separated on cooling was filtered to yield 0.97 g (88.1%) of 1,1-bis(p-methoxyphenylsulphonyl)-2,2-bis(phenyl)ethylene. Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 142-143° C.

Anal. calcd. for C_{28}H_{24}O_{6}S: C, 64.59; H, 4.65; S, 12.32.
Found: C, 64.38, H, 4.51; S, 12.19.

\[ \lambda_{\text{max}} \text{ ethanol} \ 252 (\varepsilon 18,162), 230 (24,323), 209 (40,841); \ \lambda_{\text{max}}^{\text{KBr}} \ 192, 202, 316, 400, 474, 554, 571, 610, 626, 640, 668, 706, 747, 761, 801, 831, 952, 976, 1025, 1090S-aryl), 1110, 1154s(SO}_2), 1177, 1264, 1299, 1312s(SO}_2), 1336, 1464, 1446, 1492, 1576, 1593, 2322, 2941, 2970 and 3440 cm^-1; MS, m/z (% int): 384 (37), 370 (2), 320 (10), 285 (25), 284 (28), 214 (28), 213 (23), 212 (26), 178 (100), 176 (32), 155 (32), 152 (18), 126 (4), 123 (7), 107 (10) and 77 (16).

Oxidation of 1,1-bis(p-fluorophenylsulphonyl)-2,2-bis(phenyl)ethylene

Into a 250 ml round-bottomed flask fitted with a reflux condenser, 1.0 g of 1,1-bis(p-fluorophenylsulphonyl)-2,2-bis(phenyl)-ethylene, 5.0 g of chromic acid and 30 ml of glacial acetic acid were introduced. The reaction mixture was refluxed for 10 hours and poured into 250 ml of ice cold water. The solid separated was filtered and washed with water. The crude product thus obtained was recrystallised from petroleum ether (40-60°) to give colourless needles, m.p. 46-47° C. The melting point of this compound was not depressed on admixture with benzophenone.
Oxidation of 1,1-bis(p-chlorophenylsulphonyl)-2,2-bis(phenyl)ethylene

To a solution of 5.0 g of chromic acid in 40 ml of glacial acetic acid, taken in 100 ml round-bottomed flask fitted with a reflux condenser, 1.0 g of 1,1-bis(p-chlorophenylsulphonyl)-2,2-bis(phenyl)ethylene was added. The reaction mixture was refluxed for 12 hours and the resultant solution was poured into 300 ml ice cold water. The solid separated was collected on Buchner and washed with water. The compound was recrystallised from petroleum ether (40-60°) to give colourless needles, m.p. 46-47° C. No depression in melting point was observed on admixture with benzophenone.

Oxidation of 1,1-bis(p-methoxyphenylsulphonyl)-2,2-bis(phenyl)ethylene

Into a 100 ml round-bottomed flask fitted with a reflux condenser, 1.0 g of 1,1-bis(p-methoxyphenylsulphonyl)-2,2-bis(phenyl)ethylene, 5.0 g of chromic acid and 40 ml of glacial acetic acid were introduced. The mixture was heated under reflux for 12 hours and then poured into 300 ml of ice cold water. The crude product separated was filtered and recrystallised from petroleum ether (40-60°) to give colourless needles, m.p. 46-47° C. The melting point of this compound was not depressed on admixture with benzophenone.

Section (vii)

Isomerisation of (Z)-1,2-bis(p-fluorophenylthio)stilbene to (E)-1,2-bis(p-fluorophenylthio)stilbene

(Z)-1,2-Bis(p-fluorophenylthio)stilbene (0.15 g) was taken in a
small test tube and heated at 110° C in an oil bath for 5 minutes. The melt was cooled and the solid was recrystallised from methanol to give colourless needles (0.13 g), m.p. 136-137 ° C. It was found to be identical (melting point and mixed melting points) with the sample of (E)-1,2-bis(p-fluorophenylthio)stilbene.

**Isomerisation of (Z)-1,2-bis(p-chlorophenylthio)stilbene to (E)-1,2-bis(p-chlorophenylthio)stilbene**

In a small test tube, 0.2 g of (Z)-1,2-bis(p-chlorophenylthio)-stilbene was taken and heated in an oil bath at 140° C for 5 minutes. The melt was cooled and solid obtained was recrystallised from methanol. The colourless needles obtained (0.174 g) melted at 186-187° C. It showed no depression in melting point on admixture with an authentic sample of (E)-1,2-bis(p-chlorophenylthio)stilbene.

**Isomerisation of (Z)-1,2-bis(p-methoxyphenylthio)stilbene to (E)-1,2-bis(p-methoxyphenylthio)stilbene**

About 0.15 g of (Z)-1,2-bis(p-methoxyphenylthio)stilbene was introduced into a small test tube and heated to 190° C in an oil bath for 5 minutes. The melt was solidified on cooling which on recrystallisation from methanol gave 0.123 g of a product which did not depress the melting point (197-198° C) of an authentic sample of (E)-1,2-bis(p-methoxyphenylthio)stilbene.
Isomerisation of (Z)-1,2-bis(p-fluorophenylsulphonyl)stilbene to (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene

Into a small test tube, about 0.25 g of (Z)-1,2-bis(p-fluorophenylsulphonyl)stilbene was introduced and heated above its melting point (180°C) for 5 minutes in an oil bath. The melt was cooled and the solid obtained was recrystallised from glacial acetic acid. The colourless needles obtained (0.19 g) did not depress the melting point (267-268°C) of an authentic sample of (E)-1,2-bis(p-fluorophenylsulphonyl)stilbene.

Isomerisation of (Z)-1,2-bis(p-chlorophenylsulphonyl)stilbene to (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene

(Z)-1,2-Bis(p-chlorophenylsulphonyl)stilbene (0.15 g) was taken in a test tube and heated to 210°C in an oil bath. The heating was continued for 5 minutes and cooled. The solidified mass was recrystallised from glacial acetic acid to give colourless needle shaped crystals (0.124 g), m.p. 300-301°C. It was found to be identical (melting point and mixed melting point) with an authentic sample of (E)-1,2-bis(p-chlorophenylsulphonyl)stilbene.

Isomerisation of (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene to (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene

In a small test tube, 0.15 g of (Z)-1,2-bis(p-methoxyphenylsulphonyl)stilbene was taken and heated to 180°C in an oil bath for 5 minutes. The melt was cooled and the solidified mass was recrystallised from glacial acetic acid to give 0.12 g of the product.
It did not depress the melting point (227-228°C) of an authentic sample of (E)-1,2-bis(p-methoxyphenylsulphonyl)stilbene.

**Isomerisation of (E)-1-bromo-2-p-fluorophenylthiostilbene to (Z)-1-bromo-2-p-fluorophenylthiostilbene**

A solution of (E)-1-bromo-2-p-fluorophenylthiostilbene (0.5 g) in benzene (250 ml) was irradiated with ultraviolet light for 15 hours. The residue obtained, on evaporation of the solvent was subjected to fractional crystallisation from glacial acetic acid. Light yellow needles (0.24 g, 48.0%), m.p. 135-136°C, obtained did not show any depression in melting point on admixture with an authentic sample of (Z)-1-bromo-2-p-fluorophenylthiostilbene. The ultraviolet and infrared spectral properties of both the compounds were found to be identical.

**Isomerisation of (E)-1-bromo-2-p-chlorophenylthiostilbene to (Z)-1-bromo-2-p-chlorophenylthiostilbene**

(E)-1-Bromo-2-p-chlorophenylthiostilbene (0.5 g) was dissolved in 250 ml of benzene. The solution was irradiated with ultraviolet light for 20 hours. The residue obtained, on evaporation of the solvent was subjected to fractional crystallisation from glacial acetic acid to give 0.15 g (30.0%) of pale yellow needles, melting at 171-172°C. No depression in the melting point of this compound was observed on admixture with an authentic sample of (Z)-1-bromo-2-p-chlorophenylthiostilbene. The ultraviolet and infrared spectra of both the compounds were found to be identical.
Isomerisation of (E)-1-bromo-2-p-methoxyphenylthiostilbene to (Z)-1-bromo-2-p-methoxyphenylthiostilbene

About 0.5 g of (E)-1-bromo-2-p-methoxyphenylthiostilbene was dissolved in 250 ml of benzene. The solution was exposed to ultraviolet light for 18 hours. The solvent was evaporated and the residue obtained was subjected to fractional crystallisation from glacial acetic acid when pale yellow needles (0.17 g, 34.0%) melting at 185-186° C were obtained. There was no depression in the mixed melting point of this compound on admixture with an authentic sample of (Z)-1-bromo-2-p-methoxyphenylthiostilbene. Both the compounds showed identical ultraviolet and infrared spectral properties.

Attempted reaction of 1,1-dichloro-2,2-bis(phenyl)ethylene with p-fluorobenzenethiol in presence of sodium ethoxide

To a solution of sodium ethoxide prepared by dissolving 0.230 g (0.01 g atom) of sodium in 25 ml of absolute ethanol, 1.28 g (0.01 mole) of p-fluorobenzenethiol was added. This mixture was added to a boiling solution of 2.1 g (0.005 mole) of 1,1-dichloro-2,2-bis(phenyl)ethylene dissolved in 150 ml of absolute ethanol and taken in a 250 ml round-bottomed flask fitted with a reflux condenser. The resultant solution was heated under reflux for 18 hours and poured into 750 ml of ice cold water. The solid separated was collected by filtration and washed with water. The solid melted at 77-78° C. It was found to contain no sulphur and showed no depression in melting point on admixture with 1,1-dichloro-2,2-bis(phenyl)ethylene.
Attempted reaction of 1,1-dichloro-2,2-bis(phenyl)ethylene with p-chlorobenzenethiol in presence of sodium ethoxide

Sodium p-chlorobenzenethiolate prepared by dissolving 0.230 g (0.01 g atom) of sodium and 1.44 g (0.01 mole) of p-chlorobenzethiol in 25 ml of absolute ethanol was added to a refluxing solution of 2.1 g (0.005 mole) of 1,1-dichloro-2,2-bis(phenyl)ethylene dissolved in 150 ml of absolute ethanol. The reaction mixture was refluxed for 20 hours and then poured into 750 ml of ice cold water. The solid separated was collected by filtration and washed with water. The compound melted at 77-78° C. No depression in melting was observed on admixture with 1,1-dichloro-2,2-bis(phenyl)ethylene.

Attempted reaction of 1,1-dichloro-2,2-bis(phenyl)ethylene with p-methoxybenzenethiol in presence of sodium ethoxide

p-Methoxybenzenethiol (1.40 g, 0.01 mole) was added to a solution of sodium ethoxide prepared by dissolving sodium (0.23 g, 0.01 g atom) in absolute ethanol (25 ml). This solution was then added to a refluxing solution of 1,1-dichloro-2,2-bis(phenyl)ethylene (2.1 g, 0.005 mole) in absolute ethanol (150 ml). The reaction mixture was refluxed for 18 hours and poured into 750 ml of ice cold water. The solid obtained was collected by filtration and washed with water. The solid melted at 77-78° C. There was no depression in melting point of this compound on admixture with 1,1-dichloro-2,2-bis(phenyl)ethylene.
REFERENCES


