(2.1&2.2). PURPOSE:

2.1. The overall objective of the present work was to prepare a number of new (E)- and (Z)-monosulphides, (E)- and (Z)-monosulpones, (E)- and (Z)-bromo-sulphides, (E)- and (Z)-bromosulphones and to establish their configurations by spectral and other physico-chemical methods. In order to accomplish this objective the following units of work were planned.

1. Preparation of (E) - and (Z) -1- p-bromophenyl-2-phenyl-1-p-chloro phenylthio ethylenes and (E) - and (Z) -2 - p-bromophenyl-1-phenyl-1-p-chlorophenylthio ethylenes.

2. Oxidation of (E)– and (Z) -1- p-bromophenyl- 2-phenyl-1-p-chloro phenylthio ethylenes to (E)- and (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylsulphonyl ethylenes.

3. Oxidation of (E)- and (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylthio ethylenes to (E)- and (Z)-2-p-bromophenyl-1-phenyl-1-p-chloro-phenylsulphonyl ethylenes.


5. Bromination of (E)- and (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylthio ethylenes and to isolate (E)- and (Z)–1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenylthioethylenes.


11. Oxidation of the \((E)\)- and \((Z)\)-2-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl-2-\(p\)-chlorophenylthio ethylenes to \((E)\)- and \((Z)\)-1,2-bis(\(p\)-chlorophenylsulphonyl)-1-\(p\)-bromo-phenyl-2-phenylethylenes.

2.2. The overall objective of the present work was to prepare a number of new \((E)\)- and \((Z)\)-selenyl sulphides, and \((E)\)- and \((Z)\)-selenonyl sulphones and to establish their configurations by spectral and other physico-chemical methods. In order to accomplish this objective the following units of work were planned.

13. Preparation of \((E)\)– and \((Z)\)–1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylenes from \((E)\)– and \((Z)\)–2-p-bromophenyl-1-phenyl-1-p-chlorophenyl thioethylenes


16. Structural elucidation of all the synthesised compounds by infrared spectroscopy, \(^1\)HNMR spectroscopy and mass spectrometry. Biological evaluation of all the synthesised compounds.
2.3. EXPERIMENTAL

Melting points were determined in open capillaries on Mel-Temp.apparatus, Laboratory devices, Cambridge, U.S.A. and are uncorrected.

Elemental Analysis

Elemental Analysis were determined with a Carlo Erba 1106 elemental Analyzer obtained from Central drug Research Institute, Lucknow.

Infrared absorption measurements

The infrared absorption spectra were recorded using KBr pellets on Perkin-Elmer SPECTRUM 100FT-IR spectrometer.

Nuclear Magnetic Resonance Spectrum measurements

\(^1\)H NMR spectra were recorded at 400 MHz on a Mercury plus (varian 400MHz) AR&D, Aurigene Discovery Technologies Ltd, Hyderabad and their chemical shifts are reported in δ ppm with respect to TMS as internal standard.

GC-Mass Spectrometry

GC-Mass spectral recordings were measured by means of HP 6890 gas chromatograph equipped with an HP 5973 Mass Selective Detector.

Source and purification of thiol

\(p\)-chloro benzenethiol was obtained from M/s Aldrich Chemical Company, Inc., Wisconsin, U.S.A. and was used without further purification.

\(p\)- Chlorobenzenethiol  
M.P.  
49-51°C
Source and purification of Phenylselenyl bromide

Phenylselenyl bromide was obtained from M/s Aldrich Chemical Company, Inc., Wisconsin, U.S.A. and was used without further purification.

| Phenylselenyl bromide | M.P. | 60-62 °C |

2.3.1. Benzyl p-bromophenyl ketone; [1-(4-bromophenyl)-2-phenylethanone]

It was prepared according to the procedure of M.S. Newman and D.E.Reid\(^1\) and Md.Manzoor Hussain et.al\(^2\).

Into a one litre round-bottomed flask fitted with a reflux condenser and a calcium chloride guard tube, a solution of 115.8 g (0.85 moles) of phenyl acetic acid in 300 ml of dry benzene was taken and 100 ml of thionyl chloride was added slowly. The reaction mixture was refluxed for 10 hours on a water bath. The excess of solvent and thionyl chloride were removed under reduced pressure. The crude phenyl acetyl chloride obtained, 116 g (88.2%) was used without further purification.

A mixture of 134 g (1 mole) of anhydrous aluminium chloride and 580.9g (3.7 moles)of dry bromo benzene were taken in a one liter three necked round bottomed flask fitted with a mercury sealed stirrer, a dropping funnel protected with a calcium chloride tube and a condenser guarded with a calcium chloride tube. The mixture was stirred and to the slurry obtained, 116 g (0.7488 moles) of crude phenyl acetyl chloride was added slowly during a period of 60 minutes. The reaction mixture was heated at 70 °C for 90 minutes, cooled and then poured on to a mixture of 300 g of ice and 100 ml of conc. hydrochloric acid. The organic layer was separated and washed with water for several times, dried over anhydrous calcium chloride, the residue obtained was subjected to distillation under reduced pressure. The fraction distilling at 196-200 °C/30 mm was collected, which solidified on cooling to yield 131 g (68%) of benzyl p-bromophenyl ketone. On recrystallisation from 95% ethanol, colourless plates of pure benzyl p- bromophenyl ketone were obtained m.p. 115-116 °C (Literature\(^1\) m.p. 114-115°C).
1H NMR (400 MHz, CDCl₃) : δ 7.18-7.3 (m, 5H), 7.5-7.65(d, 2H),
7.8- 7.9 (d, 2H), 4.25(s, 2H).
IR (KBr, cm⁻¹) : 1400-1520(Ar-H), 2985(-CH),
3024(=C-H), 1723(C=O),555(C-Br).
MS (70eV) (m/z %) : 274 M⁺
Anal for C₁₄H₁₁BrO : C, 61.11; H, 4.03; Br, 29.04.
Found : C, 60.01; H, 3.91; Br, 28.90.

2.3.2. p-Bromobenzyl phenyl ketone; [2-(4-bromophenyl)-1-phenylethanone]

It was prepared following a procedure similar to the preparation of benzyl p-
bromophenyl ketone¹,².

In a one litre round-bottomed flask fitted with a reflux condenser and calcium
chloride guard tube, 58.85gm (0.2732 moles) of p-bromophenylacetic acid and 100 ml of dry
benzene were taken and 50 ml of thionyl chloride was added slowly. The mixture was
refluxed for 10 hours on a water bath. Then the excess of solvent and thionyl chloride were
removed under reduced pressure when 55.2gm (86.5%) crude p-bromo phenylacetyl chloride
was obtained.

Into a 500 ml three-necked round-bottomed flask fitted with a mercury-sealed stirrer,
dropping funnel guarded with a calcium chloride tube and a condenser guarded with a
calcium chloride tube, 43.8 (0.3268 mole) of anhydrous aluminium chloride and 120 ml of
dry benzene were taken. The stirrer was started and to the slurry obtained, 55.2gm (0.2364
moles) crude p-bromophenylacetyl chloride was added slowly during a period of 30 minutes.
The reaction mixture was held at 70 °C for 90 minutes, cooled and then poured on to a
mixture of 150 g of ice and 100 ml of conc. hydrochloric acid. The product obtained was
extracted with ether, the ether solution was dried over anhydrous sodium sulphate, decanted
and ether evaporated off to yield 52.81gm (81.0%) of \( p \)-bromobenzyl phenyl ketone. It was recrystallised from 95% ethanol to give colourless crystals of pure \( p \)-bromobenzyl phenyl ketone, m.p. 122-124 °C (Literature\(^3\) m.p. 123°C).

\[
\begin{align*}
\text{O} & \quad \text{Br} \\
\end{align*}
\]

H NMR (400 MHz, CDCl\(_3\)) : \( \delta \) 7.05-7.17(m, 5H), 7.21(s, 2H), 7.4-7.53 (m, 4H).

IR (KBr cm\(^{-1}\)) : 1400-1525(Ar-H), 2995(-CH), 3040(=C-H), 1766(C=O), 625(C-Br).

MS (70eV) (m/z %) : 274 M\(^+\)

Anal for C\(_{14}\)H\(_{11}\)BrO : C, 61.11; H, 4.03; Br, 29.04.

Found : C, 60.01; H, 3.91; Br, 28.90.

2.3.3. \( p \)-Bromophenyl phenyl acetylene

It was prepared according to the procedure of M.S. Newman and D.E.Reid\(^1\) and Md.Manzoor Hussain et.al\(^2\).

A mixture of 49.32 g (0.179 moles) of pure benzyl \( p \)-bromophenyl ketone and 11.5 g (0.05528moles) of phosphorous pentachloride was taken in a 250 ml round-bottomed flask fitted with a reflux condenser guarded with a calcium chloride tube. The flask was heated at 60° C for 3 hours and distilled under reduced pressure. The distillate collected at 180-185 °C /5 mm solidified on cooling to give 37.66g (63.78 %) of \( 1-p \)-bromophenyl-1,1-dichloro-2-phenylethane. It was recrystallised from methanol to give light yellow crystals melting at 157-159°C.
A solution of sodium \( t \)-butoxide was prepared by dissolving 29.9 g (1.3g. atom) of sodium in two litres of \( t \)-butyl alcohol and taken in a three litre round-bottomed flask fitted with a reflux condenser, guarded with a calcium chloride tube. This solution was heated on a mantle to boiling and a solution of 37.72 g (0.1143 moles) of 1-\( p \)-bromophenyl-1,1-dichloro-2-phenylethane was added and refluxed for 6 hours. The \( t \)-butyl alcohol was removed by distillation and the residue obtained was poured into two liters of water. The product separated was filtered on a Buchner and washed with water and dried. Recrystallisation of the product from 95% ethanol gave 23.08 gm (78.4%) of \( p \)-bromophenyl phenyl acetylene melting at 112–114°C (Literature\(^1\) m.p. 112-113 °C).

2.3.4. Synthesis of Monosulphides.
2.3.4.1. Method: 1.
2.3.4.1.1. Preparation of \((E)\)- and \((Z)\)-1-\( p \)-bromophenyl-2-phenyl-1-\( p \)-chlorophenyl thioethylenes (1and 2) from benzyl \( p \)-bromophenyl ketone.

These compounds have been prepared by following a procedure\(^2,4\) similar to preparation of \((E)\)- and \((Z)\)-1-benzyl-2-phenyl-1-phenyl thioethylene.

A solution of 27.514 g (0.1 moles) benzyl \( p \)-bromo phenyl ketone and 21.6 g (0.15 moles) of \( p \)-chlorothiophenol in 100 ml of methylene chloride was taken in a 250 ml conical flask fitted with an air condenser guarded with a calcium chloride tube. The solution was stirred with a magnetic stirrer at room temperature and 4.532 g (0.034 moles) of anhydrous aluminium chloride was added in small portions over a period of 10 minutes. The reaction mixture turned turbid as the reaction proceeds. After the addition,
the mixture was further stirred for another 60 minutes then poured into 75 ml of water. The resulting mixture was extracted with 100 ml of methylene chloride. The extract was washed with brine, dried over anhydrous MgSO\(_4\), and the solvent was evaporated to give 19.2 g the solid which on recrystallisation from 95% ethanol yielded 15.4 g (43.3%) of (E)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylthio ethylene (1) m.p. 124-126 °C.

![Chemical Structure](image)

(1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta\) 7.1-7.15 (s, 1H), 7.25-7.65 (m, 8H), 7.75(m, 5H).

IR (KBr, cm\(^{-1}\)) : 455, 472, 485, 507, 535, 587, 690, 714, 753, 811, 828, 886, 932, 948, 961, 1008, 1090 (s) (S-aryl) 1106, 1154, 1175, 1233, 1299, 1396, 1444, 1473, 1487, 1586, 1638(m) (C=C), 1677, 1689, 1725, 1765, 1840, 1905, 1953, 2298, 2398, 3013, 3131.

MS (70eV) (m/z %) : \(399\) M\(^+\), 257,212,157,143.

Anal.Calcd for C\(_{20}\)H\(_{14}\)ClBrS : C, 59.79; H, 3.51; Br, 19.89; Cl, 8.82; S 7.98.

Found : C, 59.59; H, 3.30; Br, 19.11; Cl, 8.80; S 7.91.

The alcoholic solution obtained after separating (E)-1-p-bromo phenyl-2-phenyl-1-p-chlorophenylthioethylene (1) on evaporation of the solvent gave 12.48 g (35.1%) of (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenyl thioethylene (2) as solid. On recrystallization of this with 95% ethanol gave needle shaped crystals having melting point 102-103°C.
\[ \text{H NMR (400 MHz, CDCl}_3\text{):} \delta \ 7.1-7.15 \ (s, 1H), 7.19-7.75 (m, 8H), \\
7.8-7.9 (m, 5H); \]

\[ \text{IR (KBr cm}^{-1}) \ : \ 485, 508, 540, 587, 610, 630, 691, 717, 742, \\
811, 837, 874, 915, 933, 954, 1011, 1090 \ (s) \ (S-aryl), \\
1179, 1206, 1273, 1302, 1396, 1471, 1486, \\
1511, 1581, 1679 \ (m) \ (C=C), 1899, 2988, 3055. \]

\[ \text{MS (70eV) (m/z \%):} \ 399 \ M^+ , 257, 212, 157, 143. \]

\[ \text{Anla. Calcd for C}_{20}\text{H}_{14}\text{ClBrS :} \ C, 59.79; \ H, 3.51; \ Br, 19.89; \ Cl, 8.82; \ S 7.98. \]

\[ \text{Found :} \ C, 59.66; \ H, 3.42; \ Br, 19.77; \ Cl, 8.81; \ S 7.95. \]

2.3.4.1.2. Preparation of (E)- and (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenyl thioethylenes (3 and 4), from p-bromobenzyl phenyl ketone.

These compounds have been prepared by following a procedure similar to preparation of (E)- and (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenyl thioethylenes (1 and 2) from benzyl p-bromophenyl ketone as above. (3) m.p. 131-133 °C; (4) m.p. 97-98 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.1-7.50(m, 10H, Ar-H), 7.57-7.58(d, 2H, Ar-H), 7.9-8.0 (d, 2H, Ar-H).

IR (KBr cm$^{-1}$): 452, 478, 487, 501, 533, 587, 691, 713, 754, 815, 823, 876, 937, 949, 964, 1010, 1091 (s) (S-aryl) 1116, 1153, 1177, 1234, 1301, 1398, 1444, 1473, 1487, 1586, 1635(m) (C=C), 1678, 1692, 1727, 1767, 1842, 1915, 1954, 2294, 2393, 3097, 3178.

Anal. Calcd for C$_{20}$H$_{14}$Cl BrS: C, 59.79; H, 3.51; Br, 19.89; Cl, 8.82; S 7.98.
Found: C, 59.59; H, 3.30; Br, 19.11; Cl, 8.80; S 7.91.

(4)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.0-7.27(m, 6H, Ar-H), 7.3-7.57(m, 4H, Ar-H), 7.59-7.60 (d, 2H, Ar-H), 7.9-8.0(d, 2H, Ar-H).

IR (KBr cm$^{-1}$): 477, 626, 689, 740, 759, 816, 866, 913, 937, 1001, 1013, 1024, 1056 (w) (S-aryl), 1179, 1293, 1362, 1401, 1438, 1478, 1487, 1581, 1677 (w) (C=C), 1690, 1710, 1761, 1778, 1886, 2484, 2590, 2647, 2676, 2913, 3052.

Anal. Calcd for C$_{20}$H$_{14}$ClBrS: C, 59.79; H, 3.51; Br, 19.89; Cl, 8.82; S 7.98.
Found: C, 59.66; H, 3.42; Br, 19.77; Cl, 8.81; S 7.95.
2.3.4.2. Method 2.

2.3.4.2.1. Preparation of \((E)\)- and \((Z)\)-1-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylenes (1 and 2) and \((E)\)- and \((Z)\)-2-\(p\)-bromo phenyl-1-phenyl-1-\(p\)-chlorophenylthioethylenes (3 and 4) from \(p\)-bromo phenyl phenylacetylene.

A solution of 30.84 g (0.12 moles) of \(p\)-bromophenyl phenylacetylene in 150 ml of \(n\)-heptane was taken in a 250 ml round-bottomed flask fitted with a reflux condenser guarded with a calcium chloride tube. The flask was heated, and 7.2 g (0.05 moles) of \(p\)-chlorothiophenol was added to the boiling mixture. The reaction mixture was refluxed for 24 hours. The solution was washed successively with 2% sodium hydroxide solution, water and dried over calcium chloride. The \(n\)-heptane layer was decanted and evaporated. The residue left over weighed 17.6 g was subjected to fractional crystallisation. Four fractions were obtained after fractional crystallization.

The first fraction weighed 8.6 gm (19.58%) and obtained in the form of needle shaped crystals. The second fraction was collected as crystalline solid on further cooling and it was weighed 16.4 g (37.34%). The third fraction was collected as solid on further cooling of mother liquor and it was weighed 3.5g (7.96%) and the fourth fraction was collected on still further cooling as solid and it was weighed 4.1 g (9.33%).

The first fraction obtained as solid was recrystallised from absolute alcohol to give needle shaped crystals of \((E)\)-1-\(p\)-bromo phenyl-2-phenyl-1-\(p\)-chlorophenylthioethylene (1). The IR spectra and melting point of this was found to be same as that of \((E)\)-1-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenylthioethylene obtained earlier by method 1.

The mother liquor which was obtained after removal of first fraction on further cooling also forms solid. It was recrystallised from methanol to give colourless crystals of \((E)\)-2-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene (3). The IR spectra and melting point of this was found to be same as that of \((E)\)-2-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene obtained earlier by method 1.

The third fraction obtained as solid on fractional crystallization, was found to be \((Z)\)-1-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene (2). The IR spectra and melting point of this was found to be same as that of \((Z)\)-1-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene obtained earlier by method 1.

The mother liquor after removing (2) on cooling forms a needle shaped crystals. It was \((Z)\)-2-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene (4). The IR spectra and
melting point of this was found to be same as that of \((Z)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene obtained by earlier method 1.

2.3.5. Synthesis of Monosulphones.

2.3.5.1. Method: 3

2.3.5.1.1. Oxidation of \((E)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene (1) to \((E)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (5).

A solution of 0.6013 g (0.0015 moles) of \((E)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene (1) in 20 ml of acetic acid was taken in a 50 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 8 ml of 30% hydrogen peroxide was added and refluxed for two hours. The solid separated on cooling was filtered to yield 0.516 g (79.6%) of \((E)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (5). On recrystallisation from 95% ethanol gave an analytical sample with m.p. 210-212°C

\[ \text{IR (KBr cm}^{-1}) \] 462, 488, 509, 533, 565, 588, 598, 630, 661, 712, 757, 774, 822, 837, 845, 890, 911, 926, 958, 1014, 1029, 1090 (s) (S-aryl), 1142 (s) (SO), 1307 (s) (SO), 1442, 1474, 1492, 1575, 1627 (m) (C=C), 1678, 1734, 1819, 1890, 1906, 2010.

\[ \text{MS (70eV) (m/z \%)} \] 431 M\(^{+}\), 257, 212, 175, 157.

\[ \text{AnalCalcld for C}_{20}\text{H}_{14}\text{BrClO}_{2}\text{S} \] C, 55.38; H, 3.25; Br, 18.42; Cl, 18.17; S, 7.39.

\[ \text{Found} \] C, 55.32; H, 3.20; Br, 18.39; Cl, 18.15; S, 7.30.
2.3.5.1.2. Oxidation of \((Z)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene (2) to \((Z)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (6).

A solution of 0.8018 g (0.002 moles) of \((Z)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl thioethylene (2) in 25 ml of acetic acid was taken in a 50 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 two hours. The solid separated on cooling was filtered to yield 0.642 g (74.2%) of \((Z)-1-p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (6). On recrystallisation from 95% ethanol gave an analytical sample with m.p. 218-220°C.

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 6.8-6.95 \text{ (d, 2H), 7.1-7.15 \text{ (d, 2H), 7.2-7.6 \text{ (m, 9H), 7.95(s, 1H).}}
\]

\[
\text{IR (KBr cm}^{-1}\text{): } 472, 493, 513, 589, 597, 610, 619, 628, 666, 714, 758, 829, 843, 921, 942, 964, 1011, 1031, 1085 \text{ (S-aryl), 1150 (SO}_2\text{), 1173, 1241, 1263, 1281, 1322 \text{ (SO}_2\text{), 1397, 1441, 1474, 1484, 1563, 1578, 1627 \text{ (m)(C=C), 1677, 1809, 1911, 2854.}}
\]

\[
\text{MS (70eV) (m/z %): } 431 \text{ M}^+, 257,212,175,157.
\]

\[
\text{Anal.Calcd for C}_{20}\text{H}_{14}\text{O}_2\text{BrClS: } C, 55.38; H, 3.25; Br, 18.42; Cl, 18.17; S, 7.39.
\]

\[
\text{Found: } C, 55.34; H, 3.22; Br, 18.32; Cl, 18.15; S, 7.34.
\]

2.3.5.1.3. Oxidation of \((E)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene (3) to \((E)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (7).
A solution of 1.2g (0.003 moles) of \((E)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene (3) in 50 ml of acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 12 ml of 30\% hydrogen peroxide was added and refluxed for two hours. The solid separated on cooling was filtered to yield 0.768 g (64.6 \%) of \((E)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (7). On recrystallisation from 95\% ethanol gave an analytical sample, of \((E)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene with m.p. 143-145°C.

\[
\begin{align*}
\text{Br} & \quad \text{H} \\
\text{O} & \quad \text{S} \\
\text{Cl} & 
\end{align*}
\]

\((7)\)

\(\text{HNMR}(400\text{MHz}, \text{CDCl}_3) : \delta 6.96(\text{d},2\text{H}), 7.0-7.2(\text{d},2\text{H}), 7.25-7.6(\text{m},9\text{H}), 7.9(\text{s},1\text{H}).\)

\(\text{IR (KBr cm}^{-1}) : 498, 524, 675, 734, 768, 823, 947, 960, 1017, 1034, 1093 \text{ (S-aryl), 1148 (s) (SO}_2\text{), 1183, 1317 (s) (SO}_2\text{), 1398, 1443, 1485, 1543, 1596, 1632 (m) (C=C), 1664, 1695, 1734, 1763, 1905, 1945, 2282, 2388, 2899.\)

\text{Anal. Calcd for C}_{20}\text{H}_{14}\text{BrCl O}_2\text{S:} \quad \text{C}, 55.38; \text{H}, 3.25; \text{Br}, 18.42; \text{Cl}, 18.17; \text{S}, 7.39.

\text{Found :} \quad \text{C}, 55.32; \text{H}, 3.20; \text{Br}, 18.39; \text{Cl}, 18.15; \text{S}, 7.30.

2.3.5.1.4. Oxidation of \((Z)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl thioethylene (4) to \((Z)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (8).

A solution of 1.6036g (0.004 moles) of \((Z)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylthioethylene (4) in 60 ml of acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 15 ml of 30\% hydrogen peroxide was added and refluxed for two hours. The solid separated on cooling was filtered to yield 1.315g (82.6 \%) of \((Z)-2-p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl ethylene (8). On recrystallisation from 95\% ethanol gave an analytical sample with m.p. 139-140°C.
\( ^1 \text{H NMR (400 MHz, CDCl}_3 \text{)} : \delta 6.8-6.95 (d, 2H), 7.1-7.15 (d, 2H), 7.2-7.6 (m, 9H), 7.95 (s, 1H). \)

IR (KBr cm\(^{-1}\)) : 458, 626, 651, 687, 818, 998, 1012, 1028, 1071, 1092 (s) (S-aryl), 1145 (s) (SO\(_2\)), 1178, 1312 (s) (SO\(_2\)), 1398, 1483, 1537, 1584, 1629 (m) (C=C), 1657, 1725, 1763, 2283, 2899.

Anal. Calcd for C\(_{20}\)H\(_{14}\)O\(_2\) BrClS: C, 55.38; H, 3.25; Br, 18.42; Cl, 18.17; S, 7.39.

Found : C, 55.34; H, 3.22; Br, 18.32; Cl, 18.15; S, 7.34.

2.3.6. Synthesis of (E & Z)-Bromo sulphides.

2.3.6.1. Method: 4

2.3.6.1.1. Preparation of (E)- and (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl thioethylenes (9 and 10) from (E)- or (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylthioethylene (1 or 2).

About 10.6238 g (0.0265 moles) of (E)- or (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenyl thio ethylene (1 or 2) was dissolved in 100 ml of glacial acetic acid and the solution was taken in a 250 ml conical flask fitted with a magnetic stirrer. The stirrer was set in motion and a solution of 4g (0.05 moles) of bromine in 15 ml of glacial acetic acid was added dropwise. During addition decolourisation was observed and stirring was continued for an about 24 hours. The solid separated was filtered to yield 6.98 g (61.7%) of (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl thioethylene (10).

It was purified by recrystallisation from 95% ethanol and ether mixture to give a yellow crystals m.p. 147-149°C
$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 7.03-7.09 (d, 2H), 7.1-7.26 (d, 2H), 7.26-7.28 (d, 2H), 7.37-7.55(m, 7H).

IR (KBr cm$^{-1}$) : 485, 508, 540, 587, 610, 630, 691, 717, 742, 811, 837, 874, 915, 954, 1011, 1090 (s) (S-aryl), 1396, 1444, 1473, 1511, 1586, 1657 (w) (C=C), 1696, 1754, 1799, 1947, 2279, 2384, 2568, 2862, 3128.

MS (70eV) (m/z %) : 477 M$^+$, 336,338,334, 212,214,176,143.

Anal. Calcd for C$_{20}$H$_{13}$Br$_2$ClS : C, 49.98; H, 2.73; Br, 33.25; Cl, 7.38; S, 6.67.

Found : C, 49.91; H, 2.70; Br, 33.20; Cl, 7.32; S, 6.64.

The filtrate from the above reaction mixture after separating the (Z)-1-bromo-2-$p$-bromophenyl-1-phenyl-2-$p$-chlorophenyl thioethylene (10) on dilution with water gave 3.98 g (35.2%) of (E)-1-bromo-2-$p$-bromophenyl-1-phenyl-2-$p$-chlorophenyl-thioethylene (9) as solid. This was purified by recrystallisation from 95% ethanol to give an analytical sample, with m.p. 138-140$^\circ$C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta 7.03-7.09(d, 2H)\), \(\delta 7.11-7.26 (d, 2H)\), 7.28 (d, 2H), 7.3-7.38 (m, 5H), 7.52-7.55 (m, 2H).

IR (KBr cm\(^{-1}\)) : 497, 602, 645, 691, 723, 798, 854, 913, 945, 1012, 1068, 1094 (s) (S-aryl), 1157, 1187, 1269, 1298, 1347, 1394, 1444, 1483, 1514, 1579, 1654 (w) (C=C), 1694, 1758, 1799, 1877, 2279, 2568, 2862, 3050.

MS (70eV) (m/z %) : 477 M\(^+\), 336, 338, 334, 212, 214, 176, 143.

Anal. Calcd for C\(_{20}\)H\(_{13}\)Br\(_2\)ClS : C, 49.98; H, 2.73; Br, 33.25; Cl, 7.38; S, 6.67.

Found : C, 49.91; H, 2.72; Br, 33.23; Cl, 7.34; S, 6.59.

2.3.6.1.2 Preparation of (E)- and (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenyl thioethylenes (11 and 12) from (E)- or (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenyl thioethylene (3 or 4).

About 11.098 g (0.0276 moles) of (E)- and (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylthio ethylene (3 or 4) was dissolved in 150 ml of glacial acetic acid and the solution was taken in a 500 ml conical flask fitted with a magnetic stirrer. The stirrer was set in motion and a solution of 4 g (0.05 moles) of bromine in 25 ml of glacial acetic acid was added drop wise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional 60 minutes. The solid separated was filtered to yield 8.5 g (63.5%) of (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenyl thioethylene (12). It was purified by recrystallisation from 95% ethanol to give an analytical sample, with m.p. 134-136°C.
$^1$H NMR (400 MHz, CDCl$_3$) : δ 6.9-7.22(m, 5H, Ar-H), 7.25-7.41(m, 4H, Ar-H), 7.46-7.55(d, 2H, Ar-H), 7.57-7.97(d, 2H, Ar-H).

IR (KBr cm$^{-1}$) : 493, 503, 512, 550, 595, 610, 634, 698, 717, 747, 811, 847, 884, 923, 961, 1012, 1090 (s) (S-aryl), 1398, 1440, 1473, 1521, 1587, 1641 (w) (C=C), 1686, 1744, 1799, 1947, 2279, 2384, 2559, 2871, 3129.

Anal. Calcd for C$_{20}$H$_{13}$Br$_2$ClS : C, 49.98; H, 2.73; Br, 33.25; Cl, 7.38; S, 6.67.

Found : C, 49.91; H, 2.70; Br, 33.20; Cl, 7.32; S, 6.64.

The filtrate from the above reaction mixture after separating the (Z)-1-bromo-1-$p$-bromophenyl-2-phenyl-2-$p$-chlorophenylthioethylene (12), on dilution with water gave 2.8g (21.2 %) of (E)-1-bromo-1-$p$-bromophenyl-2-phenyl-2-$p$-chlorophenylthioethylene (11), as solid. This was purified from 95% ethanol to give an analytical sample with m.p.128-130°C.

![11]
2.3.7. Synthesis of \((E)\)-Bromosuphone, \((E)\)-Sulphide-Sulphone and \((E)\)-Disulphones.

2.3.7.1. Method: 5

These compounds have been prepared by two different schemes. Both the schemes yielded the same product. The identity of the compound obtained was confirmed by melting points, mixed melting points, elemental analysis and spectral analysis.

2.3.7.1.1. Oxidation of \((E)\)-1-bromo-2-\(p\)-bromophenyl-1-phenyl-2-\(p\)-chlorophenyl thioethylene (9) to \((E)\)-1-bromo-2-\(p\)-bromophenyl-1-phenyl-2-\(p\)-chlorophenyl sulphonyl ethylene (14) or \((E)\)-1-bromo-1-\(p\)-bromophenyl-2-phenyl-2-\(p\)-chlorophenyl thioethylene (11) to \((E)\)-1-bromo-1-\(p\)-bromophenyl-2-phenyl-2-\(p\)-chlorophenylsulphonyl ethylene (16).

A solution of 4.367 g (0.009 moles) of \((E)\)-1-bromo-2-\(p\)-bromophenyl-1-phenyl-2-\(p\)-chlorophenyl thioethylene (9) in 60 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 50 ml of 30% hydrogen peroxide was added and refluxed for two hours. The product separated on cooling was collected by filtration, yield 3.85 g (89.6%). Recrystallisation of the product from 95% ethanol gave an analytical sample of \((E)\)-1-bromo-2-\(p\)-bromophenyl-1-phenyl-2-\(p\)-chlorophenyl sulphonylethylene (14) m.p. 215-217 °C.

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{Cl} \\
\text{Br} & \quad \text{O} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\((14)\)

\(^{1}\text{H NMR} (400 \text{ MHz}, \text{CDCl}_3)\) : \(\delta 6.71-6.78\ (d, 2\text{H}), 6.9-7.05\ (d, 2\text{H}), 7.2-7.4\ (m, 5\text{H}), 7.5-7.56\ (m, 2\text{H}), 7.66-7.68\ (d, 2\text{H})\).

\text{IR (KBr cm}^{-1}\) : \(471, 513, 555, 589, 619, 628, 666, 693, 749, 785, 844, 960, 1067, 1081\ (s) (S-aryl), 1149\ (s) (SO}_2\), 1187, 1279, 1313\ (s) (SO}_2\), 1388, 1444, 1483, 1573, 1627\ (m) (C=C), 1814, 1911, 1959, 2104, 2836, 3089, 3127.

\text{MS (70eV) (m/z %)} : \(509\text{M}^+, 338, 336, 334, 214, 212, 176, 174, 143\).
Anal. Calcd for C\textsubscript{20}H\textsubscript{13}Br\textsubscript{2}ClO\textsubscript{2}S:  C, 46.86; H, 2.56; Br, 31.17; Cl, 6.92; S, 6.25.
Found : C, 46.85; H, 2.53; Br, 31.12; Cl, 6.91; S, 6.22.

A solution of 4 g (0.00833 moles) of (E)-1-bromo-1-\textit{p}-bromophenyl-2-phenyl-2-\textit{p}-chlorophenyl thioethylene (11) in 60 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 50 ml of 30\% hydrogen peroxide was added and refluxed for two hours. The product separated on cooling was collected by filtration, yield 3.85 g (89.6\%). Recrystallisation of the product from 95\% ethanol gave an analytical sample of (E)-1-bromo-1-\textit{p}-bromophenyl-2-phenyl-2-\textit{p}-chlorophenylsulphonyl ethylene (16) m.p. 199-201°C.

![Chemical Structure](image)

\(\text{1H NMR (400 MHz, CDCl}\textsubscript{3})\) : \(\delta 7.2-7.27 \text{ (d, 2H), 7.51-7.55 \text{ (m, 5H), 7.66-7.7 \text{ (m, 3H), 7.8-7.98 \text{ (m, 3H).}}\}

\(\text{IR (KBr cm}^{-1}\) : 471, 493, 515, 565, 593, 632, 675, 699, 759, 804, 845, 976, 1067, 1083 \text{ (s) (S-aryl), 1152 \text{ (s) (SO}_2\text{), 1178, 1244, 1267, 1320 \text{ (s) (SO}_2\text{), 1398, 1444, 1477, 1565, 1579, 1595, 1654 \text{ (m) (C=C), 1765, 1798, 1815, 1914, 1968, 2108, 2836, 3041, 3126.}}\)

Anal. Calcd for C\textsubscript{20}H\textsubscript{13}Br\textsubscript{2}ClO\textsubscript{2}S:  C, 46.86; H, 2.56; Br, 31.17; Cl, 6.92; S, 6.25.
Found : C, 46.83; H, 2.46; Br, 31.11; Cl, 6.89; S, 6.23.
2.3.7.1.2. Conversion of \((E)-1\text{-}p\text{-}bromophenyl\text{-}1\text{-}phenyl\text{-}2\text{-}p\text{-}chlorophenylsulphonyl\text{-}2\text{-}p\text{-}chlorophenylsulphonyl ethylene (14)\) to \((E)-1\text{-}p\text{-}bromophenyl\text{-}1\text{-}phenyl\text{-}2\text{-}p\text{-}chlorophenylsulphonyl\text{-}2\text{-}p\text{-}chlorophenyl thioethylene (18)\) or Conversion of \((E)-1\text{-}bromo\text{-}1\text{-}p\text{-}bromophenyl\text{-}2\text{-}phenyl\text{-}2\text{-}p\text{-}chlorophenylsulphonyl ethylene (16)\) to \((E)-2\text{-}p\text{-}bromophenyl\text{-}1\text{-}phenyl\text{-}1\text{-}p\text{-}chlorophenylsulphonyl\text{-}2\text{-}p\text{-}chlorophenyl thioethylene (20)\).

To a hot solution of 1.19 g (0.00232) moles of \((E)-1\text{-}bromo\text{-}2\text{-}p\text{-}bromophenyl\text{-}1\text{-}phenyl\text{-}2\text{-}p\text{-}chlorophenylsulphonyl ethylene (14)\) in 40 ml of absolute ethanol taken in a 100 ml round-bottomed flask fitted with a reflux condenser protected with a calcium chloride guard tube, a solution of sodium salt of \(p\text{-}chlorobenzenethiolate\) prepared from 60 mg (2.5 mg atom) of sodium, 10 ml of absolute ethanol and 0.280 g (0.00194 moles) of \(p\text{-}chlorothiophenol\) was added. The mixture was refluxed for 7 hours. The colourless product separated on cooling was collected by filtration on a buchner to yield 1.03 g (81.7%) of \((E)-1\text{-}p\text{-}bromo phenyl\text{-}2\text{-}phenyl\text{-}1\text{-}p\text{-}chlorophenylsulphonyl\text{-}2\text{-}p\text{-}chlorophenyl thioethylene (18)\).

Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 194-196 °C.

\[
\text{(18)}
\]

\(^1\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 6.8\text{-}6.9 \text{(m, 5H), 7.0\text{-}7.07 \text{(m, 2H), 7.17\text{-}7.33 \text{(m, 5H),}\n7.5\text{-}7.66\text{(m, 5H)}}\]

\[
\text{IR (KBr cm}^{-1}) \text{: } 504, 576, 586, 626, 656, 695, 714, 740, 834, 876, 915, 943, 1023, 1035, 1090 \text{(s) (S-aryl), 1154 \text{(w) (SO}_2\text{), 1165, 1189, 1224, 1301, 1325 \text{(m) (SO}_2\text{), 1398, 1454, 1484, 1598, 1673 \text{(w) (C=C), 1724, 1745, 1778, 1876, 1957, 2332, 2393, 2567, 2723, 2891, 3052, 3126.}}\]
To a hot solution of 1.19 g (0.00232 moles) of \((E)-1\)-bromo-1-\(p\)-bromophenyl-2-phenyl-2-\(p\)-chlorophenylsulphonyl ethylene (16) in 40 ml of absolute ethanol taken in a 100 ml round-bottomed flask fitted with a reflux condenser protected with a calcium chloride guard tube, a solution of sodium salt of \(p\)-chlorobenzenethiolate prepared from 60 mg (2.5 mg atom) of sodium, 10 ml of absolute ethanol and 0.280 g (0.00194 mmoles) of \(p\)-chlorothiophenol was added. The mixture was refluxed for 7 hours. The colourless product separated on cooling was collected by filtration on a buchner to yield 1.09 g (81.95%) of \((E)-2-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenylsulphonyl-2-\(p\)-chlorophenyl thioethylene (20). Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 68-69°C.

\[
\text{Cl} \quad \text{S} \quad \text{O} \quad \text{S} \quad \text{Cl} \\
\text{Br} \\
\text{S} \quad \text{O} \quad \text{S} \quad \text{Cl}
\]

(20)

\(^1\text{H NMR (400 MHz, CDCl}_3\) : \(\delta 6.9-7.0\) (m, 5H), 7.1-7.3 (m, 5H), 7.4-7.5 (d, 2H), 7.6-7.66 (m, 5H).

\text{IR (KBr cm}^{-1} \) : 524, 586, 595, 629, 676, 699, 718, 743, 835, 877, 925, 945, 1021, 1037, 1095 (s) (S-aryl), 1155 (w) (SO₂), 1173, 1187, 1234, 1308, 1323 (m) (SO₂), 1399, 1458, 1489, 1599, 1671 (w) (C=C), 1725, 1746, 1787, 1891, 1956, 2336, 2394, 2563, 2724, 2899, 3065, 3134.

\text{MS (70eV) (m/z %)} : 400,398,321,320.

\text{Anal.Calcd for C}_{26}\text{H}_{17}\text{BrCl}_2\text{O}_2\text{S}_2} : \text{C}, 54.18; \text{H}, 2.97; \text{Br}, 13.86; \text{Cl}, 12.30; \text{S}, 11.13.

\text{Found} : \text{C}, 53.98; \text{H}, 2.74; \text{Br}, 13.77; \text{Cl}, 12.16; \text{S}, 11.04.
2.3.7.3. Oxidation of (E)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylsulphonyl-2-p-chlorophenyl thioethylene (18) or (E)-2-p-bromophenyl-1-phenyl-1-p-chlorophenyl sulphonyl-2-p-chlorophenyl thioethylene (20) to (E)-1,2-bis(p-chlorophenylsulphonyl)-1-p-bromophenyl-2-phenyl ethylene (22).

A solution of 0.506 g (0.00088 moles) of (E)-1-p-bromophenyl-2-phenyl-1-p-chlorophenyl sulphonyl - 2- p- chloro phenyl thio ethylene (18) or (E)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylsulphonyl-2-p-chlorophenyl thioethylene (20) 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 added 8 ml of 30% hydrogen peroxide. The solution was refluxed for one hour and the colourless crystals separated on cooling were collected by filtration to yield 0.448g (83.2%) of (E) - 1, 2-bis (p-chlorophenylsulphonyl)-1-p-bromophenyl-2-phenyl ethylene (22). It was recrystallised thrice from 95% ethanol to give an analytical sample with m.p. 253-255° C.

\[
\begin{align*}
\text{HNMR(400MHz,CDCl}_3) : & \delta 6.7-7.24(m,5H,Ar-H), 7.26-7.34(m,4H,Ar-H), 7.43-7.47(m, 4H, Ar-H), 7.53-7.57(d, 2H, Ar-H), 7.76(d,2H, Ar-H). \\
\text{IR (KBr cm}^{-1} ) : & 433, 467, 513, 587, 605, 624, 655, 686, 714, 731, 767, 834, 923, 965, 1014, 1080 (s) (S-aryl), 1128, 1150 (s) (SO_2), 1284, 1298, 1327 (s) (SO_2), 1378, 1395, 1444, 1474, 1488, 1567, 1589, 1654 (w) (C=C), 1774, 1905, 2047, 2265, 2754, 2845, 3078. \\
\text{MS (70eV) (m/z %)} : & 431,367,288,255,182. \\
\text{Anal. Calcd for C}_{26}\text{H}_{17}\text{BrCl}_2\text{O}_4\text{S}_2:} & \text{C, 51.33; H, 2.82; Br, 13.13; Cl, 11.66; S, 10.54.} \\
\text{Found :} & \text{C, 51.22; H, 2.66; Br, 13.08; Cl, 11.57; S, 10.48.}
\end{align*}
\]
2.3.8. Synthesis of (Z)-Bromosulphone, (Z)-Sulphide-Sulphone and (Z)-Disulphones.

2.3.8.1 Method: 6

These compounds also have been prepared by two different schemes. Both the schemes yielded the same product. The identity of the compound obtained was confirmed by melting points, mixed melting points, elemental analysis and spectral analysis.

2.3.8.1.1 Oxidation of (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl thioethylene (10) to (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl sulphonyl ethylene (13) and (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenyl thioethylene (12) to (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenylsulphonyl ethylene (15).

In a 100 ml round-bottomed flask fitted with a reflux condenser a solution of 1.997 g (0.00416 moles) of (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl thioethylene (10) in 50 ml of acetic acid was taken. The solution was heated to boiling and 20 ml of 30% hydrogen peroxide was added and refluxed for two hours. The product separated on cooling was collected by filtration, yield 1.57 g (73.4 %). Recrystallisation of the product from 95% ethanol gave an analytical sample of (Z)-1-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenylsulphonyl ethylene (13), m.p. 215-217 °C.

![Chemical structure](image)

(13)

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 6.71-6.78(d, 2H, Ar- H), 6.9-7.05(d, 2H, Ar- H), 7.2-7.4(m, 5H, Ar-H), 7.5-7.56(m, 2H, Ar-H), 7.77-7.79(d, 2H, Ar- H).

IR (KBr cm$^{-1}$) : 471, 493, 514, 565, 590, 629, 669, 698, 755, 795, 842, 966, 1069, 1085 (s) (S-aryl), 1150 (s) (SO$_2$), 1173, 1243, 1263, 1321 (s) (SO$_2$), 1397, 1440, 1473, 1563,
1577, 1590, 1656 (m) (C=C), 1814, 1910, 1959, 2104, 2836, 3041, 3126.

MS (70eV) (m/z %) : 509 M⁺, 338, 336, 334, 214, 212, 176, 174, 143.

Anal. Calcd for C₂₀H₁₃Br₂ClO₂S: C, 46.86; H, 2.56; Br, 31.17; Cl, 6.92; S, 6.25.
Found : C, 46.85; H, 2.52; Br, 31.11; Cl, 6.80; S, 6.19.

In a 100 ml round-bottomed flask fitted with a reflux condenser a solution of 1.997g (0.00416 moles) of (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenyl thioethylene (12) in 50 ml of acetic acid was taken. The solution was heated to boiling and 20 ml of 30% hydrogen peroxide was added and refluxed for two hours. The product separated on cooling was collected by filtration, yield 1.57 g (73.4 %). Recrystallisation of the product from 95% ethanol gave an analytical sample (Z)-1-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenylsulphonyl ethylene (15), m.p. 128-129°C.

![Diagram](image)

(15)

¹H NMR (400 MHz, CDCl₃) : δ 7.27(s, 1H, Ar-H), 7.46-7.78(m, 7H, Ar-H), 7.80-7.98(m, 5H, Ar-H).
IR (KBr cm⁻¹) : 473, 503, 542, 575, 614, 631, 679, 700, 754, 786, 944, 960, 1025, 1084 (s) (S-aryl), 1146 (s) (SO₂), 1176, 1187, 1240, 1279, 1314 (s) (SO₂), 1388, 1444, 1483, 1573, 1629 (m) (C=C), 1661, 1707, 1725, 1792, 1814, 1911, 1959, 2104, 2836, 3089, 3127.

Anal. Calcd for C₂₀H₁₃Br₂ClO₂S: C, 46.86; H, 2.56; Br, 31.17; Cl, 6.92; S, 6.25.
Found : C, 46.81; H, 2.54; Br, 31.09; Cl, 6.89; S, 6.21.
2.3.8.1.2. Conversion of \((Z)-1\text{-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenyl sulphonyl ethylene}(13)\) to \((Z)-1\text{-p-bromophenyl-2-phenyl-1-p-chlorophenylsulphonyl -2-p-chlorophenyl thioethylene}\) (17) and Conversion of \((Z)-1\text{-bromo-1-p-bromophenyl-2-phenyl-2-p-chlorophenylsulphonyl ethylene}\) (15) to \((Z)-2-p\text{-bromophenyl-1-phenyl-1-p-chlorophenylsulphonyl-2-p-chlorophenyl thioethylene}\) (19).

About 0.330 g (0.00229 moles) of \(p\)-chlorothiophenol was added to an ethanolic solution of sodium ethoxide prepared from 690 mg (3 mg atom) of sodium dissolved in 10 ml of absolute ethanol. This solution was then added to a hot solution of 1.428 g (0.00279 moles) of \((Z)–1\text{-bromo-2-p-bromophenyl-1-phenyl-2-p-chlorophenylsulphonyl ethylene}\) (13), in 150 ml of absolute ethanol contained in a 250 ml round-bottomed flask fitted with a reflux condenser and protected with calcium chloride guard tube. The mixture was refluxed for 6 hours. The colorless product separated on cooling was filtered to yield 0.83 g (54.9%) of \((Z)-1\text{-p-bromophenyl-2-phenyl-1-p-chlorophenyl sulphonyl -2-p-chlorophenyl thioethylene}\) (17). Recrystallisation of the product thrice from 95% ethanol gave an analytical sample, m.p. 128-130 °C.

\[
\begin{align*}
\text{(17)}
\end{align*}
\]

\(^1\text{HNMR (400MHz, CDCl}_3\text{)}\) : \(\delta\) 6.9-7.26(m, 5H, Ar-H), 7.28-7.50(m, 4H, Ar-H), 7.51-7.68 (m, 6H, Ar-H), 7.86-7.88(d, 2H, Ar-H).

\(\text{IR (KBr cm}^{-1}\text{)}\) : 514, 577, 592, 629, 654, 666, 704, 716, 742, 789, 834, 879, 898, 917, 944, 1034, 1056, 1092 (s) (S-aryl), 1152 (w) (SO\(_2\)), 1168, 1192, 1214, 1311, 1326 (m) (SO\(_2\)), 1388, 1458, 1494, 1598, 1671 (w) (C=C), 1734, 1754, 1765, 1875, 1958, 2342, 2394, 2567, 2743, 2894, 3054, 3128.

\(\text{MS (70eV) (m/z %)}\) : 321,320.
About 0.330 g (0.00229 moles) of $p$-chlorothiophenol was added to an ethanolic solution of sodium ethoxide prepared from 690 mg (3 mg atom) of sodium dissolved in 10 ml of absolute ethanol. This solution was then added to a hot solution of 1.428 g (0.00279 moles) of (Z)-1-bromo-1-$p$-bromophenyl-2-phenyl-2-$p$-chlorophenylsulphonyl ethylene (15), in 150 ml of absolute ethanol contained in a 250 ml round-bottomed flask fitted with a reflux condenser and protected with calcium chloride guard tube. The mixture was refluxed for 6 hours. The colorless product separated on cooling was filtered to yield 0.83 g (54.9%) of (Z)-2-$p$-bromophenyl-1-phenyl-1-$p$-chlorophenylsulphonyl-2-$p$-chlorophenylthioethylene(19).

Recrystallisation of the product thrice from 95% ethanol gave an analytical sample, m.p. 73-75°C.

$^{1}$H NMR (400 MHz, CDCl$_3$) : $\delta$ 6.9-7.0(m, 5H), 7.12-7.31(m, 5H), 7.44-7.540(d, 2H), 7.547-7.563(m, 5H).

IR (KBr cm$^{-1}$) : 515, 579, 598, 630, 644, 667, 714, 726, 743, 788, 844, 889, 899, 927, 955, 1037, 1057, 1093 (s) (S-aryl), 1153 (w) (SO$_2$), 1167, 1193, 1217, 1316, 1325 (m) (SO$_2$), 1389, 1457, 1493, 1599, 1672 (w) (C=C), 1735, 1758, 1769, 1875, 1959, 2343, 2395, 2576, 2787, 2895, 3053, 3132.

Anal. Calcd for C$_{26}$H$_{17}$ Br Cl$_2$O$_2$S$_2$: C, 54.18; H, 2.97; Br, 13.86; Cl, 12.30; S, 11.13.
Found : C, 53.98; H, 2.71; Br, 13.54; Cl, 12.11; S, 10.94.
2.3.8.3. Oxidation of \((Z)-1\)-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl sulphonyl-2-\(p\)-chlorophenyl thioethylene (17) or \((Z)-2\)-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl sulphonyl-2-\(p\)-chlorophenyl thioethylene (19) to \((Z)-1,2\)-bis(\(p\)-chlorophenyl sulphonyl)-1-\(p\)-bromophenyl-2-phenyl ethylene (21).

A solution of 1.01g (0.00175 moles) of \((Z)-1\)-\(p\)-bromophenyl-2-phenyl-1-\(p\)-chlorophenyl sulphonyl-2-\(p\)-chlorophenyl thioethylene (17) or \((Z)-2\)-\(p\)-bromophenyl-1-phenyl-1-\(p\)-chlorophenyl sulphonyl-2-\(p\)-chlorophenyl thioethylene (19) in 50 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 added 6 ml of 30% hydrogen peroxide. The solution was refluxed for one hour and the colorless crystals separated on cooling were collected by filtration to yield 0.772 g (71.9\%) of \((Z)-1,2\)-bis(\(p\)-chlorophenyl sulphonyl)-1-\(p\)-bromophenyl-2-phenylethylene (21). It was recrystallised from 95\% ethanol to give needle shaped crystals with, m.p. \(244-246^\circ\)C.

\[
\begin{align*}
\text{Br} &\quad \text{Cl} \\
\text{S} &\quad \text{S} \\
\text{O} &\quad \text{O} \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]

\((21)\)

\(^1\text{H NMR (400 MHz, CDCl}_3\) : \(\delta 6.9-7.29\text{(m, 5H, Ar-H), 7.30-7.38(m, 6H, Ar-H), 7.39-7.45(m, 2H, Ar-H), 7.52-7.55(d, 2H, Ar-H), 7.72(d, 2H, Ar-H).}

\text{IR (KBr cm}^{-1}\) : 454, 485, 526, 596, 626, 624, 655, 686, 702, 714, 767, 824, 923, 970, 1010, 1067, 1084 (s) (S-aryl), 1157 (s) (SO\(_2\)), 1235, 1277, 1314 (s) (SO\(_2\)), 1389, 1395, 1446, 1488, 1521, 1570, 1589, 1638 (w) (C=C), 1769, 1793, 1832, 1902, 1958, 2047, 2294, 2654, 2847, 3078.

\text{MS (70eV) (m/z \%)} : 431, 367, 288, 255, 182.

\text{Anal. Calcd for C}_{26}\text{H}_{17}\text{BrCl}_2\text{O}_4\text{S}_2: C, 51.33; H, 2.82; Br, 13.13; Cl, 11.66; S, 10.54.}

\text{Found} : C, 51.22; H, 2.79; Br, 13.07; Cl, 11.55; S, 10.50.
2.3.9.1 Method: 7

2.3.9.1.1. Preparation of (E)– and (Z)–1-<sup>p</sup>-bromophenyl-2-phenyl-1-phenylselenyl-2-<sup>p</sup>-chlorophenyl thio ethylene, (23 and 24) from (E)-1-<sup>p</sup>-bromophenyl-2-phenyl-1-<sup>p</sup>-chlorophenylthio-ethylene (1).

About 3.66g (0.01 moles) of (E)–1-<sup>p</sup>-bromophenyl-2-phenyl-2-<sup>p</sup>-chlorophenylthio-ethylene (1) was dissolved in 100 ml of glacial acetic acid and the solution was taken in a 250 ml conical flask fitted with a magnetic stirrer. The stirrer was set in motion and a solution of 2.36 g (0.01 mmoles) of Phenyl selenyl bromide in 30 ml of glacial acetic acid was added dropwise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional thirty minutes. The solid separated was filtered to yield 3.12 g (59.7%) of (Z)–1-<sup>p</sup>-bromo phenyl-2-phenyl-1-phenylselenyl-2-<sup>p</sup>-chlorophenylthio- ethylene (24). It was purified by recrystallisation from 95% ethanol to give an analytical sample, m.p. 98-99°C

\[
\text{Cl} \quad \text{S} \quad \text{Se} \quad \text{Br}
\]

\[
\text{(24)}
\]

\[^1\text{HNMR (CDCl}_3, 400 \text{ MHz)} : \delta 7.71-7.69(\text{d, 2H}), 7.50-7.48 (\text{d, 2H}), 7.4-7.38 (\text{m, 3H}), 7.27-7.10(\text{m, 11H}).
\]

\[\text{IR (KBr cm}^{-1} ) : 3010, 2999(\text{Ar-H}), 1580(\text{C=C}), 1473, 1444 \text{ (Ringstretcing)}, 1390,1175(\text{Ar-S}), 1106,834(\text{Ar-Se});\]

\[\text{MS (70eV) (m/z %)} : 555 \text{ M}^+, 402,400,398,320,319,258,256.\]

\[\text{Anal.calcd. for } \text{C}_{26}\text{H}_{18}\text{BrClSeS} : \text{C, 56.08; H, 3.26; S, 5.76.}
\]

\[\text{Found} : \text{C, 55.95; H, 3.21; S, 5.56.}\]
The filtrate from the above reaction mixture after separating the (Z) – 1-p-bromo phenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenylthio-ethylene (24) on dilution with water gave 1.59g (30.45%) of (E)–1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenyl thioethylene (23), as solid. This was purified by recrystallisation from 95% ethanol to give an analytical sample, m.p. 87-89 °C.

\[
\text{(23)}
\]

\[^1\text{HNMR (CDCl}_3, 400\text{MHz)}\] : δ 7.97-7.95(m,6H),7.64-7.62(d,4H), 7.27(d,8H,-Ar).

IR (KBr cm\(^{-1}\)) : 3020(Ar-H), 2959, 1570(C=C), 1472, 1434(Ringstretching), 1067(Ar-S), 897,841(Ar-Se).

MS (70eV) (m/z %) : 555 M\(^+\), 402,400,398,320,319,258,256.

Anal.calcd. for C\(_{26}\)H\(_{18}\)BrClSeS : C, 56.08; H, 3.26; S, 5.76.

Found : C, 56.01; H, 3.02; S, 5.56.

2.3.9.1.2. Preparation of (E)– and (Z)– 1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenylthioethylene (23 and 24) from (Z)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylthioethylene (2).

A solution of 3.66g (0.01moles) of (Z)-1-p-bromophenyl-2-phenyl-2-p-chloro phenylthioethylene (2) in 160 ml of glacial acetic acid was taken in a 500 ml conical flask fitted with magnetic stirrer. The stirrer was started and a solution of 2.36 g (0.01moles) of Phenyl selenyl bromide in 30 ml of glacial acetic acid was added drop wise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional thirty minutes. The solid separated was
filtered to yield 3.45g (66.09%) of (Z) – 1-p-bromophenyl-2-phenyl-1-phenylselenyl-2- p-chlorophenylthioethyylene (24). On recrystallisation from 95% ethanol gave an analytical sample, m.p. 98-99°C. It was found to be identical (melting point and mixed melting point) with an authentic sample of (Z) - 1-p-bromophenyl-2-phenyl-1-phenyl selenyl-2- p-chloro phenylthioethylene prepared earlier.

The filtrate from the above reaction mixture after separating (Z) – 1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenylthioethylene on dilution with water gave 1.27g (24.32%) of (E) – 1-p-bromophenyl-2-phenyl-1-phenyl selenyl-2-p-chlorophenylthioethylene (23) as solid. This was purified from 95% ethanol gave an analytical sample. The Melting point and 1R spectrum were same as that of(E)-1-p-bromophenyl-2-phenyl-1-phenylselenyl-2- p-chloro phenylthioethylene prepared earlier.

2.3.9.1.3. Oxidation of (E)-1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenylthio ethylene, (23) to (E)– 1-p-bromophenyl-2-phenyl-1-phenylselenonyl-2-p-chloro phenyl sulphonylethylene (27).

A solution of 2.61 g (0.005 moles) of (E) – 1-p-bromophenyl-2-phenyl-1-phenyl selenyl-2-p-chloro phenylthioethylene (23) in 60 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 20 ml of 30% hydrogen peroxide was added and refluxed for two hours. The product separated on cooling was collected by filtration, yield 2.33 g (79.6%). Recrystallisation of the product from 95% ethanol gave an analytical sample of (E) –1-p-bromophenyl-2-phenyl-1-phenylselenonyl-2-p-chloro phenyl sulphonylethylene (27) m.p. 156-158°C.
1H NMR (CDCl₃, 400 MHz): δ 7.956(d, 2H-Ar), 7.65-7.52(m, 7H-Ar),
7.42-7.39(d,2H-Ar),7.27-6.896(m,7H-Ar-H).

IR (KBr cm⁻¹): 3063, 3027(Ar-H), 1971, 1931, 1605(C=C),
1508, 1494, 1445(Ring stretching),
1179(Ar-S), 833(Ar-SO₂), 937(Ar-SeO₂).

MS (70eV) (m/z %): 434,432,430,368, 366,
352,351, 258, 256.

Anal. Calcd. for C₂₆H₁₈BrClSeSO₄:
C, 50.30; H, 2.92; S, 5.17.

Found:
C, 50.22; H, 2.87; S, 5.11.

2.3.9.1.4. Oxidation of (Z)–1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-
chlorophenylthio ethylene, (24) to (Z)–1-p-bromophenyl-2-phenyl-1-phenylselenonyl-2-
p-chloro phenyl sulphonylethylene (28).

In a 100 ml round-bottomed flask fitted with a reflux condenser a solution of 1.997 g
(0.00358 moles) of (Z) – 1-p-bromophenyl-2-phenyl-1-phenylselenyl-2-p-chlorophenylthio
ethylene (24) in 50 ml of acetic acid was taken. The solution was heated to boiling and 20 ml
of 30% hydrogen peroxide was added and refluxed for two hours. The product separated on
cooling was collected by filtration, yield 1.57 g (73.4 %). Recrystallisation of the product
from 95% ethanol gave an analytical sample of (Z) – 1-p-bromophenyl-2-phenyl-1-
phenylselenonyl-2-p-chloro phenyl sulphonylethylene (28), m.p. 112-114 °C.

![Diagram](image.png)

1H NMR (CDCl₃, 400 MHz): δ 7.95(d, 2H-Ar), 7.65-7.52(m, 7H-Ar),
7.429-7.39(d, 2H-Ar), 7.27-6.896(m, 7H-Ar-H).
IR (KBr cm\(^{-1}\)) : 3063, 3027 (Ar-H), 1971, 1930,
1632 (C=C), 1508, 1494,
1445 (Ringstretcing), 1209 (Ar-S),
956 (Ar-SeO\(_2\)), 833 (Ar-SO\(_2\)).

MS (70eV) (m/z %) : 434, 432, 430, 368, 366, 352, 351, 258, 256.

Anal. calcd. for C\(_{26}\)H\(_{18}\)BrClSeSO\(_4\) : C, 50.30; H, 2.92; S, 5.17.
Found : C, 50.22; H, 2.87; S, 5.11.

2.4.1. Method: 8

2.4.1.1. Preparation of (E) – and (Z) – 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chloro phenylthioethylene (25 and 26) from (E)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylthioethylene (3).

About 7.32 g (0.01825 moles) of (E)-1-p-bromophenyl-2-phenyl-1-p-chlorophenylthioethylene (3) was dissolved in 200 ml of glacial acetic acid and the solution was taken in a 500 ml conical flask fitted with a magnetic stirrer. The stirrer was set in motion and a solution of 4.74 g (0.02 moles) of Phenyl selenylbromide in 60 ml of glacial acetic acid was added dropwise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional thirty minutes. The solid separated was filtered to yield 6.97 g (66.76%) of (Z)-1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene (26). It was purified by recrystallisation from 95% ethanol to give an analytical sample, m.p. 214-216 °C
$^1$HNMR (CDCl$_3$, 400MHz) : δ 7.50-7.40(d, 2H), 7.27-7.15 (d, 2H),
7.10- 6.8 (m, 14H).
IR (KBr cm$^{-1}$) : 3045(Ar-H), 2975, 2556, 1932, 1682(C=C),
1586, 1486, 1427(Ringstretching) 1399,
1210(Ar-S), 927, 850 (Ar -Se).
Anal. calcd. for C$_{26}$H$_{18}$BrClSeS : C, 56.08; H, 3.26; S, 5.76.
Found : C, 56.07; H, 3.21; S, 5.65.

The filtrate from the above reaction mixture after separating the (Z)–1-$p$-
bromophenyl-2-phenyl-2-phenylselenyl-1-$p$-chloro phenylthioethylene (26), on dilution with
water gave 2.8g (26.82%) of (E)–1-$p$-bromophenyl-2-phenyl-2-phenyl selenyl-1-$p$-chloro
phenylthioethylene (25), as solid. This was purified from 95% ethanol to give an analytical
sample, m.p.63-65° C.

(25)

$^1$HNMR (CDCl$_3$, 400MHz) : δ 7.63-7.62(d, 2H,-Ar), 7.61-7.60(d, 2H,-Ar),
7.59-7.49(m, 9H), 7.33-7.22(m, 5H, Ar-H).
IR (KBr cm$^{-1}$) : 3050(Ar-H) 1570(C=C), 1472,
1434(Ringstretching), 1067, 1018(Ar-S),
897,841 (Ar-Se).
Anal. calcd. for C$_{26}$H$_{18}$BrClSeS : C, 56.08; H, 3.26; S, 5.76.
Found : C, 55.98; H, 3.02; S, 5.66.
2.4.1.2. Preparation of (E)– and (Z)– 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene (25 and 26) from (Z)-2-p-bromophenyl-1-phenyl-1-p-chlorophenylthioethylene (4).

A solution of 3.66 g (0.00912 moles) of (Z)– 1-p-bromophenyl-2-phenyl-1-p-chlorophenylthioethylene (4) in 150 ml of glacial acetic acid was taken in a 500 ml conical flask fitted with a magnetic stirrer. The stirrer was started and a solution of 2.36 g (0.01 moles) of Phenyl selenyl bromide in 30 ml of glacial acetic was added dropwise. During addition decolourisation was observed with immediate precipitation. The addition took about 15 minutes and stirring was continued for an additional thirty minutes. The solid separated was filtered to yield 3.19 g (61.2%) of the crude (Z)– 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene (26). On recrystallisation from 95% ethanol gave an analytical sample of (Z)– 1-p-Bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene. No depression in the mixed melting point of this compound was observed on mixing with (Z)– 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene prepared earlier.

The filtrate from the above reaction mixture after separating (Z)– 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene on dilution with water gave 1.54 g (29.5%) of (E)– 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene (25) as solid. This was purified from 95% ethanol to give an analytical sample. The Melting point and infrared spectrum of this compound was similar to that of (E) - 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene obtained earlier.


In a 250 ml round-bottomed flask fitted with a reflux condenser a solution of 2.617 g (0.00469 moles) of (E) – 1-p-bromophenyl-2-phenyl-2-phenylselenyl-1-p-chlorophenylthioethylene (25) in 75 ml of acetic acid was taken. The solution was heated to boiling and 25 ml of 30% hydrogen peroxide was added and the solution refluxed for two hours. The product separated on cooling was collected by filtration, yield 1.64 g (58.6%).
Recrystallisation of the product from 95% ethanol gave an analytical sample of \((E) – 1\)-p-bromophenyl-2-phenyl-2-phenyl selenonyl-1-p-chloro phenylsulphonyl ethylene (29), m.p. 152-154°C.

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{image.png}
\end{center}}
\]

\((29)\)

\(^1\)HNMR (CDCl\(_3\), 400 MHz) \: \delta \: 7.95(d, 2H,-Ar), 7.65-7.52(m, 7H,-Ar), 7.429-7.391(d, 2H,-Ar), 7.270-6.895(m, 7H,-Ar-H).

IR(KBr cm\(^{-1}\)) \: 3063,3027(Ar-H),1971,1931,1605(C=C), 1508, 1494, 1445(Ringstretching), 1179(Ar-S), 937(Ar-SeO\(_2\)), 833(Ar-SO\(_2\)).

Anal.calcd. for \(\text{C}_{26}\text{H}_{18}\text{BrClSeSO}_4\) \: C, 50.30; H, 2.92; S, 5.17.

Found \: C, 50.22; H, 2.87; S, 5.11.


A solution of 7.14 g (0.013 moles) of \((Z) – 1\)-p-bromophenyl-2-phenyl-2-phenylseleneny1-1-p-chlorophenylthioethylene (26) in 200 ml of acetic acid was taken in a 500 ml round-bottomed flask fitted with a reflux condenser. The solution was heated to boiling and 60 ml of 30% hydrogen peroxide was added and heated under reflux for two hours. The product separated on cooling was collected by filtration to yield 6.22 g (81.3%) of \((Z) – 1\)-p-bromophenyl - 2- phenyl- 2- phenyl selenony1- 1- p-chlorophenyl- sulphonylethylene (30).
Recrystallisation of the product from 95% ethanol gave an analytical sample, m.p. 219-220 °C.

\[
\text{(30)}
\]

\[^1\text{HNMR (CDCl}_3,\text{ 400 MHz)}\]: \(\delta\) 7.95 (d, 2H,-Ar), 7.65-7.52 (m, 7H,-Ar),
7.42-7.39 (d,2H-Ar), 7.27-6.89 (m, 7H,-Ar-H).

\[
\text{IR (KBr cm}^{-1})\]: 3063, 3027 (Ar-H), 1971, 1931,
1632 (C=C), 1508, 1494,
1445 (Ringstretching), 1209 (Ar-S),
956 (Ar-SeO\(_2\)), 833 (Ar-SO\(_2\)).
\]

Anal.calcd. for \(\text{C}_{26}\text{H}_{18}\text{BrClSeSO}_4\): C, 50.30; H, 2.92; S, 5.17.

Found: C, 50.22; H, 2.87; S, 5.11.

2.4.2. REFERENCES:


