CHAPTER III
EXPERIMENTAL

Melting points were determined on a Mel-temp apparatus and are uncorrected. The elemental analyses were performed by Dr. R.D. MacDonald, Australian Micro Analytical Service, CSIRO, University of Melbourne, Parkville, Victoria, Australia.

Ultraviolet absorption measurements.— The ultraviolet absorption spectra were determined with a Beckman Model DU-2 Ultraviolet Spectrophotometer. The solvent used was 95\% ethanol and it was purified by distillation after treatment with lead acetate and potassium hydroxide.

Infrared absorption measurements.— The infrared absorption spectra were recorded with a Perkin-Elmer Infrared Spectrophotometer Model 700 in nujol mulls.

Reagents.—

1,3-Dinitrobenzene\textsuperscript{13}.— Methylformanilide was prepared according to the procedure of Pieser and Jones.\textsuperscript{13} Into a one litre three necked flask fitted with a mechanical stirrer, a separatory funnel and a condenser, was taken 67.5 g. of methylformanilide and 50 ml. of dry o-dichlorobenzene. The flask was placed in an ice bath and 67.5 g. of phosphorus
oxyzochloride was added slowly with stirring. At room temperature 44.6 g. of anthracene was added with stirring and the mixture was heated on a steam bath for 3 hours. The viscous mass separated was subjected to steam distillation. The dark oil left after steam distillation on cooling solidified to a mass of yellow crystals. The product on recrystallization from glacial acetic acid yielded 45.2 g. (87.8%) of shining yellow needles, m.p. 102-103° (literature118 m.p. 98.4-99.4°).

A number of aryl aldehydes and other reagents used were obtained from commercial sources and purified when necessary.

General procedure for the preparation of sodium aryl-sulphinates116,..”

Into a two litre beaker provided with a mechanical stirrer and a thermometer were placed 300 g. (2.38 mole) of anhydrous sodium sulphite, 210 g. (2.5 mole) of sodium bicarbonate, and 1.2 litres of water. The solution was heated on a water-bath at 70-80° and was maintained at this temperature; and an appropriate arylsulphonyl chloride (1.27 mole) was added in portions of 5-10 g. with stirring. The addition took about three hours and the mixture was heated with stirring for one more hour. The reaction mixture was allowed to stand for 6 to 10 hours and the solid sodium arylsulphinate formed was collected on a Buchner, dried and recrystallized from water.
According to the general procedure described above the following three sodium arylsulphinates were prepared:

1) Sodium benzenesulphinate,
2) Sodium p-toluenesulphinate and
3) Sodium p-chlorobenzenesulphinate

General procedure for the preparation of arylsulphonylacetic acids.

The procedure followed was essentially that of Gabriel. Recrystallized sodium arylsulphinate (0.5 mole) and chloroacetic acid (0.6 mole) were dissolved in water (150 ml) and the mixture was made alkaline; and the pH was adjusted to 10.

The solution was heated under reflux on a sand bath for 2 hours, cooled and extracted thrice with 50 ml portions of benzene to remove any aryl methyl sulphone formed during this reaction. The aqueous solution was acidified to Congo red with dilute hydrochloric acid when crystals of arylsulphonylacetic acid began to separate. The solution was left overnight in the refrigerator to complete the separation of the compound. The product was collected on a Föhrner funnel, washed with cold water, dried and recrystallized. However, in the case of phenylsulphonylacetic acid, the acidified solution has to be extracted with ether to get the compound.
The relevant data on the sulphonyl acetic acids prepared are given in Table I-20.

**Table I-20**

**Arylsulphonylacetic acid, \( \text{ArSO}_2\text{CH}_2\text{COOH} \)**

<table>
<thead>
<tr>
<th>No.</th>
<th>( R )</th>
<th>Yield</th>
<th>m.p., °C</th>
<th>Lit.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}_6\text{H}_5 )</td>
<td>61</td>
<td>110-111</td>
<td>111-112</td>
<td>136</td>
</tr>
<tr>
<td>2</td>
<td>( \text{p} = \text{CH}_3 \text{C}_6\text{H}_4 )</td>
<td>70</td>
<td>115-116</td>
<td>116-117</td>
<td>136</td>
</tr>
<tr>
<td>3</td>
<td>( \text{p} = \text{ClC}_6\text{H}_4 )</td>
<td>56</td>
<td>122-123</td>
<td>122</td>
<td>137</td>
</tr>
</tbody>
</table>

General procedure for the condensation of arylsulphonylacetic acids with different aryl aldehydes:

The procedure followed was almost essentially that of Balish and Seshanathia Rao. A solution of arylsulphonylacetic acid (0.01 mole) in glacial acetic acid (6 ml.) was mixed with an aryl aldehyde (0.01 mole) and a catalytic amount (0.2 ml.) of benzylamine, and the whole mixture was refluxed for 90 minutes. In certain condensations the heating was continued for 100-120 minutes. The reaction mixture was cooled, treated with dry ether (50 ml.) and refrigerated overnight. Any product separated was collected by filtration and the filtrate was diluted with more ether, the ethereal layer was washed successively with a saturated solution of sodium bicarbonate (15 ml.), sodium bisulphite (15 ml.), dilute hydrochloric acid (20 ml.) and
finally with water. Evaporation of the dried ethereal layer yielded in many cases a solid product. However, in some instances a syrupy substance separated was solidified on treatment with a small amount of methanol or isopropanol.

(2)-1-(p-Acetamidophenyl)-2-(benzenesulphonyl)ethene.-
A mixture of 5 g. (0.025 mole) of benzenesulphonylacetic acid, 4.08 g. (0.025 mole) of p-acetamidobenzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid was heated under reflux for 100 minutes. This solution after working up gave a brown syrupy substance which was solidified on treatment with a small amount of methanol. The brown product separated (3.8 g., 50.6%) was recrystallized from aqueous ethanol to give light brown crystals, m.p. 82-83°.

Anal. Calc. for C_{16}H_{13}NO_3S.H_2O: C, 60.17; H, 5.37.
Found: C, 60.35; H, 5.16.

λ_max
ethanol 315 nm (ε 27,970), 290 (13,420), 203 (18,510); λ_Nujol
678, 701, 719, 747, 795, 802, 836, 860, 978 (m) (CH out-of-plane), 995, 1022, 1080 (s) (S-aryl), 1139 (s) (SO_2), 1168, 1198, 1257, 1290, 1298 (s) (SO_2), 1358, 1401, 1440, 1450, 1500, 1521, 1570, 1607, 1677 (s), and 3320 cm\(^{-1}\).

(2)-1-(m-Bromophenyl)-2-(benzenesulphonyl)ethene.- The condensation was effected by refluxing a mixture of 2 g. (0.01
nole) of benzenesulphonylacetonic acid, 1.85 g. (0.01 mole) of
\( \text{p} \)-bromobenzaldehyde and 0.2 ml. of benzylamine in 6 ml. of
glacial acetic acid for 90 minutes. The reaction mixture after
working up gave an oil which on treatment with a few ml.
of methanol solidified to yield 1.5 g. (46.4\%\) of the product.
Recrystallization of the crude compound from isopropanol gave
an analytical sample, colourless needle shaped crystals
melting at 103-104\°.

Anal. Calcd. for \( \text{C}_{14}\text{H}_{13}\text{BrO}_{3}\text{S} \): C, 52.04; H, 3.43.
Found: C, 51.89; H, 3.33.

\( \gamma_{\text{ethanol}} \) max 271 nm (\( \epsilon \) 21,990), 225 (19,870), 210 (18,410);

\( \nu_{\text{Nujol}} \) max 670, 690, 720, 756, 764, 772, 630, 870, 890, 930, 966,
985 (w) (CH out-of-plane), 993, 1027, 1074, 1078 (s) (S-aryl),
1149 (s) (SO\(_2\)), 1175, 1188, 1232, 1297 (s) (SO\(_3\)), 1316 (s),
1374, 1422, 1445, 1463, 1556, 1580, 1610 and 1547 (w) (C=O) cm\(^{-1}\).

\( \text{(E)}\)-1-\((\text{p}-\text{Bromophenyl})\)-2-\((\text{benzenesulphonyl})\)ethene. - It
was prepared by heating under reflux a mixture of 2 g. (0.01
mole) of benzenesulphonylacetonic acid, 1.85 g. (0.01 mole) of
\( \text{p} \)-bromobenzaldehyde and 0.2 ml. of benzylamine in 6 ml. of
glacial acetic acid for 90 minutes. The reaction mixture
yielded 2.0 g. (61.9\%) of the product. The sulphone on
recrystallization from 95\% ethanol thrice afforded fine
colourless needles, m.p. 154-155\°.
Anal. Calcd. for C_{16}H_{14}BrO_{4}: C, 52.04; H, 3.43.

Found: C, 52.16; H, 3.51.

\( \lambda_{\text{max}} \) ethanol 284 nm (6 28,160), 220 (14,800), 204 (15,500);

\( \lambda_{\text{max}} \) Nujol 650, 690, 700, 720, 740, 784, 820, 857, 978 (m) (CH out-of-plane), 1070, 1095 (m) (C-aryl), 1156 (s) (C=C), 1179, 1194, 1253, 1302 (s) (SO_{2}), 1379, 1445, 1460, 1556, 1570 and 1615 cm\(^{-1}\).

(E)-1-(m-Bromo-p-methoxyphenyl)-2-(benzenesulphonyl) ethane.- Two grams (0.01 mole) of benzenesulphonylacetic acid, 2.15 g. (0.01 mole) of m-bromo-p-methoxybenzaldehyde and 0.2 ml. of benzylamine were taken in 6 ml. of glacial acetic acid and the mixture was heated under reflux for 90 minutes. The reaction mixture yielded a syrupy liquid which on treatment with methanol gave 2.65 g. (58%) of crystalline product. These crystals on further recrystallization thrice from 95° ethanol afforded an analytical sample; colourless needles, m.p. 157-158°.

Anal. Calcd. for C_{18}H_{13}BrO_{3}S: C, 51.41; H, 3.71.

Found: C, 51.42; H, 3.75.

\( \lambda_{\text{max}} \) ethanol 308 nm (r 22,450), 204 (22,830), 238 (19,940), 213 (19,430); \( \lambda_{\text{max}} \) Nujol 670, 690, 718, 738, 788, 818, 830, 858, 880, 890, 940, 968 (m) (CH out-of-plane), 1010, 1045, 1080 (s).
(E)-1-(m-Chlorophenyl)-2-(benzenesulphonyl)ethene. A mixture of 4.0 g. (0.02 mole) of benzenesulphonylacetic acid and 2.51 g. (0.02 mole) of m-chlorobenzaldehyde in 12 ml. of glacial acetic acid was refluxed for 90 minutes in the presence of 0.4 ml. of benzylamine. A light yellow oily layer was separated when the reaction mixture was worked up. However, the addition of a small amount of methanol afforded a crystalline product 3.3 g. (80.3%). Recrystallization of the latter from isopropanol yielded colourless shining flakes, m.p. 98.5-99.5°.

Anal. Calcd. for C₁₄H₁₄ClO₃S: C, 60.33; H, 3.98.
Found: C, 60.44; H, 4.04.

\[ \lambda_{\text{max}}^{\text{ethanol}} \quad 271 \text{ nm} (\varepsilon 21,020), 270 (18,620), 211 (13,060); \]
\[ \lambda_{\text{max}}^{\text{Nujol}} \quad 680, 692, 723, 762, 779, 838, 884, 912, 970 \text{ (m) (C=O out-of-plane)}, 1000, 1092 \text{ (m) (3-aryl)}, 1130 \text{ (s) (SO₂), 1195, 1240, 1275, 1303 (m) (SO₂), 1360, 1462, 1560, 1582, 1614, and 1645 (w) (C=O) cm}^{-1}. \]

(E)-1-(2,3-Dimethoxyphenyl)-2-(benzenesulphonyl)ethene. To 12 ml. of glacial acetic acid were added 5.0 g. (0.025 mole)
of benzenesulphonylacetic acid, 4.15 g. (0.025 mole) of 2,5-dimethoxybenzaldehyde and 0.5 ml. of benzylamine; and the mixture was heated under reflux for 90 minutes. The resultant reaction mixture was worked up to yield 4.9 g. (64.4\%) of the product. This material on recrystallization from methanol afforded an analytical sample, colourless shining prisms melting at 114-115°.

Anal. Caled. for C_{18}H_{16}O_{8}: C, 63.13; H, 5.30.
Found: C, 63.04; H, 5.32.

$\lambda_{\text{ethanol}}$ 281 nm ($\epsilon$ 19,160), 213 (22,360), 203 (23,580).

$\nu_{\text{IR, Nujol}}$ 692, 713, 740, 755, 764, 790, 818, 840, 855, 878, 932, 1000 (m) (CH out-of-plane), 1018, 1072, 1098 (m) (aryl), 1156 (s) (CO), 1180, 1220, 1235, 1272, 1280, 1297 (s) (CO), 1316, 1320, 1362, 1438, 1456, 1468, 1492, 1582, 1618 and 1680 (w) (C=O) cm$^{-1}$.

(E)-1-(2,5-Dimethoxyphenyl)-2-(benzenesulphonyl)ethene.

The condensation was accomplished by refluxing a mixture of 5.0 g. (0.025 mole) of benzenesulphonylacetic acid, 4.15 g. (0.025 mole) of 2,5-dimethoxybenzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid. On working up, the reaction mixture yielded 3.8 g. (50\%) of the product which on recrystallization from aqueous acetic acid gave light yellow plates, m.p. 135-136°.
Anal. Calc.: for C_{10}H_{14}O_{4}S: C, 63.13; H, 5.30.
Found: C, 63.17; H, 5.25.

\[ \lambda_{\text{max}} \] ethanol 277 nm (€ 13,140), 226 (14,210), 204 (18,430);

\[ \nu_{\text{max}}' \] Nujol 680, 690, 710, 726, 734, 758, 770, 812, 828, 845,
694, 944, 965 (m) (CH out-of-plane), 1000, 1028, 1080, 1087,
(s) (S-aryl), 1145 (s) (CO\(_2\)), 1185, 1406, 1240, 1275, 1305 (s)
(C\(_\text{ar}\)), 1378, 1414, 1446, 1509, 1578, 1605 and 1675 (v) (C=O) cm\(^{-1}\)

(2)-2-(3,4-Dimethoxyphenoxy)-2-(benzenesulphonyl)ethene.

A mixture of 7.5 g. (0.0375 mole) of benzenesulphonylacetic acid, 6.23 g. (0.0375 mole) of 3,4-dimethoxybenzaldehyde and
0.8 ml. of benzylamine in 20 ml. of glacial acetic acid was
heated under reflux for 90 minutes. The resultant reaction
mixture yielded 5.15 g. (45.2\%) of the product which on recrystallisation from 95% ethanol four times afforded, colourless
heavy plates melting at 144-145°.

Anal. Calc.: for C_{16}H_{16}O_{4}S: C, 63.13; H, 5.30.
Found: C, 63.40; H, 5.35.

\[ \lambda_{\text{max}} \] ethanol 322 nm (€ 18,030), 294 (13,990), 232 (15,310),
204 (23,250); \[ \nu_{\text{max}}' \] Nujol 695, 762, 780, 815, 852, 872, 940, 980,
960, 1000 (m) (ch out-of-plane), 1020, 1042, 1062, 1084,
1098 (m) (S-aryl), 1158 (s) (CO\(_2\)), 1168, 1232, 1297 (s) (CO\(_2\)),
1304, 1360, 1394, 1432, 1458, 1470, 1520, 1592, 1610, 1622
and 1638 (v) (C=O) cm\(^{-1}\).

**E)-1-(o-Fluoroaryl)-2-(bromophenyl)ethene.**

Bromophenylacetic acid (3.0 g., 0.025 mole) dissolved in glacial acetic acid (15 ml.) was treated with o-fluorobenzaldehyde (3.76 g., 0.025 mole) in the presence of benzylamine (0.5 ml.) and was refluxed for 90 minutes. The reaction mixture after working up gave 2.8 g. (38.9%) of the compound which on recrystallization from 95° ethanol gave colourless long needles, m.p. 91-92°.


Found: C, 66.44; H, 5.54.

\(\lambda_{\text{max}}\) ethanol 324 nm (ε 9,154), 275 (20,500), 227 (18,310),

206 (22,310); \(\lambda_{\text{max}}\) Nujol 687, 714, 727, 776, 785, 805, 820, 834, 860, 925, 946, 973, 990 (m) (CH out-of-plane), 1040, 1095 (s) (C(S)aryl), 1140 (s) (SO\(_2\)), 1176, 1250, 1280, 1308 (s) (C=C)\), 1374, 1392, 1443, 1450, 1486, 1567, 1600, 1635 and 1675 (v) (C=O) cm\(^{-1}\).

**E)-1-(o-Fluoroaryl)-2-(bromophenyl)ethene.**

Three grams (0.15 mole) of bromophenylacetic acid, 1.96 g. (0.015 mole) of o-fluorobenzaldehyde and 0.3 ml. of benzylamine in 10 ml. of glacial acetic acid was heated under reflux for 90 minutes. The reaction mixture yielded 1.8 g. (45.2%) of
the product. Two recrystallizations from 95° ethanol afforded an analytically pure sulphone as colourless shining crystals, m.p. 85-86°.

Anal. Calcd. for C_{14}H_{13}F_0S: C, 64.12; H, 4.23.
Found: C, 64.24; H, 4.20.

\[ \lambda_{\text{max}} \text{ ethanol} \quad 269 \text{ nm (\varepsilon 21,940), 203 (15,780)}; \]

\[ \nu_{\text{max}} \text{ Nujol} \quad 682, 703, 718, 745, 778, 820, 840, 852, 868, 
968 (m) (CI out-of-plane), 995, 1082 (s) (S-ary1), 1142 (s) (SO_2), 1183, 1210, 1282, 1300 (s) (SO_2), 1372, 1450, 1568, 
1602, 1640 (w) (C=O) and 1680 cm\(^{-1}\).

(E)-1-(p-Isopropylphenyl)-2-(benzenesulphonyl)ethene.

A mixture of 5.0 g. (0.025 mole) of benzenesulphonylacetic acid, 3.71 g. (0.025 mole) of p-isopropylbenzaldehyde and
0.5 ml. of bengylamine in 15 ml. of glacial acetic acid was heated under reflux for 100 minutes. On working up, the
reaction mixture afforded 2.5 g. (35.2%) of the product. This material on recrystallization from aqueous ethanol gave
colourless lustrous flakes melting at 104-104.5°.

Anal. Calcd. for C_{17}H_{18}O_2S: C, 71.29; H, 6.33.
Found: C, 71.10; H, 6.12.

\[ \lambda_{\text{max}} \text{ ethanol} \quad 284 \text{ nm (\varepsilon 25,900), 224 (15,160), 204 (16,950)}; \]

\[ \nu_{\text{max}} \text{ Nujol} \quad 680, 720, 735, 752, 797, 805, 824, 861, 960, \]
974 (m) (C=O out-of-plane), 998, 1018, 1057, 1082 (s) (C=aryl), 1145 (s) (C=O), 1179, 1196, 1284, 1306 (s) (C=O), 1374, 1415, 1456, 1500, 1556, 1570 and 1606 cm\(^{-1}\).

\[(E)-1-(o-Methylphenyl)-2-(bromobenzensulphonyl)ethene\] -

Four grams (0.02 mole) of benzenesulphonylacetic acid was condensed with 2.40 g. (0.02 mole) of o-methylbenzaldehyde in 12 ml. of glacial acetic acid by refluxing the solution for 90 minutes in the presence of 0.5 ml. of benzylamine. On working up, the reaction mixture yielded 0.3 g. (43.4\%) of the product. This sulphone was recrystallised thrice from isopropanol to give colourless, shining crystals melting at 64-64.5\°C.


Found: C, 69.30; H, 5.44.

\(\lambda_{\text{max}}\) ethanol 278 nm (\(\varepsilon 19,810\)), 228 (15,390), 204 (23,090)

\(\lambda_{\text{max}}\) nujol 685, 715, 745, 753, 785, 820, 834, 833, 976 (m)

(C=O out-of-plane), 995, 1020, 1081 (s) (C=aryl), 1140 (s) (C=O), 1175, 1213, 1275, 1300 (s) (C=O), 1373, 1411, 1472, 1590 and 1603 cm\(^{-1}\).

\[(E)-1-(1-Naphthyl)-2-(bromobenzensulphonyl)ethene\] - It was prepared by heating under reflux a mixture of 7.5 g.
(0.0375 mole) of benzene-sulphonylacetic acid and 5.05 g. (0.0375 mole) of 1-naphthaldehyde in 25 ml. of glacial acetic acid in the presence of 0.8 ml. of benzylamine for 100 minutes. The resultant reaction mixture when worked up gave a light yellow oil which on treatment with ethanol afforded 4.2 g. (38.2%) of the product. The crude product on recrystallization twice from 95% ethanol afforded an analytical sample, colourless lustrous plates, m.p. 102-103°.

Anal. Calc'd. for C_{14}H_{14}O_{3}: C, 73.45; H, 4.79.
Found: C, 73.67; H, 4.88.

λ\text{max} \text{ethanol} \quad 322 \text{ nm (11,900), 246 (17,010), 221 (43,620), 206 (31,320); λ\text{Nujol} \quad 698, 720, 746, 770, 780, 808, 840, 855, 875, 894, 930, 980 (m) CH out-of-plane), 1038, 1098 (m) (\text{oxy}), 1158 (s) (\text{co}), 1277, 1312 (s) (\text{co}), 1353, 1382, 1466, 1592, 1616, 1656 and 1682 cm⁻¹.

(E)-1-(1-Pyrenyl)-2-(benzenesulphonyl)ethene. The condensation was accomplished by refluxing a mixture of 2.0 g. (0.01 mole) of benzene-sulphonylacetic acid, 2.30 g. (0.01 mole) of 1-pyrenyl carboxaldehyde and 0.2 ml. of benzylamine in 6 ml. of glacial acetic acid for 100 minutes. Ether (25 ml.) was added to the cooled reaction mixture and the resulting solution was refrigerated for overnight. The yellow crystalline solid separated was collected on a Büchner (1.7 g.) and the
mother liquor after working up further yielded 1.3 g. of the material. The total yellow product (7.5 g., 68%), after three crystallizations from acetic acid gave an analytical sample, m.p. 195-196°.

Anal. Calcd. for C_{34}H_{46}O_{8}: C, 78.23; H, 4.38.
Found: C, 77.93; H, 4.40.

\( \text{ethanol} \) max 280 nm (ε 21,680), 235 (44,030), 202 (32,840);

\( \text{Nujol} \) max 674, 700, 723, 742, 760, 792, 800, 818, 830, 874, 895, 922, 948 (m) (CN out-of-plane), 967 (v.w.), 1008, 1076 (s) (S-aryl), 1139 (s) (SO₂), 1178, 1220, 1275, 1290, 1304 (s) (SO₂), 1360, 1430, 1448, 1578, and 1660 (w) (C=O) cm⁻¹.

-(E)-1-(p-Acetamido-phenyl)-2-(p-tolyl-sulphonyl)ethene

A mixture of 5.35 g. (0.025 mole) of p-tolyl-sulphonyl-acetic acid, 4.0 g. (0.025 mole) of p-acetamido-benzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid was heated under reflux for 60 minutes. On working up the reaction mixture yielded 7.5 g. (31.7%) of the product. Recrystallization of the crude sulphone from aqueous ethanol thrice afforded light brown crystals, m.p. 178-179°.

Anal. Calcd. for C_{41}H_{38}N_{2}O_{9}S: C, 64.73; H, 5.43.
Found: C, 64.48; H, 5.37.

\( \text{ethanol} \) max 315 nm (ε 25,200), 231 (11,850), 203 (17,150).
ν<sub=max</sub>Nujol 650, 672, 702, 722, 812, 852, 874, 990 (m) (CH out-of-plane), 1080, 1020, 1040, 1095 (s) (C=aryl), 1143 (s) (CO<sub>n</sub>), 1190, 1203, 1242, 1270, 1290, 1305 (s) (NO<sub>2</sub>), 1333 (s), 1376, 1417, 1460, 1507, 1539, 1590, 1692 and 3330 cm<sup>-1</sup>.

(E)-1-(m-Bromophenyl)-2-(p-tolylsulphonyl)ethene.— The condensation was effected by refluxing a mixture of 4.28 g. (0.02 mole) of p-tolylsulphonylacetic acid, 3.7 g. (0.02 mole) of m-bromobenzaldehyde and 0.4 ml. of benzylamine in 12 ml. of glacial acetic acid for 90 minutes. The reaction mixture yielded 4.1 g. (60.8%), of the product, which on recrystallisation from 95% ethanol afforded an analytical sample melting at 121-122°.

Anal. Calc'd. for C<sub>16</sub>H<sub>13</sub>BrNO<sub>2</sub>Cl: C, 53.44; H, 3.89.
Found: C, 53.42; H, 3.89.

ν<sub>max</sub> ethanol

ν<sub>max</sub>Nujol 278 nm (ε 16,930), 226 (12,930), 209 (14,690).

ν<sub>max</sub>Nujol 654, 675, 700, 746, 812, 832, 854, 860, 985 (s) (CH out-of-plane), 1023, 1090 (m) (C=aryl), 1144 (s) (NO<sub>2</sub>), 1184, 1200, 1280, 1307, 1320 (s), 1320 (a) (NO<sub>2</sub>), 1376, 1460, 1555 (w), 1580 and 1600 cm<sup>-1</sup>.

(E)-1-(m-Bromophenyl)-2-(p-tolylsulphonyl)ethene.—

Heating a mixture of 2.14 g. (0.01 mole) of p-tolylsulphonylacetic acid, 1.85 g. (0.01 mole) of m-bromobenzaldehyde and
0.2 ml. of benzylamine in 6 ml. of glacial acetic acid under reflux for 90 minutes yielded 2.2 g. (65.3%) of the sulphone. The product on recrystallization from methanol gave colourless flakes, m.p. 99-99.5°.

Found: C, 53.64; H, 3.89.

$\lambda_{\text{max}}^\text{ethanol}$ 273 nm ($\epsilon$ 25,860), 222 (24,230);

$\lambda_{\text{max}}^\text{Nujol}$ 676, 697, 720, 760, 768, 788, 837, 878, 898, 972 (m) (Π out-of-plane), 1002, 1030, 1080, 1090 (s) (s-aryl), 1152 (s) (C=O), 1196, 1235, 1280, 1306 (s) (C=O), 1320, 1380, 1428, 1450, 1470, 1560, 1586, 1615 and 1685 (w) (C=O) cm⁻¹.

(E)-1-(p-Bromophenyl)-1-(p-tolylsulphonyl)ethene.— A mixture of 2.13 g. (0.01 mole) of p-tolylsulphonylacetic acid, 1.85 g. (0.01 mole) of p-bromobenzaldehyde and 0.2 ml. of benzylamine in 6 ml. of glacial acetic acid was heated under reflux for 90 minutes. The product obtained (2.8 g., 83.1%), on recrystallization from 95% ethanol afforded an analytical sample, colourless shining leaflets, m.p. 161-162°.

Found: C, 53.70; H, 4.10.

$\lambda_{\text{max}}^\text{ethanol}$ 285 nm ($\epsilon$ 31,300), 210 (18,030), 202 (23,390);
\( \nu_{\text{max}} \) Nujol

676, 708, 760, 792, 800, 820, 828, 865, 948, 980 (s) (CH out-of-plane), 1018, 1060, 1094 (s) (\( \alpha \)-aryl), 1148 (s) (\( \gamma \)-ph), 1180, 1192, 1219, 1246, 1297, 1310 (s) (\( \alpha \)-a), 1380, 1402, 1460, 1490, 1520, 1540, 1560, 1592, 1620, 1650 (w) (C=\( \equiv \)) and 3050 cm\(^{-1}\).

(E)-1-(\( \alpha \)-Bromo-\( p \)-methoxyphenyl)-2-(\( p \)-tolylsulphonyl)ethene.- Into 6 ml. of glacial acetic acid were added, 2.14 g. (0.01 mole) of \( p \)-tolylsulphonylacetic acid, 2.15 g. (0.01 mole) of \( \alpha \)-bromo-\( p \)-methoxybenzaldehyde and 0.2 ml. of benzylamine, and the mixture was heated under reflux for 100 minutes. On working up, the reaction mixture yielded 2.6 g. (70.8\%o) of the sulphone. It was recrystallized from isopropanol to give colourless shining needles melting at 140-140.5º.

Anal. Calc. for \( \text{C}_{30}\text{H}_{20}\text{Br}_{2}\text{O}_{4} \): C, 52.31; H, 4.12.

Found: C, 51.95; H, 4.19.

\( \nu_{\text{max}} \) ethanol

293 nm (\( \epsilon \) 26,520), 337 (24,360), 213 (23,080), 204 (23,080); \( \nu_{\text{max}} \) Nujol 630, 675, 700, 759, 772, 808, 835, 870, 897, 958 (m) (CH out-of-plane), 1016, 1048, 1076 (m) (\( \alpha \)-aryl), 1132 (s) (\( \gamma \)-ph), 1176, 1230, 1260, 1284, 1298 (m) (\( \alpha \)-a), 1368, 1400, 1430, 1450, 1482, 1540, 1584 and 1596 cm\(^{-1}\).

(E)-1-(\( \alpha \)-Chlorophenyl)-2-(\( p \)-tolylsulphonyl)ethene.- \( p \)-Tolylsulphonylacetic acid (10.7 g., 0.05 mole) was condensed
with o-chlorobenzaldehyde (7.0 g., 0.05 mole) in glacial acetic acid (25 ml.) in the presence of benzylamine (0.7 ml.) by refluxing the reaction mixture for 90 minutes. The compound on recrystallisation from isopropanol yielded (6.9 g., 47.3%) colourless leaflets, m.p. 102-103°.

Anal. Calcd. for C_{15}H_{15}ClO_{2}S: C, 61.85; H, 4.47.
Found: C, 61.53; H, 4.51.

\[
\text{ethanol} \quad 274 \text{ nm (ε 21,380), 222 (16,420), 203 (19,590);} \\
\nu_{\text{max}} \quad 650, 662, 692, 734, 800, 820, 842, 956 \text{ (m) (CH out-of-plane), 1016, 1027, 1040, 1079 (s) (C-aryl), 1100, 1116, 1138 (s) (SO_{2}), 1176, 1189, 1222, 1275, 1292 (s), 1310 (s) (SO_{2}), 1365, 1430, 1444, 1480, 1548, 1590 and 1656 (m) cm}^{-1}.
\]

(E)-1-(m-Chlorophenyl)-2-(p-tolylsulphonyl)ethene

A mixture of 4.28 g. (0.02 mole) of p-tolylsulphonylacetic acid and 2.81 g. (0.02 mole) of o-chlorobenzaldehyde in 12 ml. of glacial acetic acid was refluxed for 90 minutes in the presence of 0.4 ml. of benzylamine. On working up, the reaction mixture afforded 4.8 g. (89.2%) of the product. This sulphone on repeated recrystallisations from methanol gave an analytical sample, shining colourless leaflets, m.p. 84-86°.

Anal. Calcd. for C_{16}H_{15}ClO_{2}S: C, 61.85; H, 4.47.
Found: C, 61.49; H, 4.54.
\( \lambda_{\text{max}} \) ethanol 271 nm (6 26,530), 219 (25,930), 203 (25,800)

\( \lambda_{\text{max}} \) Nujol 660, 677, 705, 776, 820, 845, 876, 890, 982 (s)
(\( \text{C}^2 \text{H}_{\text{out-of-plane}} \)), 1000, 1030, 1040, 1090 (s) (S-aryl),
1140 (s) (\( \text{C}^2 \text{O}_2 \)), 1174, 1192, 1232, 1298 (s) (\( \text{C}^2 \text{O}_2 \)), 1321,
1376, 1419, 1468, 1475, 1493, 1560, 1589, 1614 and 1660 (w)
(\( \text{C}^2 \text{C} \)) cm\(^{-1} \).

(E)-1-(2,3-Dimethoxyphenyl)-2-(p-tolylsulphonyl)ethane.

The condensation was accomplished by refluxing a mixture of
5.35 g. (0.025 mole) of p-tolylsulphonylacetic acid, 4.16 g.
(0.025 mole) of 2,3-dimethoxybenzaldehyde and 0.5 ml. of
benzylamine, in 15 ml. of glacial acetic acid for 90 minutes.
The yield was 5.15 g. (64.7%) and the compound crystallized
as colourless needles from 95% ethanol melting at 127-128°.

Anal. Calcd. for C\(_{27}\)H\(_{20}\)O\(_4\)S: C, 64.12; H, 5.70.
Found: C, 64.38; H, 5.75.

\( \lambda_{\text{max}} \) ethanol 282 nm (6 21,370), 217 (25,270), 203 (23,180)

\( \lambda_{\text{max}} \) Nujol 660, 722, 752, 776, 818, 845, 876, 930, 980, 994 (s)
(\( \text{C}^2 \text{H}_{\text{out-of-plane}} \)), 1018, 1078 (s) (S-aryl), 1088, 1140 (s)
(\( \text{C}^2 \text{O}_2 \)), 1167, 1182, 1205, 1228, 1268, 1290 (s) (\( \text{C}^2 \text{O}_2 \)), 1370,
1418, 1440, 1460, 1474, 1570, 1594, 1608 and 1650 (w) (\( \text{C}^2 \text{C} \)) cm\(^{-1} \).
(E)-1-(2,3-Dimethoxyphenyl)-2-(p-tolylsulphonyl)ethene.

About 5.35 g. (0.025 mole) of p-tolylsulphonylacetic acid was condensed with 4.16 g. (0.025 mole) of 2,5-dimethoxybenzaldehyde in 15 ml. of glacial acetic acid in the presence of 0.5 ml. of benzylamine by refluxing the solution for 90 minutes. The reaction mixture afforded 4.6 g. (57.8%) of the sulphone. Recrystallization of the product twice from 95% ethanol gave an analytical sample, colourless shining plates, m.p. 119-120°.

Anal. Calcd. for C_{17}H_{18}O_{4}S: C, 64.12; H, 5.70.
Found: C, 64.30; H, 5.79.

λ max

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>288 nm (ε 25,300), 221 (14,060), 209 (16,610);</th>
</tr>
</thead>
</table>

ν max

| 655, 700, 720, 727, 794, 800, 826, 831, 977 (m) |
| (CH out-of-plane), 1018, 1052, 1082 (s) (S-aryl), 1140 (s) (SO_{2}), 1178, 1208, 1240, 1282, 1301 (s) (SO_{2}), 1340, 1360, 1375, 1416, 1454, 1500, 1550 and 1602 cm^{-1}. |

(8)-1-(3,4-Dimethoxyphenyl)-2-(p-tolylsulphonyl)ethene.

A mixture of 5.35 g. (0.025 mole) of p-tolylsulphonylacetic acid, 4.16 g. (0.025 mole) of 3,4-dimethoxybenzaldehyde and 0.5 ml. benzylamine in 15 ml. of glacial acetic acid was refluxed for 90 minutes and the reaction mixture yielded 3.0 g. (37.7%) of the sulphone. This material on recrystallization from methanol afforded colourless plates melting at 126-127°.
Anal. Calcd. for C₁₂H₁₆O₈S: C, 64.12; H, 5.70
Found: C, 64.23; H, 5.80.

$\lambda_{\text{max}}^\text{ethanol}$ 321 nm (ε 18,680), 293 (14,960), 237 (18,610), 204 (24,960); $\lambda_{\text{max}}^\text{Nujol}$ 657, 697, 730, 744, 762, 805, 844, 877, 927, 940, 980 (s) (C=O out-of-plane), 1020, 1078 (s) (C=aryl), 1138 (s) (C=O), 1168, 1215, 1245, 1260, 1280, 1290, 1330 (m) (C=O), 1372, 1405, 1438, 1460, 1483, 1508, 1574, 1585, 1603, 1680 (w) (C=O) cm⁻¹.

(E)-1-(o-Ethoxyphenyl)-2-(p-tolylsulphonyl)ethene.

Into 15 ml. of glacial acetic acid were added 5.35 g. (0.025 mole) of p-tolylsulphonyl acetic acid, 3.76 g. (0.025 mole) of o-ethoxybenzaldehyde and 0.3 ml. of benzylamine; and the mixture was refluxed for 90 minutes. On working up, the reaction mixture yielded 3.8 g. (50.3%) of the crystalline product. Recrystallization of the sulphone from 95% ethanol gave long needles, m.p. 108-109°.

Anal. Calcd. for C₁₂H₁₆O₈S: C, 67.51; H, 6.0.
Found: C, 67.49; H, 5.97.

$\lambda_{\text{max}}^\text{ethanol}$ 323 nm (ε 8,686), 274 (19,390), 220 (17,570), 205 (20,130); $\lambda_{\text{max}}^\text{Nujol}$ 655, 700, 723, 752, 776, 808, 834, 856, 920, 980 (m) (C=O out-of-plane), 1015, 1039, 1080 (m) (C=aryl)
1112, 1138 (s) (s=s), 1166, 1242, 1274, 1303 (s) (s=s),
1368, 1448, 1482, 1592 and 1640 (w) (cm⁻¹) cm⁻¹.

(E)-1-(o-Fluorophenyl)-2-(p-tolylsulphonyl)ethane.-
Heating a mixture of 3.21 g. (0.015 mole) of p-tolylsulphonylacetic acid, 1.36 g. (0.015 mole) of o-fluorobenzaldehyde and 0.2 ml. of benzylamine in 9 ml. of glacial acetic acid under reflux for 90 minutes, yielded 1.6 g. (38.7%) of the product. Recrystallization of the sulphone from aqueous ethanol thrice gave colourless shining crystals melting at 73-74°.

Found: C, 65.48; H, 4.81.
λ<sub>max</sub> ethanol 270 nm (ε 22,950), 204 (19,190).

λ<sub>max</sub> H₂O 672, 720, 772, 786, 802, 822, 828, 854, 862,
888, 984 (s) (CH out-of-plane), 1022, 1042, 1096 (s) (S=aryl),
1127, 1136 (s) (s=s), 1187, 1280, 1285, 1342, 1302 (s) (s=s),
1324 (s), 1388, 1466, 1496, 1600, 1622 and 1650 (w) (cm⁻¹) cm⁻¹.

(Z)-1-(p-Fluorophenyl)-2-(p-tolylsulphonyl)ethane.-
A mixture of 3.21 g. (0.015 mole) of p-tolylsulphonylacetic acid and 1.36 g. (0.015 mole) of p-fluorobenzaldehyde in 9 ml. of glacial acetic acid was refluxed for 90 minutes in the presence of 0.2 ml. of benzylamine. The light yellow product,
obtained, (1.8 g., 43.5°) on recrystallization from aqueous acetic acid afforded an analytical sample, colourless flakes, m.p. 96.3-97°.

Found: C, 63.16; H, 4.61.

\[ \text{ethanol} \] max 274 nm (ε 39,360), 204 (31,610);

\[ \text{Nujol} \] max 660, 700, 762, 786, 808, 837, 863, 938, 972 (m)
(CH out-of-plane), 1010, 1037, 1078 (s) (S-aryl), 1100,
1135 (s) (SO₂), 1152, 1178, 1227, 1275 (s), 1299 (s) (SO₂),
1312 (s), 1370, 1390, 1406, 1446, 1498, 1588, 1604 and
1645 (w) (C=O) cm⁻¹.

(E)-1-(p-Hydroxyphenyl)-2-(p-tolylsulphonyl)ethene.

The condensation was effected by refluxing a mixture of 5.35 g. (0.025 mole) of p-tolylsulphonylacetic acid and 3.05 g. (0.025 mole) of p-hydroxybenzaldehyde in 15 ml. of glacial acetic acid in the presence of 1.0 ml. of benzylamine for 120 minutes. On working up, the reaction mixture yielded only a light brown syrupy substance. This material on treatment with methanol afforded a crystalline product (1.3 g., 19.0%) after refrigeration for several days. Re-
crystallisation of the latter from n-hexane gave light brown crystals, m.p. 108-110°.

Found: C, 64.73; H, 5.42.

$\lambda_{\text{max}}$ ethanol 310 nm ($< 10.560$), 228 (15.730), 206 (15.590);

$\nu_{\text{max}}^{\text{IR}}$ 690, 740-810 (br), 860, 902, 995 (w) (CH out-of-plane), 1068 (m) ($^{6}$-aryl), 1196, 1165 (m) ($^{10}$O$_{a}$), 1190, 1240, 1305, 1320 (w) ($^{6}$O$_{b}$), 1335, 1400, 1409, 1532, 1620, 1660 (w) ($^{6}$c=c), 1695, 2450, 2925, 3060 and 3625 cm$^{-1}$.

(E)-1-(p-Isopropylphenyl)-2-(p-tolylsulphonyl)ethane-

p-Tolylsulphonylacetic acid (5.35 g., 0.025 mole) dissolved in acetic anhydride (15 ml.) was treated with p-isopropyl-

benzaldehyde (3.71 g., 0.025 mole) in the presence of

benzylamine (0.5 ml.) and was refluxed for 90 minutes. The

reaction mixture on working up yielded 4.5 g. (59.8%) of the

sulphone. Recrystallization of the compound three-times from

95° ethanol afforded an analytical sample, colourless shining

plates melting at 135-136°.

Anal. Calc. for C_{18}H_{18}O_{3}: C, 71.97; H, 6.71.

Found: C, 71.88; H, 6.69.

$\lambda_{\text{max}}$ ethanol 278 nm ($< 13.660$), 230 (12.910), 204 (16.770);

$\nu_{\text{max}}^{\text{IR}}$ Nujol 674, 707, 733, 765, 820, 860, 984, 940, 997 (m)

(CH out-of-plane), 1020, 1050, 1094 (s) ($^{6}$-aryl), 1147 (s) ($^{10}$O$_{a}$),
1165, 1180, 1207, 1245, 1282, 1304 (m) (S=O), 1360, 1415, 1462, 1504, 1576, 1602 and 1652 (w) (C=O) cm$^{-1}$.

$(E)-1$-{(o-Methylphenyl)}-2-{(p-tolylsulphonyl)ethene}.

A mixture of 4.28 g. (0.02 mole) of p-tolylsulphonylactic acid, 2.49 g. (0.02 mole) of o-methylbenzaldehyde and 0.3 ml. of benzylamine in 12 ml. of glacial acetic acid was refluxed for 90 minutes. The reaction mixture yielded 1.8 g. (33.1%) of the sulphone. It was recrystallized from isopropanol as colourless long needles, m.p. 88-89$^\circ$.

Anal. Calc. for C$_{16}$H$_{14}$O$_{3}$S: C, 70.55; H, 5.92.

Found: C, 70.25; H, 5.96.

$\lambda$ ethanol max 280 nm (e 27,730), 225 (20,480), 204 (32,030).

$\lambda_{\text{Nujol max}}$ 635, 700, 730, 750, 804, 832, 850, 958 (s) (CH out-of-plane), 1017, 1030, 1080 (s) (s-aryl), 1139 (s) (S=O), 1180, 1207, 1298 (s) (S=O), 1368, 1450, 1590 and 1605 cm$^{-1}$.

$(E)-1$-{(2-Naphthyl)}-2-{(p-tolylsulphonyl)ethene}.

A solution of p-tolylsulphonylactic acid (4.28 g., 0.02 mole) dissolved in 12 ml. of glacial acetic acid was treated with 3.1 g. (0.02 mole) of 2-naphthaldehyde in the presence of 0.4 ml. of benzylamine and was refluxed for 100 minutes. The reaction mixture yielded 3.6 g. (58.3%) of the product. Recrystallization from acetic acid afforded pure sulphone as
colourless prisms melting at 159.5-160.5°.

Anal. Calcd. for C₈H₁₄O₈S: C, 73.98; H, 5.23.
Found: C, 74.16; H, 5.31.

\( \lambda_{\text{ethanol max}} \) 307 nm (ε 22,780), 269 (33,240), 229 (26,100),
211 (22,850), 204 (22,630); \( \gamma_{\text{Nujol max}} \) 670, 710, 750, 775,
810, 820, 840, 850, 870, 900, 910, 972, 985 (m) (CH out-of-plane), 1022, 1088 (s) (β-aryl), 1150 (s) (νC=S), 1238,
1290, 1308 (m) (νC=O), 1380, 1460, 1595 and 1616 (m) cm⁻¹.

(8)-1-[(1)-Pyrene]-2-(p-tolylsulphonyl)ethene.- Into
6 ml. of glacial acetic acid, 2.14 g. (0.01 mole) of p-tolylsulphonylacetic acid, 2.30 g. (0.01 mole) of 1-pyrene
carboxaldehyde and 0.2 ml. of benzylamine were added; and the mixture was heated under reflux for 100 minutes. On
working up, the reaction mixture yielded 2.5 g. (85.4%) of the material. Recrystallization of the sulphone from
acetic acid four times, afforded an analytical sample, fine
light yellow crystals, m.p. 189-190°.

Found: C, 78.51; H, 4.78.

\( \lambda_{\text{ethanol max}} \) 280 nm (ε 22,790), 236 (44,350), 203 (33,610);
\( \gamma_{\text{Nujol max}} \) 660, 716, 735, 774, 790, 815, 830, 844, 950,
965 (m) (CH out-of-plane), 1020, 1088 (m) (β-aryl),
1142 (s) (300), 1180, 1190, 1235, 1290, 1315 (m) (300),
1377, 1458 and 1594 cm⁻¹.

(E)-1-(2-Pyridyl)-2-(p-tolylsulphonyl)ethene. - By
heating a mixture of 5.35 g. (0.025 mole) of p-tolylsulphonyl-
acetic acid, 2.66 g. (0.025 mole) of pyridine-2-aldehyde
and 0.6 ml. of benzylamine in 15 ml. of glacial acetic acid
under reflux for 100 minutes yielded 2.0 g. (30.9%) of
the compound. It was recrystallized thrice from cyclohexane
to give an analytical sample, fine long needles, m.p. 87-88°.

Anal. Calc. for C₁₄H₁₅NO₂S/2H₂O: C, 56.94; H, 5.80.
Found: C, 56.55; H, 5.91.

λ ethanol 262 nm (ε 520), 228 (17,000), 201 (13,340);

υ max Nujol 694, 750, 790, 810, 844, 946, 958 (s) (CH out-of-
plane), 1010, 1032, 1084 (s) (S-aryl), 1100, 1140 (s) (C=S),
1375, 1290 (s) (300), 1370, 1402, 1444, 1580 and 1660 (w)
(C=S) cm⁻¹.

(E)-1-(p-Acetamidophenyl)-2-(p-Chlorobenzensulphonyl)ethene. - A mixture of 5.86 g. (0.025 mole) of p-chloro-
benzensulphonylacetic acid, 4.08 g. (0.025 mole) of p-
acetamidobenzaldehyde and 0.5 ml. of benzylamine in 15 ml.
of glacial acetic acid was heated under reflux for 90 minutes.
The reaction mixture yielded 5.8 g. (69.0%) of the product
which on recrystallization thrice from aqueous acetone afforded an analytical sample, orange-red crystals, m.p. 206-208°.

Anal. Calcd. for C_{14}H_{14}ClNO_{5}: C, 57.24; H, 4.21.
Found: C, 56.99; H, 4.33.

λ_{max} ethanol 317 nm (ε 26,470), 235 (15,410), 203 (20,650);

λ_{max} Hujol 700, 736, 754, 762, 806, 825, 840, 867, 943,
978 (m) (ν out-of-plane), 1025, 1047, 1084 (s) (3-aryl),
1140 (s) (ν_{06}), 1150, 1177, 1263, 1290, 1310 (s) (ν_{08}),
1374, 1405, 1458, 1506, 1528, 1672 (m) (ν_{c=c}), 1694
and 3300 cm⁻¹.

(E)-1-(o-Bromophenyl)-3-(p-chlorobenzensulphonyl)-ethene.- The condensation was effected by refluxing a mixture of 5.66 g. (0.025 mole) of p-chlorobenzensulphonyl-acetic acid, 4.63 g. (0.025 mole) of o-bromobenzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid for 90 minutes. The reaction mixture yielded 5.4 g. (60.4%) of the product. Recrystallisation of the sulphone from methanol gave fine colourless needles melting at 140-150°.

Anal. Calcd. for C_{14}H_{14}ClNO_{5}: C, 47.01; H, 2.89.
Found: C, 46.82; H, 2.57.
\( \lambda_{\text{max}} \) ethanol 276 nm (< 17,820), 222 (13,310), 202 (17,360);

\( \lambda_{\text{max}} \) Nujol 660, 700, 756, 806, 870, 944, 983 (m) (C=C out-of-plane), 1018, 1078 (s), 1090 (s) (3-aryl), 1145 (s) (SO\(_2\)), 1180, 1200, 1242, 1280, 1316 (s) (SO\(_2\)), 1370, 1398, 1476, 1484, 1560, 1580, 1610, 1770 and 1895 cm\(^{-1}\).

\((E)-(p\text{-bromophenyl})-2-(p\text{-chlorobenzensulphonyl})\)-ethanone, p-Chlorobenzensulphonylacetic acid (4.69 g., 0.02 mole) was condensed with p-bromobenzaldehyde (3.70 g., 0.02 mole) in glacial acetic acid (17 ml.) in the presence of benzyleamine (0.5 ml.) by refluxing the solution for 90 minutes. The reaction mixture yielded 5.35 g. (74.9\%) of the sulphone. Two crystallisations from acetic acid afforded an analytical sample of the sulphone as fine colourless needles, m.p. 184-185°.

Anal. Calc. for C\(_{14}\)H\(_{10}\)BrClO\(_2\)S: C, 47.01; H, 2.82.
Found: C, 47.02; H, 2.83.

\( \lambda_{\text{max}} \) ethanol 285 nm (< 25,340), 220 (13,310), 202 (17,360);

\( \lambda_{\text{max}} \) Nujol 660, 700, 756, 806, 870, 944, 983 (m) (C=C out-of-plane), 1018, 1078 (s), 1090 (s) (3-aryl), 1145 (s) (SO\(_2\)), 1180, 1200, 1242, 1280, 1316 (s) (SO\(_2\)), 1370, 1398, 1476, 1484, 1560, 1580, 1610, 1770 and 1895 cm\(^{-1}\).
(E)-1-(m-Bromo-p-napthoxyphenyl)-2-(p-chlorobenzensulphonyl)ethene.- p-Chlorobenzensulphonylacetic acid (2.35 g., 0.01 mole) dissolved in 6 ml. of glacial acetic acid was treated with m-bromo-p-methoxybenzaldehyde (2.15 g., 0.01 mole) in the presence of 0.2 ml. of benzylamine and the solution was refluxed for 90 minutes. The reaction mixture yielded 2.4 g. (62.6%) of the sulphone which on recrystallization from 95° ethanol gave colourless puffy crystals melting at 149-150°.

Anal. Calc. for C_{18}H_{14}BrClO_{3}S: C, 46.46; H, 3.12.
Found: C, 46.40; H, 3.07.

\lambda_{\text{octanol}} \text{max} 311 \text{ nm} (\varepsilon 24,680), 203 (23,910),
230 (26,110), 202 (27,400); \gamma_{\text{Nujol}} \text{max} 682, 704, 755, 773,
817, 820, 850, 890, 915, 925, 992 (s) (CH out-of-plane), 1040,
1060, 1085 (m) (S-aryl), 1150 (s) (C=O), 1187, 1200, 1245,
1267, 1296, 1310 (s), 1320 (s) (C=O), 1380, 1398, 1464,
1502, 1600, 1614 and 1680 (v) (C=C) cm\(^{-1}\).

(E)-1-(o-Chlorophenyl)-2-(p-chlorobenzensulphonyl)-ethene.- Into 15 ml. of glacial acetic acid 4.69 g. (0.02 mole) of p-chlorobenzensulphonylacetic acid, 2.81 g. (0.02 mole) of o-chlorobenzaldehyde and 0.4 ml. of benzylamine were added; and the mixture was refluxed for 90 minutes. The product, isolated (5.50 g., 87.2%) from the reaction mixture, on recrystallization from methanol afforded an analytical
sample, fine long needle shaped crystals, m.p. 130.5-131.8°.

Anal. Calcd. for C_{14}H_{10}ClO_{5}: C, 53.70; H, 3.22;
Cl, 22.64. Found: C, 53.43; H, 3.17; Cl, 22.90.

λ_{max 276 nm} \ (\varepsilon \ 19,320), 226 (14,280),
203 (21,380); λ_{Nujol max} 676, 746, 756, 819, 828, 852,
962 \ (m) (C=Cl out-of-plane), 1014, 1040, 1085 \ (s) (C=Oaryl),
1144 \ (s) (C\equiv C), 1198, 1278, 1303, 1320 \ (s) (C\equiv C), 1375,
1458, 1576 and 1602 \ cm^{-1}.

(R)-1-(m-Chlorophenyl)-2-(p-chlorobenzensulphonyl)-
ethene.- By heating a mixture of 4.60 g. (0.02 mole) of
p-chlorobenzensulphonylacetic acid, 2.41 g. (0.07 mole) of
m-chlorobenzaldehyde and 0.4 ml. of benzylamine in 12 ml. of
acetic acid under reflux for 90 minutes gave 3.3 g.
(84.7%) of the sulphone. This material on recrystallization
from 95% ethanol yielded colourless long needles, m.p.
130-131°.

Anal. Calcd. for C_{14}H_{10}ClO_{5}: C, 53.70; H, 3.22;
Cl, 22.64. Found: C, 53.77; H, 3.21; Cl, 22.80.

λ_{max ethanol 275 nm} \ (\varepsilon \ 23,700), 205 (21,040);
λ_{Nujol max} 592, 700, 757, 790, 832, 840, 856, 899, 926,
1000 (s) (C\(^\text{N}\) out-of-plane), 1024, 1100 (s) (C=O),
1160 (s) (C=O), 1185, 1212, 1284, 1297, 1315 (s) (C=O),
1330, 1402, 1430, 1470, 1570, 1590, 1624 (m) (C=C) and
1907 cm\(^{-1}\).

(F)-1-(p-Chlorophenyl)-2-(p-chlorobenzensulphonyl)ethane. - A mixture of 3.86 g. (0.025 mole) of p-chloro-
benzene sulphonic acid and 3.51 g. (0.025 mole) of
p-chlorobenzaldehyde in 15 ml. of glacial acetic acid was
refluxed for 90 minutes in the presence of 0.5 ml. of
benzylamine. On working up, the reaction mixture yielded
fine colourless shining needles (4.4 g., 85\%). Further
recrystallization of the material twice from 95\% ethanol
afforded an analytical sample melting at 167-167.5\°C.
(literature\(^{66}\) m.p. 163-164\°C, yield 30.2\%).

\(\lambda_{\text{max}}\) ethanol
285 nm (\(\epsilon 20,830\)), 219 (18,660),
203 (23,600); \(\lambda_{\text{max}}\) Nujol
670, 696, 720, 745, 799, 826, 860,
975 (m) (C\(^\text{N}\) out-of-plane), 1004, 1078 (s) (C=O), 1135 (s)
(C=O), 1160, 1196, 1272, 1300 (s) (C=O), 1366, 1447, 1568
and 1600 cm\(^{-1}\).

(F)-1-(2,4-Dichlorophenyl)-2-(p-chlorobenzene-
sulphonyl)ethane. - p-Chlorobenzene sulphonyl acetic acid
(4.69 g., 0.07 mole) dissolved in 12 ml. of glacial acetic
acid was treated with 2,4-dichlorobenzaldehyde (3.56 g., 0.02 mole) in the presence of benzylamine (0.4 ml.) and was refluxed for 100 minutes. The reaction mixture yielded 5.5 g. (70.3%) of the sulphone which on recrystallization from 95° ethanol gave fine needles, m.p. 153-154°.

Anal. Caled. for C₁₄H₉Cl₂O₃S: C, 46.3%; H, 2.61.

Found: C, 46.43; H, 2.65.

λ max ethanol 282 nm (ε 27,800), 228 (20,970), 204 (26,020); Λ max Nujol 662, 700, 742, 764, 805, 829, 846, 868, 960, 979 (s) (C= out-of-plane), 1013, 1053, 1094 (s)
(C-aryl), 1150 (s) (C=O), 1185, 1201, 1284, 1317 (s) (S=O),
1323 (s), 1382, 1466, 1582 and 1619 cm⁻¹.

(E)-1-(3,4-Dichlorophenyl)-2-(p-chlorobenzensulphonyl)ethene.- The condensation was accomplished by refluxing a mixture of 4.69 g. (0.02 mole) of p-chlorobenzensulphonylecetic acid and 3.50 g. (0.02 mole) of 3,4-dichlorobenzaldehyde in 17 ml. ofacial acetic acid in the presence of 0.4 ml. of benzylamine for 100 minutes. The reaction mixture yielded 4.0 g. (57.6%) of the product which on recrystallization twice from 95° ethanol afforded an analytical sample, colourless needles, m.p. 164-165°.

Found: C, 43.27; H, 2.50.

λ_{\text{ethanol max}} 203 (ε 26,260), 230 (19,050), 204 (18,990);

λ_{\text{Nujol max}} 660, 705, 746, 782, 820, 840, 870, 895, 950, 975 (s) (CN out-of-plane), 1006, 1025, 1080 (s) (s-aryl), 1130 (s) (CO), 1188, 1210, 1377, 1396 (s) (CO), 1310, 1380, 1463, 1542, 1568, 1600, 1638 and 1660 (w) (C=O) cm\(^{-1}\).

(E)-1-(p-Dimethylaninophenyl)-2-(n-chlorobenzensulphonyl)ethene.- Heating under reflux a mixture of 5.96 g. (0.025 mole) of p-chlorobenzensulphonylacetic acid, 3.73 g. (0.025 mole) of p-dimethylaninobenzaldehyde and 0.4 ml. of benzylamine in 15 ml. of glacial acetic acid for 100 minutes, yielded 6.5 g. (81.0\%) of the sulphone. This compound on recrystallization thrice from aqueous acetic acid gave an analytical sample, light orange coloured crystals, m.p. 158°-159° (literature\(^{66}\) 162°-164°, yield 1.8\%).

λ_{\text{ethanol max}} 240 nm (ε 25,400), 203 (25,230);

λ_{\text{Nujol max}} 718, 724, 756, 790, 819, 839, 850, 863, 932, 980 (m) (CN out-of-plane), 1017, 1070, 1080, 1090 (s) (s-aryl), 1112, 1142 (s) (C=O), 1154, 1205, 1238, 1276, 1306, 1316 (s) (C=O), 1330, 1376, 1410, 1460, 1526, 1547, 1573, 1598 and 1665 (w) (C=O) cm\(^{-1}\).
(E)-1-(2,3-Dimethoxyphenyl)-2-(p-chlorobenzensulphonyl)ethene.— Into 12 ml. of glacial acetic acid, 4.65 g. (0.02 mole) of p-chlorobenzensulphonylacetic acid, 3.32 g. (0.02 mole) of 2,3-dimethoxybenzaldehyde and 0.4 ml. of benzylamine were added; and refluxed for 100 minutes. The reaction mixture on working up, yielded 5.45 g. (80.6%) of the sulphone. Recrystallization of this product from 95% ethanol four times, afforded fine needle shaped crystals melting at 125-126°.

Anal. Calcd. for C_{15}H_{15}ClO_{3}: C, 56.72; N, 4.46.
Found: C, 56.73; N, 4.41.

$\lambda_{\text{max}}$ ethanol 295 nm ($\varepsilon$ 23,810), 219 (24,340), 203 (25,370). $\nu_{\text{max}}$ Nujol 725, 765, 782, 836, 850, 890, 935, 986, 1004 (s) (CH out of plane), 1025, 1076, 1094 (s) (S-aryl), 1130 (s) ($v_2$), 1173, 1180, 1195, 1211, 1230, 1277 (s) 1295 (s) ($v_1$), 1382, 1400, 1425, 1450, 1470, 1576, 1614 and 1670 (w) ($v_1$) cm$^{-1}$.

(E)-1-(2,3-Dimethoxyphenyl)-2-(p-chlorobenzensulphonyl)ethene.— By refluxing a mixture of 5.06 g. (0.025 mole) of p-chlorobenzensulphonylacetic acid, 4.16 g. (0.025 mole) of 2,3-dimethoxybenzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid for 100 minutes yielded 3.75 g. (44.3%) of the sulphone. Three crystallizations from
isopropanol afforded pure sulphone as colourless lustrous plates, m.p. 114-115°

Anal. Calc. for C_{18}H_{18}O_{10}: C, 56.72; H, 4.46.
Found: C, 57.09; H, 4.40.

\(\lambda_{\text{max}}\) ethanol 279 nm (ε 17,489), 236 (13,970), 203 (17,440); \(\lambda_{\text{max}}\) Nujol 860, 707, 735, 750, 772, 810, 823, 841, 857, 868, 958, 1000 (m) (c=c out-of-plane), 1020, 1035, 1053, 1065 (s) (c=c), 1110, 1148 (s) (c=c), 1184, 1210, 1246, 1287, 1300 (s) (c=c), 1330, 1346, 1380, 1400, 1445, 1467, 1506, 1582, 1603, 1664 (s) (c=c), 1690, 1720 and 3100 cm\(^{-1}\).

(E)-1-(3,4-dimethoxyphenyl)-2-(p-chlorobenzensulphonyl)ethene. - p-Chlorobenzensulphonylacetic acid (4.69 g., 0.02 mole) was condensed with 3,4-dimethoxybenzaldehyde (3.32 g., 0.02 mole) in the presence of benzylamine (0.4 ml.) in glacial acetic acid (12 ml.) by heating under reflux for 100 minutes. The reaction mixture on working up, yielded 3.10 g. (45.9%) of the sulphone. Two recrystallizations of the product from isopropanol afforded an analytical sample, colourless lustrous flakes, m.p. 147-147.5° (literature 144-146°, yield 10.2%).
(E)-1-(c-Ethoxyphenyl)-2-(p-chlorobenzene sulphonyl)-ethene. - The condensation was accomplished by refluxing a mixture of 3.86 g. (0.025 mole) of p-chlorobenzene sulphonyl-acetic acid, 3.76 g. (0.025 mole) of c-ethoxybenzaldehyde and 0.5 ml. of benzylamine in 15 ml. of glacial acetic acid for 100 minutes. The reaction mixture yielded 3.4 g. (42.1%) of the sulphone which on recrystallization thrice from isopropanol gave fine colourless needles melting at 110-111°.

Anal. Calcd. for C_{16}H_{15}ClO_{3}: C, 59.53; H, 4.68.
Found: C, 59.18; H, 4.58.

\[ \lambda_{\text{ethanol max}} 328 \text{ nm (e 8,340), 277 (18,050), 232 (17,330), 203 (22,980); } \nu_{\text{Nujol max}} 700, 722, 750, 775, 820, 880, 882, 948, 958 \text{ (m) (CF out-of-plane), 1015, 1040, 1085 (s) (c-aryl), 1138 (s) (CO), 1170, 1180, 1252, 1282, 1300 (s) } \]
1305 (s) (C=O), 1340, 1355, 1442, 1470, 1490, 1564, 1600 and 1680 (w) (C=C) cm\(^{-1}\).

\((E)\)-1-(o-Fluorophenyl)-2-(p-chlorobenzensulphonyl)ethene.— p-Chlorobenzensulphonylacetic acid (3.82 g., 0.015 mole) was condensed with o-fluorobenzaldehyde (1.86 g., 0.015 mole) in glacial acetic acid (10 ml.) in the presence of catalytic amounts of benzylamine (0.5 ml.) by refluxing the solution for 90 minutes. An yellow syrupy liquid obtained after working up, yielded a solid product (4.1 g., 92.3\%) on treatment with few ml. of isopropanol. It was re-crystallized from 95% ethanol, m.p. 103-104\(^\circ\).

Anal. Calcd. for C\(_{14}\)H\(_{10}\)ClO\(_3\)S: C, 56.66; H, 3.39; Cl, 11.95. Found: C, 56.90; H, 3.45; Cl, 12.10.

\(\lambda\) max ethanol 272 nm (\(\varepsilon\) 26,570), 235 (12,040), 203 (24,290);

\(\lambda\) max Nujol 697, 704, 740, 782, 772, 812, 822, 838, 855, 960 (s) (CH out-of-plane), 1006, 1028, 1080 (s) (\(\pi\)-aryl), 1142 (s) (SO\(_2\)), 1219, 1230, 1275, 1303 (s) (SO\(_2\)), 1363, 1382, 1445, 1470, 1564 and 1606 cm\(^{-1}\).

\((E)\)-1-(p-Fluorophenyl)-2-(p-chlorobenzensulphonyl)ethene.— Heating a mixture of 3.52 g. (0.015 mole) of p-chlorobenzensulphonylacetic acid, 1.86 g. (0.015 mole) of p-fluorobenzaldehyde and 0.2 ml. of benzylamine in 10 ml,
of glacial acetic acid under reflux for 20 minutes yielded
2.3 g. (51.8%) of colourless needles. This material on
recrystallisation thrice from methanol afforded an analytical
sample, m.p. 110-111.5°.

Anal. Calcd. for C_{14}H_{12}O_2: C, 56.6%; H, 3.3%.
Found: C, 56.7%; H, 3.5%.

\( \lambda_{\text{ethanol max}} \) 270 nm (\( \varepsilon = 23,000 \)), 236 (11,770), 224 (12,000),
203 (20,700); \( \lambda_{\text{max}} \) 600, 740, 762, 780, 810, 834, 890,
930, 958, 1008 (m) (\( \delta \) out-of-plane), 1078 (s) (\( \sigma^{-}\)-aryl),
1132 (s) (\( \sigma_{b} \)), 1167, 1220, 1268, 1285, 1300, 1307 (s) (CO\(_2\)),
1365, 1400, 1448, 1490, 1580, 1603 and 1640 (v) (C=O) cm\(^{-1}\).

(E)-1-(p-Isopropylphenyl)-2-(p-chlorobenzensulphonyl)-
ethene.- The condensation was effected by refluxing a mixture
of 5.86 g. (0.025 mole) of p-chlorobenzensulphonylacetic
acid, 3.71 g. (0.025 mole) of p-isopropylbenzaldehyde in 15 ml.
of glacial acetic acid in the presence of 0.5 ml. of benzyl-
amine for 100 minutes. The reaction mixture yielded 3.4 g.
(47.4%) of the sulphone which on recrystallisation from 95°
ethanol gave colourless lustrous plates melting at 77-77.5°.

Anal. Calcd. for C_{14}Hi4O_2S: C, 63.66; H, 5.34.
Found: C, 63.54; H, 5.32.

\( \lambda_{\text{ethanol max}} \) 289 nm (\( \varepsilon = 27,130 \)), 226 (15,360), 203 (21,280);
\( \nu_{\text{max}} \) 754, 820, 846, 862, 981 (v) (C-H out-of-plane),
1000, 1016, 1057, 1095 (s) (s-aryl), 1148 (s) (C-O), 1182,
1280, 1315 (s) (C=O), 1378, 1419, 1458, 1504, 1558, 1576
and 1602 cm\(^{-1}\).

\((E)-1-(p\text{-Methylphenyl})-2-(p\text{-chlorobenzensulphonyl})\)-
ethane = p-Chlorobenzensulphonylacetic acid (4.6 g, 0.02 mole) dissolved in
acetic acid (15 ml.) was treated with p-methylbenzaldehyde (2.40 g, 0.02 mole) in
the presence of benzylamine (0.4 ml.) and was refluxed for
90 minutes. The reaction mixture yielded 4.6 g. (78.8\%) of
the product. The sulphone on recrystallization thrice
from methanol afforded an analytical sample, colourless fine
needles, m.p. 135.5-136\.

Anal. Calc. for \( C_{16}H_{13}ClO_3 \): C, 61.55; H, 4.47.
Found: C, 61.47; H, 4.49.

\( \nu_{\text{max}} \) ethanol 292 nm (e 21,380), 226 (14,370), 204 (25,720);

\( \nu_{\text{max}} \) \text{Nujol} 700, 750, 769, 811, 840, 860, 873, 950, 980 (m)
(C-H out-of-plane), 1010, 1038, 1080 (s) (s-aryl), 1109,
1137 (s) (C=O), 1170, 1212, 1274, 1304 (s) (C=O), 1375, 1390,
1453, 1570, 1593 and 1610 cm\(^{-1}\).

\((E)-1-(p\text{-Methylphenyl})-2-(p\text{-chlorobenzensulphonyl})\)ethane =
Refluxing a mixture of 5.86 g. (0.025 mole) of p-chloro-
benzenesulphonylacetic acid, 2.0 g. (0.025 mole) of
p-methylbenzaldehyde and 0.6 ml. of benzylamine in 12 ml.
of glacial acetic acid for 90 minutes yielded 4.7 g. (67.6%) of
the sulphone. The product on repeated crystallizations
from 95% ethanol gave colourless leaflets, m.p. 124-125°.

Anal. Calc. for C₁₆H₁₅ClO₃N: C, 61.5%; N, 4.47.
Found: C, 61.61; N, 4.59.

λ<sub>max</sub> ethanol 283 nm (ε 24,960), 227 (15,970),
203 (20,760); \( \lambda_{Nujol} \) max 698, 740, 758, 765, 805, 827, 860,
974 (m) (CN out-of-plane), 1007, 1035, 1079 (s) (C-aryl),
1110, 1138 (s) (C=C), 1178, 1198, 1267, 1303 (m) (C=C),
1367, 1402, 1430, 1503, 1567 and 1598 cm⁻¹.

(E)-1-(p-Methoxyphenyl)-2-(p-chlorobenzenesulphonyl)-
ethene.- A mixture of 3.86 g. (0.025 mole) of p-chloro-
benzenesulphonylacetic acid 3.40 g. (0.025 mole) of p-methoxy-
benzaldehyde and 0.6 ml. of benzylamine in 15 ml. of glacial
acetic acid was heated under reflux for 100 minutes. The
reaction mixture after being kept in the refrigerator for
a day gave colourless shining flakes (1.8 g., m.p. 138-140°).
The mother liquor yielded an additional 3.0 g. of the sulphone
and the total yield was 4.8 g. (62.2%). Recrystallization of
the product from 95% ethanol gave an analytical sample, m.p.
144-145° (lit. 142.5-143.5°; yield 19%).
ethanol  
max  310 nm (ε 28,980), 233 (27,710), 203 (26,360); ν<sub>ν</sub><sub><sub>Nujol</sub>max</sub> 692, 712, 742, 754, 802, 816, 832, 869, 948, 974 (s) (CH out-of-plane), 1010, 1022, 1074 (s) (ν<sub>γ</sub>-aryl), 1109, 1132 (s) (ν<sub>ν</sub><sub>0</sub><sub>0</sub>), 1170 (s), 1198, 1250, 1272, 1287 (s), 1304 (s) (ν<sub>ν</sub><sub>0</sub><sub>0</sub>), 1320 (s), 1372, 1387, 1412, 1432, 1452, 1504, 1567, and 1590 cm<sup>-1</sup>.

(E)-1-(o-Nitrophenyl)-<sup>ω</sup>-(<sup>ω</sup>-Chlorobenzensulphonyl)ethane.

p-Chlorobenzensulphonylacetoc acid (4.66 g., 0.02 mole) was condensed with o-nitrobenzaldehyde (3.02 g., 0.02 mole) in glacial acetic acid (12 ml.) in the presence of benzylamine (0.4 ml.) and the reaction mixture was heated under reflux for 90 minutes. The sulphone obtained (5.0 g., 77.4%), on recrystallisation from acetic acid afforded an analytical sample, shining yellow leaflets m.p. 174-175°.

Anal. Calc. for C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>N: C, 51.94; H, 3.11; Cl, 10.95. Found: C, 52.11; H, 3.11; Cl, 10.90.

ν<sub>ethanol</sub> 247 nm (ε 19,950), 203 (22,410); ν<sub>Nujol</sub>max 672, 700, 740, 759, 798, 810, 824, 838, 865, 893, 980 (s) (CH out-of-plane), 1016, 1083 (s) (ν<sub>γ</sub>-aryl), 1115, 1144 (s) (ν<sub>ν</sub><sub>0</sub><sub>0</sub>), 1176, 1197, 1238, 1282, 1300 (s), 1320 (s) (ν<sub>ν</sub><sub>0</sub><sub>0</sub>), 1341 (s), 1380, 1396, 1440, 1467, 1522, 1574, 1601 and 1623 (w) (C=O) cm<sup>-1</sup>. 
(R)-1-(p-Nitrophenyl)-2-(p-chlorobenzensulphonyl)ethene.

The condensation was accomplished by refluxing a mixture of 4.69 g. (0.02 mole) of p-chlorobenzensulphonyl acetic acid, 3.02 g. (0.02 mole) of p-nitrobenzaldehyde and 0.4 ml. of benzylamine in 10 ml. of glacial acetic acid for 90 minutes.

On working up, the reaction mixture afforded 5.1 g. (80.5%) of the sulphone which on recrystallization thrice from 95% ethanol gave light yellow shining flakes melting at 141-142°.

Anal. Calcd. for C_{14}H_{10}CINO_{4}: C, 51.94; H, 3.11;
Cl, 10.95. Found: C, 52.14; H, 3.07; Cl, 10.80.

$\lambda_{\text{max}}^{\text{ethanol}}$: 265 nm (e 35,560), 233 (19,470), 202 (23,940);

$\nu_{\text{max}}^{\text{Nujol}}$: 670, 700, 727, 755, 800, 808, 820, 840, 843, 902,

937, 982 (s) (C-H out-of-plane), 1015, 1024 (s) (S=aryl),

1146 (s) (SO$_2$), 1174, 1200, 1276 (s), 1301 (s) (SO$_2$), 1319 (s),

1350, 1373, 1392, 1462, 1528, 1560, 1576, 1615 (m) and

1647 (w) (C=O) cm$^{-1}$.

(R)-1-(p-Nitrophenyl)-2-(p-chlorobenzensulphonyl)ethene.

Heating a mixture of 5.86 g. (0.025 mole) of p-chlorobenzensulphonyl acetic acid and 1.78 g. (0.025 mole) of p-nitrobenzaldehyde in 15 ml. of glacial acetic acid for 90 minutes in the presence of 0.5 ml. of benzylamine, yielded 6.2 g. (76.7%) of the product. Recrystallization of this
material from acetic acid twice afforded an analytical sample, light yellow crystals, m.p. 197-198°.

Anal. Calc. for C_{14}H_{16}O_{4}: C, 51.04; H, 3.11; Cl, 10.98. Found: C, 51.69; H, 3.17; Cl, 11.20.

\lambda_{\text{max}} \text{ ethanol} 204 \text{ nm (e 16,780), 225 (14,970), 203 (27,490);}

\lambda_{\text{max}} \text{ Nujol} 660, 688, 700, 732, 746, 803, 819, 832, 840, 858, 958, 1066 (s) (CC out-of-plane), 1040, 1083 (s) (C=O), 1120, 1140 (s) (C=O), 1292, 1275, 1304 (s), 1316 (s), 1338 (s) (SO$_2$), 1388, 1465, 1514, 1570 and 1596 (m) cm$^{-1}$.

(E)-1-(1-Naphthyl)-2-(p-chlorobenzenesulphonyl)ethene

Three grams (0.013 mole) of p-chlorobenzenesulphonylacetic acid, 2.0 g. (0.015 mole) of 1-naphthaldehyde and 0.3 ml. of benzylamine were taken in 9 ml. of glacial acetic acid and the mixture was refluxed for 100 minutes. The reaction mixture on working up yielded 2.7 g. (63.4%) of the sulphones. The product on recrystallisation from 95% ethanol afforded light cream coloured leaflets, m.p. 136.5-137°.

Anal. Calc. for C_{18}H_{18}Cl_{10}O: C, 65.79; H, 3.98; Cl, 10.78. Found: C, 65.59; H, 3.95; Cl, 10.80.

\lambda_{\text{max}} \text{ ethanol} 320 \text{ nm (e 7,474), 222 (47,760), 204 (37,670);}

\lambda_{\text{max}} \text{ Nujol} 660, 708, 743, 772, 782, 810, 835, 844, 865, 880.
A mixture of 3.52 g. (0.015 mole) of p-chlorobenzensulphonyl-
acetic acid, 2.34 g. (0.012 mole) of 9-anthraldehyde and
0.3 ml. of benzylamine in 9 ml. of glacial acetic acid was
referred for 100 minutes. The reaction mixture yielded
3.0 g. (61.5%) of the product which on recrystallization
three times from acetic acid afforded an analytical sample, m.p.
182-183°.

Anal. Calcd. for C_{16}H_{13}ClO_{3}S: C, 65.75; H, 3.95.
Found: C, 65.81; H, 4.02.

\begin{align*}
\text{ethanol} & \quad \text{max} \\
& \quad \lambda_{\text{max}} \quad 368 \text{ nm} (\epsilon \text{27,110}), \quad 271 (35,300), \\
& \quad 232 (30,740), \quad 203 (25,360); \quad \lambda_{\text{max}}^{\text{Nujol}} \quad 705, \quad 745, \quad 758, \quad 764, \\
& \quad 690, \quad 637, \quad 560, \quad 573, \quad 580, \quad 617, \quad 653, \quad 760, \quad 974, \quad 990 (s) (\text{C} \quad \text{out-of-plane}), \quad 1019, \quad 1097 (s) (\text{S-aryl}), \quad 1120, \quad 1160 (s) (\text{SO}_{2}), \\
& \quad 1182, \quad 1263, \quad 1293, \quad 1320 (s) (\text{CO}), \quad 1360, \quad 1374, \quad 1380, \quad 1400, \\
& \quad 1466, \quad 1512, \quad 1580, \quad 1594, \quad 1615, \quad 1660 (w) (\text{C} =\text{O}) \text{ and } 1700 \text{ cm}^{-1}.
\end{align*}

\[(E)-1-(9-Aanthryl)-2-(p-chlorobenzensulphonyl)ethane.\]

To 12 ml. of glacial acetic acid, 4.69 g. (0.02 mole) of
p-chlorobenzensulphonylacetic acid, 4.13 g. (0.02 mole) of
9-anthraldehyde and 0.4 ml. of benzylamine were added and the
whole mixture was refluxed for 120 minutes. On working up the reaction mixture 6.20 g. (87.0%) of the sulphone was obtained. Recrystallization of the compound from isopropanol thrice yielded yellow coloured crystals melting at 184–185°.

Found: C, 69.48; H, 3.91.

λ max ethanol 285 nm (ε 1,11,000), 221 (ε 27,040),
203 (ε 37,070); λ max Nujol 709, 724, 750, 776, 795, 825, 840, 855, 872, 889, 927, 948, 982 (m) (CH out-of-plane), 1010, 1082 (s) (S-aryl), 1110, 1135 (s) (SO_2), 1174, 1195, 1255, 1274, 1290, 1309 (s) (SO_2), 1370, 1390, 1435, 1452, 1510, 1570, 1605, 1640 and 1670 (w) (C=O) cm⁻¹.

(E)-1-(1-Pyrene)-2-(p-chlorobenzensulphonyl)ethene,

p-chlorobenzensulphonylacetic acid (2.35 g., 0.01 mole) dissolved in glacial acetic acid (6 ml.) was treated with 1-pyrenecarboxaldehyde (2.30 g., 0.01 mole) in the presence of benzylamine (0.2 ml.) and was refluxed for 120 minutes. The reaction mixture yielded 3.4 g. (84.4%) of the product which on recrystallization from acetic acid four times afforded an analytical sample, light yellow crystals, m.p. 204–205°.

Found: C, 70.98; H, 3.57.
\[ \lambda_{\text{max}} \text{ ethanol} = 280 \text{ nm} (\epsilon 27,580), 235 (50,240), 203 (38,900); \]

\[ \lambda_{\text{max}} \text{ Nujol} = 675, 705, 720, 746, 770, 782, 812, 828, 840, 854, \]

885, 944, 959 (m) (CH out-of-plane), 1007, 1080 (s) (\( \pi-\text{aryl} \)),

1136 (s) (SO\(_2\)), 1167, 1182, 1220, 1240, 1273, 1302 (s) (\( \pi-\text{O} \)),

1370, 1385, 1408, 1432, 1570 and 1584 cm\(^{-1}\).

\((\text{E})-1-(2-\text{Thienyl}-2-\text{-(p-chlorobenzensulphonyl)})\text{ethane} \)

Into 15 ml. of warm glacial acetic acid, 5.66 g., (0.028 mole) of p-chlorobenzensulphonylacetic acid, 2.98 g.,

(0.025 mole) of thiophene-\( \alpha \)-aldehyde and 0.5 ml. of benzylamine were added; and the mixture was refluxed for 100 minutes.

The reaction mixture on working up yielded 6.4 g. (90.1\%)

of the product. Recrystallization of the sulphone from acetic acid afforded an analytical sample as light pink coloured crystals, m.p. 134.5-135.5\(^\circ\) (literature 3 135-136.5\(^\circ\), yield 19\%).

\[ \lambda_{\text{max}} \text{ ethanol} = 311 \text{ nm} (\epsilon 20,790), 241 (10,660), 202 (15,990); \]

\[ \lambda_{\text{max}} \text{ Nujol} = 720, 754, 787, 798, 818, 832, 860, 962 (m) (\text{CH}

\text{ out-of-plane}), 1012, 1040, 1080 (s) (\( \pi-\text{aryl} \)), 1140 (s) (SO\(_2\)),

1160, 1218, 1272, 1310 (s) (SO\(_2\)), 1375, 1418, 1457, 1570 and 1592 cm\(^{-1}\).
REFERENCES

7. J. Tröger and A. Prechnow, ibid., (2) 72, 123 (1908).


42. A.A. Oswald and K. Griesbaum, Radical Additions of Thiols to Dieneins and Acetylenes, in N. Kharasch and
pp. 233-256.
43. A.A. Oswald, K. Griesbaum, R.E. Hudson, Jr., and
44. F. Montanari, Cazz. Chim. ital., 86, 406, 420, 428, 735,
747 (1956).
45. N. Kharasch and G.N. Viannois, J. Org. Chem., 29,
1190 (1964), and preceding papers.
47. V. Calo, G. Scorrano, and G. Modena, J. Org. Chem., 34,
2020 (1969), and preceding papers.
C, 1339, 1344 (1968).
49. R.G. Fairley, The stereochemistry of Electrophilic
Additions to Olefins and Acetylenes, in R.L. Eliesl
and N.I. Allinger, ed., "Topics in Stereochemistry,
50. A. Ponzani, G. Modena, and G. Scorrano, C.A., 68, 16447a
(1966).


69. T.J. Cran, ibid., 74, 3028 (1952).


74. F.L. Southwick and T.J. Shores, ibid., 72, 3028 (1950).

75. E.E. Lutz and C.R. Peaver, ibid., 72, 3028 (1950).


121. W.F. Truce and M.E. Poudakian, ibid., 78, 2748 (1956).


135. Gabriel, Rec., 14, 634 (1881).