

## Acyloxyoxosulphonium Intermediates in the Formation of Sulphones from Sulphoxides

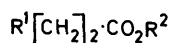
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Sulphones are the main product of the reaction of sulphoxides with (dichloroiodo)benzene in pyridine in the presence of carboxy-groups. Evidence is presented for the formation of acyloxyoxosulphonium intermediates, which may derive from inter- or intra-molecular processes.

DURST<sup>1,2</sup> has shown that the reaction of sulphuryl chloride with sulphoxides containing functions capable of neighbouring group participation, such as carboxy- or hydroxy-groups, leads to the formation of sulphones instead of  $\alpha$ -chloro-sulphoxides, which are the usual product with this<sup>3</sup> and with other chlorinating agents.<sup>4</sup> We have found that the course of the reaction of sulphoxides with (dichloroiodo)benzene (I) in pyridine may be affected by carboxy-groups not only intra-molecularly but also through an intermolecular process.

### RESULTS

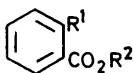
Reaction of 3-phenylsulphinylpropionic acid (II) and of 2-methylsulphinylbenzoic acid (III) with (I) affords the corresponding sulphones (IV) and (V). The  $\alpha$ -halogeno-sulphoxide (VII) is the only product of reaction of methyl 2-methylsulphinylbenzoate (VI) in the absence of water. Chlorination of optically active (+)-(VI) in the presence of silver ions<sup>4</sup> gives methyl (-)-2-chloromethylsulphinylbenzoate (VII); in the absence of Ag<sup>+</sup>, racemic material is obtained.†



(II) R<sup>1</sup> = Ph·SO, R<sup>2</sup> = H

(IV) R<sup>1</sup> = Ph·SO<sub>2</sub>, R<sup>2</sup> = H

(VIII) R<sup>1</sup> = Ph·SO, R<sup>2</sup> = Me

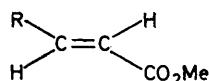


(III) R<sup>1</sup> = SO·Me, R<sup>2</sup> = H

(V) R<sup>1</sup> = SO<sub>2</sub>Me, R<sup>2</sup> = H

(VI) R<sup>1</sup> = SO·Me, R<sup>2</sup> = Me

(VII) R<sup>1</sup> = SO·CH<sub>2</sub>Cl, R<sup>2</sup> = Me



(X) R = Ph·SO

(XI) R = Ph·SO<sub>2</sub>



(XII) R<sup>1</sup> = SO·Et, R<sup>2</sup> = H

(XIII) R<sup>1</sup> = SO<sub>2</sub>Et, R<sup>2</sup> = H

(XIV) R<sup>1</sup> = SO·CHCl·Me, R<sup>2</sup> = H

(XV) R<sup>1</sup> = SO·Et, R<sup>2</sup> = Me

(XVI) R<sup>1</sup> = SO·CHCl·Me, R<sup>2</sup> = Me

(XVII) R<sup>1</sup> = SO<sub>2</sub>Et, R<sup>2</sup> = Me

(XVIII) R<sup>1</sup> = SO·CHBr·Me, R<sup>2</sup> = Me

(XIX) R<sup>1</sup> = SO<sub>2</sub>CHBr·Me, R<sup>2</sup> = Me

Chlorination of  $\beta$ -methoxycarbonyl ethyl phenyl sulphoxide (VIII) is complicated by the ready dehydrohalogenation of the initially formed  $\alpha$ -chloro-sulphoxide (IX), which cannot be isolated. The crude reaction product is a mixture of (IX) and of methyl *trans*-2-phenylsulphinyl-

acrylate (X) in a ratio of *ca.* 4 : 1; on standing or by column chromatography it is fully transformed into (X). Oxidation of the mixture leads to methyl *trans*-2-phenylsulphonylacrylate (XI). Chlorination of optically active (VIII) affords practically inactive material (see Experimental section).

When 3-ethylsulphinylbenzoic acid (XII) is treated with (I), the sulphone (XIII) is formed together with the  $\alpha$ -chloro-sulphoxide (XIV) in a ratio 3 : 1 or 1 : 3, depending on the presence or absence of water. Methyl 3-ethylsulphinylbenzoate (XV) gives, in the absence of water, the  $\alpha$ -chloro-sulphoxide (XVI), and in the presence of water the sulphone (XVII) (20%) is formed together with (XVI).

$\alpha$ -Chlorination of methyl 3-ethylsulphinylbenzoate (XV) with (I) can in principle lead to mixtures of diastereoisomeric chlorosulphoxides. However, as has already been found for a large number of substrates,<sup>4</sup> the reaction is highly stereospecific. One of the two possible diastereoisomers, (XVIa), predominates over the other, (XVIb) (ratio *ca.* 95 : 5), as shown by comparison of the <sup>1</sup>H n.m.r. spectrum of the crude mixture with those of (XVIa and b). Diastereoisomerically pure (XVIb) is obtained by inversion of the sulphanyl group of (XVIa) (see Experimental section).

When optically active (XV) [ $\alpha$ ]<sub>D</sub><sup>25</sup> + 176° (CHCl<sub>3</sub>), is used, the optical purity of (XVI) depends on the reaction conditions. Since the diastereoisomeric ratio remains constant, the different optical activity must be due to a different ratio of enantiomers. In the absence of silver nitrate, (XVI) is practically racemic, but in the presence of silver ions, the chloro-sulphoxide obtained has [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 120° (CHCl<sub>3</sub>).

Similar behaviour is observed in the  $\alpha$ -bromination of (XV) with bromine and silver nitrate, one of the two diastereoisomers (XVIIIa and b) being preferentially formed (diastereoisomeric ratio  $\geq 9 : 1$ ).

Only the major component (XVIIIa), [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 120° (CHCl<sub>3</sub>), can be isolated from the mixture. Oxidation of (-)-(XVIIIa) gives the corresponding sulphone (XIX), [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 1·8° (CHCl<sub>3</sub>). Reduction of (-)-(XVIIIa) affords (-)-(XV), [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 155° (CHCl<sub>3</sub>), 88% optically pure. Since the last reaction does not affect the sulphanyl group, this indicates that bromination of (XV) to (XVIIIa) in the presence of Ag<sup>+</sup> occurs with inversion of chirality at sulphur.

On the basis of the c.d. curves, the same absolute configuration at sulphur can be assigned to the chloro-sulphoxide (-)-(XVIa) and to the bromo-sulphoxide (-)-(XVIIIa), so that chlorination in the presence of silver nitrate also occurs with inversion of chirality at sulphur.

To see if, and to what extent, the behaviour of sulph-

<sup>3</sup> K. C. Tin and T. Durst, *Tetrahedron Letters*, 1970, 4643.

<sup>4</sup> P. Calzavara, M. Cinquini, S. Colonna, R. Fornasier, and F. Montanari, *J. Amer. Chem. Soc.*, 1973, **95**, 7431.

<sup>5</sup> (a) K. Mislow, *Rec. Chem. Progr.*, 1967, **28**, 217; (b) D. Landini, G. Modena, F. Montanari, and G. Scorrano, *J. Amer. Chem. Soc.*, 1970, **92**, 7168, and references therein.

† This is probably due to a chloride ion catalysed racemization;<sup>5</sup> the recovered sulphoxide (VI) is also racemic.

<sup>1</sup> T. Durst, K. C. Tin, and M. J. V. Marcil, *Canad. J. Chem.*, 1973, **51**, 1704.

<sup>2</sup> T. Durst and K. C. Tin, *Canad. J. Chem.*, 1971, **49**, 2374.

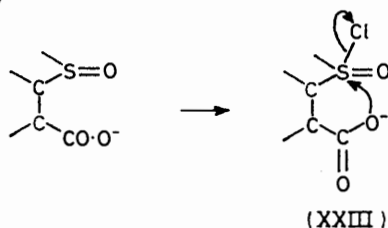
oxides (II), (III), and (XII) depends on the presence of the carboxy-group, ethyl phenyl sulphoxide (XX) was treated with (dichloriodo)benzene in pyridine in the presence and absence of benzoic acid and water.  $\alpha$ -Chloroethyl phenyl sulphoxide (XXI)\* and ethyl phenyl sulphone (XXII) were obtained in variable ratios, depending on the reaction conditions (see the Table).

Reaction of ethyl phenyl sulphoxide with (I) in pyridine

Ph-SO-Et (mol)	PhCO <sub>2</sub> H (mol)	H <sub>2</sub> O (mol)	Ratio (XXI): (XXII)
1			> 95 : 5
1		10	90 : 10
1	3		50 : 50
1	3	10	30 : 70

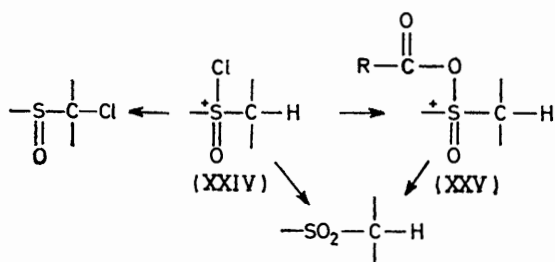
#### DISCUSSION

Formation of the sulphones (IV) and (V) from 3-phenylsulphinylpropionic acid (II) and 2-methylsulphinylbenzoic acid (III) by reaction with PhICl<sub>2</sub> indicates that a neighbouring carboxy-group prevents  $\alpha$ -chlorination, as previously found by Durst with SO<sub>2</sub>Cl<sub>2</sub>,<sup>1,2</sup> probably by nucleophilic attack at sulphur in a chloro-oxosulphonium salt intermediate (XXIII) (Scheme 1).



SCHEME 1

When the reaction of sulphoxides with (I) leads to mixtures of chloro-sulphoxides and sulphones, two competitive processes must operate, both proceeding through a common chloro-oxosulphonium intermediate (XXIV) (Scheme 2).



SCHEME 2

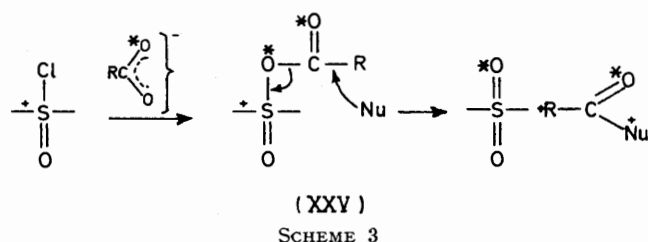
In alkyl phenyl sulphoxides, collapse of (XXIV) to an  $\alpha$ -chloro-sulphoxide is the preferred pathway, regardless of the presence of water, but in the case of the *m*-methoxycarbonyl derivative (XV) the electron-withdrawing effect makes the attack by water on (XXIV) easier. Different behaviour is encountered in the case of acid (XII): the sulphone (XIII) is formed even in the absence of water, and in the presence of water it becomes

\* As previously reported,<sup>4</sup> only one of the two possible diastereoisomeric  $\alpha$ -chloro-sulphoxides is formed.

the major product. Most of the sulphone (XIII) must thus derive from the intermolecular attack on (XXIV) by the carboxylate ion of a second molecule of substrate. The acyloxosulphonium salt (XXV) is formed, and then collapses to the final product.

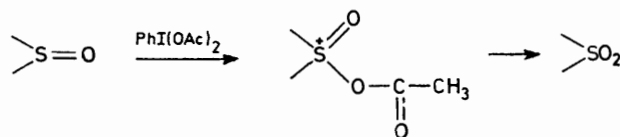
The intervention of acyloxosulphonium intermediates is confirmed by the preferential formation of ethyl phenyl sulphone (XXII) in the reaction of the corresponding sulphoxide with (I) in the presence of benzoic acid.

When the reaction was carried out by using isotopically normal benzoic acid and 10% <sup>18</sup>O-enriched water, (XXII) was only 1% <sup>18</sup>O-enriched, but when isotopically normal water and <sup>18</sup>O-enriched benzoic acid were used, a sulphone with the theoretical amount of <sup>18</sup>O was obtained. This establishes that the reaction proceeds mainly *via* attack by a nucleophile at the carbonyl carbon of the acyloxosulphonium intermediate (XXV), the nucleophile being water, benzoate ion, and perhaps chloride ion or pyridine (Scheme 3).



$\alpha$ -Chlorination, however, remains a competitive process in these conditions, and may be dominant in substrates where the  $\alpha$ -protons are particularly acidic: both dibenzyl and benzyl *p*-tolyl sulphoxide give the corresponding  $\alpha$ -chloro-sulphoxides and no sulphone even in the presence of benzoic acid and water.

It should be noted that, although intermediate (XXV) can be seen as the equivalent of the acyloxy-sulphonium intermediates of the Pummerer rearrangement,<sup>6</sup> formation of  $\alpha$ -acyloxy-sulfoxides was not detected. Intermediates similar to (XXV) are probably involved in the slow reaction of sulphoxides with (diacetoxyiodo)benzene in pyridine at 100° which gives sulphones as the only products (Scheme 4) (see Experimental section).



#### EXPERIMENTAL

*Starting Sulphoxides.*—Racemic 3-phenylsulphinylpropionic acid (II) was prepared according to Durst,<sup>1</sup> m.p. 101–102° (lit.,<sup>1</sup> 98°).

(–)-3-Phenylsulphinylpropionic acid. From a solution of the racemic acid (9.9 g, 0.05 mol) and cinchonidine (14.7 g, 0.05 mol) in boiling propan-2-ol (70 ml) a

<sup>6</sup> (a) T. Durst, *Adv. Org. Chem.*, 1969, **6**, 556; (b) G. A. Russel and G. J. Mikol, in 'Mechanism of Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, vol. 1, p. 157.

cinchonidine salt (19.5 g), m.p. 149–152°, separated on cooling. Four crystallizations from propan-2-ol afforded a salt (2.9 g), m.p. 163–164°,  $[\alpha]_D^{20} -133.9^\circ$  (*c* 1, MeOH). An aqueous solution of the salt was treated with the theoretical amount of 1*N*-sulphuric acid and extracted several times with chloroform; evaporation of the solvent afforded (–)-(II) (1.2 g), m.p. 109–111°,  $[\alpha]_D^{20} -161.1^\circ$  (*c* 1, EtOH) {lit.,<sup>7</sup>  $[\alpha]_D^{20} -185^\circ$  (*c* 1, EtOH)}.

Racemic  $\beta$ -methoxycarbonylethyl phenyl sulphoxide (VIII) was prepared by oxidation of the corresponding sulphide<sup>8</sup> (1.96 g, 0.01 mol) in methanol with NaIO<sub>4</sub> (2.24 g, 0.0105 mol) at 0°. The crude material was purified by column chromatography (SiO<sub>2</sub>, eluant diethyl ether) to afford the sulphoxide (1.8 g, 85% yield),  $n_D^{20}$  1.5511 (Found: C, 56.4; H, 5.7. C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 56.55; H, 5.7%).

(–)- $\beta$ -Methoxycarbonylethyl phenyl sulphoxide (VIII) was obtained in 81% yield by esterification of the corresponding (–)-acid (II) with diazomethane in anhydrous tetrahydrofuran (THF) at 0°. After evaporation of the solvent the crude product was purified by column chromatography (SiO<sub>2</sub>, eluant diethyl ether),  $[\alpha]_D^{20} -177^\circ$  (*c* 1, EtOH).

Racemic 2-methylsulphonylbenzoic acid (III) was synthesized, as reported,<sup>9</sup> by oxidation of the corresponding sulphide (15.7 g, 0.0934 mol) with the stoichiometric amount of peracetic acid, and carefully purified by repeated crystallization from ethyl acetate, m.p. 178–180° (lit.,<sup>9</sup> 178–180°), yield 73%.

(–)-2-Methylsulphonylbenzoic acid (III) was obtained from the racemic acid *via* its brucine salt, as previously reported,<sup>9</sup> m.p. 185.5–186°,  $[\alpha]_D^{20} -227.5^\circ$  (*c* 1, EtOH).

Racemic methyl 2-methylsulphonylbenzoate (VI) was obtained in 77% yield by esterification of the corresponding acid (III) with diazomethane in anhydrous THF at 0°, m.p. 69–70° (from ether–light petroleum) (lit.,<sup>10</sup> 69–70°).

Methyl (–)-2-methylsulphonylbenzoate (VI) was similarly obtained from the acid (III), m.p. 66–67°,  $[\alpha]_D^{20} -200^\circ$  (*c* 1, EtOH) {lit.,<sup>10</sup> m.p. 66–67°,  $[\alpha]_D^{20} -200^\circ$  (*c* 1, EtOH)}.

3-Ethylsulphonylbenzoic acid (XII), prepared by oxidation of the corresponding sulphide (13.7 g, 0.075 mol) with the stoichiometric amount of peracetic acid, had m.p. 110° (from benzene) (lit.,<sup>11</sup> 102°) (9.6 g, 64.5% yield).

(+)-3-Ethylsulphonylbenzoic acid (XII) was obtained from the racemic acid *via* its brucine salt,<sup>11</sup> m.p. 69–71°,  $[\alpha]_D^{20} +200^\circ$  (*c* 1, CHCl<sub>3</sub>) {lit.,<sup>11</sup> m.p. 71°,  $[\alpha]_D^{25} +202^\circ$  (*c* 4, CHCl<sub>3</sub>)}.

Methyl 3-ethylsulphonylbenzoate (XV) was obtained in 75% yield by esterification at –10° of (XII) with diazomethane in anhydrous THF. The crude product was purified by column chromatography (SiO<sub>2</sub>, eluant diethyl ether),  $n_D^{20}$  1.5505 (Found: C, 56.7; H, 5.8. C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 56.55; H, 5.7%).

Methyl (+)-3-ethylsulphonylbenzoate (XV) was obtained by reaction of the (+)-acid (XII) with diazomethane in THF,  $n_D^{20}$  1.5543, after purification by column chromatography (SiO<sub>2</sub>, eluant diethyl ether),  $[\alpha]_D^{25} +176^\circ$  (*c* 1, CHCl<sub>3</sub>).

Ethyl phenyl sulphoxide (XX), b.p. 101–102° at 1 mmHg, was prepared as previously described.<sup>12</sup>

<sup>7</sup> U. Folli, F. Montanari, and G. Torre, *Tetrahedron Letters*, 1966, 5037.

<sup>8</sup> C. D. Hurd and L. L. Geishbein, *J. Amer. Chem. Soc.*, 1947, **69**, 2328.

<sup>9</sup> G. Barbieri, V. Davoli, I. Moretti, F. Montanari, and G. Torre, *J. Chem. Soc. (C)*, 1969, 731.

<sup>10</sup> D. Landini, F. Rolla, and G. Torre, *Internat. J. Sulphur Chem. (A)*, 1972, **2**, 43.

*Reaction of Sulphoxides with (Dichloroiodo)benzene or Bromine.*—Reactions of sulphoxides with bromine in the presence or absence of silver(I) nitrate in anhydrous pyridine and acetonitrile as solvent were carried out as previously described.<sup>13</sup> The same procedure was used for the reactions of sulphoxides with (dichloroiodo)benzene. The crude products were purified by crystallization and/or column chromatography (SiO<sub>2</sub>; eluant chloroform–ethanol 9 : 1 in the case of carboxy-derivatives, and diethyl ether or diethyl ether–light petroleum 1 : 1 in all other cases).

(a) *Reactions in the absence of water.* Acids (II) (0.4 g) and (III) (0.4 g) on reaction with (I) afforded 3-phenylsulphonylpropionic acid (IV) (0.33 g, 76% yield) and 2-methylsulphonylbenzoic acid (V) (0.31 g, 70% yield), respectively. In both cases unchanged sulphoxide was recovered. Compound (IV) had m.p. 123–125° (from benzene) (lit.,<sup>1</sup> 124–126°); compound (V) had m.p. 130–131° (lit.,<sup>1</sup> 130–132°).

Under the same conditions, the ester (VI) (0.3 g) gave a 52% yield of methyl 2-chloromethylsulphonylbenzoate (VII), m.p. 115–116° (from di-isopropyl ether) (Found: C, 46.4; H, 3.8. C<sub>9</sub>H<sub>9</sub>ClO<sub>3</sub>S requires C, 46.45; H, 3.9%); sulphoxide (VI) was recovered (0.12 g, 40%).

When optically active (–)-(VI),  $[\alpha]_D^{20} -200^\circ$  (*c* 1, EtOH),<sup>10</sup> reacted with (I) in the absence and presence of silver nitrate, the chloro-sulphoxide (VII) had  $[\alpha]_D^{25}$  0 and –305° (*c* 1, acetone), respectively. Compound (–)-(VII) had m.p. 108–110°.

Racemic acid (VIII) (420 mg) was treated with (I) (540 mg) for 1.5 h; column chromatography (SiO<sub>2</sub>, eluant diethyl ether–light petroleum 1 : 3) of the reaction mixture gave a mixture (250 mg) of methyl 2-chloro-2-phenylsulphonylpropionate (IX) and methyl *trans*-2-phenylsulphonyl acrylate (X) in a ratio of 4 : 1 (by <sup>1</sup>H n.m.r. analysis) and unchanged material (100 mg). On standing or by repeated column chromatography the mixture was fully converted into the acrylate (X), m.p. 69–70° (from cyclohexane) (Found: C, 57.2; H, 4.8. C<sub>10</sub>H<sub>20</sub>O<sub>3</sub>S requires C, 57.15; H, 4.8%).

Compound (X) was identified by comparison with a sample obtained by esterification of *trans*-2-phenylsulphonyl acrylic acid with diazomethane at –10°.<sup>14</sup>

Oxidation of the mixture of (IX) and (X) (250 mg) with *m*-chloroperbenzoic acid afforded, after repeated chromatography (SiO<sub>2</sub>, diethyl ether–light petroleum 3 : 1), methyl *trans*-2-phenylsulphonyl acrylate (200 mg) (XI) (85%), m.p. 96–97° (from cyclohexane) (Found: C, 52.9; H, 4.35. C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>S requires C, 53.1; H, 4.4%). The same sulphone (XI) was obtained by oxidation of a pure sample of (X). Chlorination of optically active (–)-(VIII),  $[\alpha]_D^{20} -177^\circ$  (*c* 1, EtOH), gave a practically inactive mixture of (IX) and (X),  $[\alpha]_D^{20} -7.9^\circ$  (*c* 5, EtOH).

Compound (XII) (1.98 g, 0.01 mol) by reaction with (I) (2.75 g, 0.01 mol) in anhydrous pyridine afforded 3- $\alpha$ -chloroethylsulphonylbenzoic acid (XIV) (1.14 g) (50%), 3-ethylsulphonylbenzoic acid (XIII) (364 mg, 17%), and unchanged sulphoxide (654 mg, 33%). Compound (XIV) had m.p. 153–154° (from benzene) (Found: C, 46.25;

<sup>11</sup> J. Holloway, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 1928, 3001.

<sup>12</sup> M. Cinquini, S. Colonna, and D. Landini, *J.C.S. Perkin II*, 1972, 296.

<sup>13</sup> M. Cinquini and S. Colonna, *J.C.S. Perkin I*, 1972, 1883.

<sup>14</sup> D. Albera, M. Bonincontro, and F. Montarari, *Gazzetta*, 1960, **90**, 709.

H, 3.9.  $C_9H_8ClO_2S$  requires C, 46.45; H, 3.9%). Compound (XIII) had m.p. 161–163° (from xylene) (lit.,<sup>11</sup> 162–164°).

Methyl 3-ethylsulphinylbenzoate (XV) (1 g, 0.0047 mol) was treated with (I) in anhydrous pyridine to give a mixture of the diastereoisomeric  $\alpha$ -chloro-sulphoxides (XVI) (732 mg, 63%); unchanged sulphoxide was recovered (250 mg, 25%). The <sup>1</sup>H n.m.r. spectrum of (XVI) in  $CDCl_3$  showed that the two diastereoisomeric chloro-sulphoxides were in a ratio of 95:5. Purification of (XVI) by column chromatography ( $SiO_2$ , diethyl ether as eluant) afforded methyl 3- $\alpha$ -chloroethylsulphinylbenzoate (XVIa), m.p. 101–102° (from cyclohexane) (Found: C, 48.7; H, 4.45.  $C_{10}H_{11}ClO_2S$  requires C, 48.7; H, 4.5%; c.d. ( $c$  0.003,  $CHCl_3$ ),  $[\theta]_{300}^0$ ,  $[\theta]_{252}^{25}$ , –42020, and  $[\theta]_{230}^0$ ).

Methyl (+)-3-ethylsulphinylbenzoate,  $[\alpha]_D^{25} +176^\circ$  ( $c$  1,  $CHCl_3$ ) (600 ml, 0.00283 mol), on reaction with (I) in anhydrous pyridine in the presence of silver(I) nitrate (1 g, 1 molar excess) gave substantially the results previously described for the racemic benzoate (XV). The diastereoisomeric mixture of  $\alpha$ -chloro-sulphoxides (XVI) after purification by column chromatography afforded (XVIa) (304 mg, 43.7%), m.p. 58–60°,  $[\alpha]_D^{25} -120^\circ$  ( $c$  1,  $CHCl_3$ ). Oxidation of (–)-(XVIa) (246 mg, 0.001 mol),  $[\alpha]_D^{25} -120^\circ$  ( $c$  1,  $CHCl_3$ ), with an excess of *m*-chloroperbenzoic acid in methylene chloride afforded methyl 3- $\alpha$ -chloroethylsulphonylbenzoate (XXVI) (236 mg, 90%) as a viscous oil,  $[\alpha]_D^{25} 0^\circ$  ( $c$  6,  $CHCl_3$ ) (Found: C, 45.9; H, 4.2.  $C_{10}H_{11}ClO_4S$  requires C, 45.8; H, 4.25%). When the reaction was repeated starting from (+)-(XV) in the absence of silver(I) nitrate a racemic mixture of the  $\alpha$ -chloro-sulphoxides (XVI) was obtained.

Methyl 3-ethylsulphinylbenzoate (XV) (212 mg, 1 mmol) was very unreactive to bromine (0.06 ml, 1.2 mmol) in anhydrous pyridine and acetonitrile. After 4 days only 5% of the  $\alpha$ -bromo-sulphoxides (XVIIIa and b), m.p. 72–78°, was obtained together with 90% starting sulphoxide (XV). By repeating the reaction in the presence of silver(I) nitrate (407 mg, 1.4 molar excess), (XV) afforded a mixture of the diastereoisomeric  $\alpha$ -bromo-sulphoxides (XVIIIa and b) (116 mg, 40%) in a ratio of 9:1 (<sup>1</sup>H n.m.r. spectrum in  $CDCl_3$ ), m.p. 80–82°. Starting sulphoxide (95 mg, 45%) was also recovered.

When (+)-(XV),  $[\alpha]_D^{25} +176^\circ$  ( $c$  1,  $CHCl_3$ ), was used, the recovered sulphoxide had  $[\alpha]_D^{25} +170^\circ$  ( $c$  1,  $CHCl_3$ ). Purification of (XVIIIa and b) by column chromatography ( $SiO_2$ , diethyl ether–light petroleum 1:1) afforded methyl (–)-3- $\alpha$ -bromoethylsulphinylbenzoate (XVIIIa), m.p. 78–79°,  $[\alpha]_D^{25} -120^\circ$  ( $c$  1,  $CHCl_3$ ); c.d. ( $c$  0.007  $CHCl_3$ ),  $[\theta]_{300}^0$ ,  $[\theta]_{256}^{25} -25410$ , and  $[\theta]_{230}^0$ .

Oxidation of (–)-(XVIIIa) (102 mg) with an excess of *m*-chloroperbenzoic acid in methylene chloride afforded methyl (–)-3- $\alpha$ -bromoethylsulphonylbenzoate (XIX) (97 mg, 90%) as a viscous liquid after purification by column chromatography ( $SiO_2$ , diethyl ether–light petroleum 3:7),  $[\alpha]_D^{25} -1.8^\circ$  ( $c$  7,  $CHCl_3$ ) (Found: C, 39.3; H, 3.7.  $C_{10}H_{11}BrO_4S$  requires C, 39.1; H, 3.6%). Reactions of phenyl ethyl, of dibenzyl, and of benzyl *p*-tolyl sulphoxide with (I) in anhydrous pyridine to give the corresponding  $\alpha$ -chloro-sulphoxides have been reported.<sup>13</sup>

(b) *Reactions in the presence of water.* The reactions

<sup>15</sup> H. Gilman and F. J. Well, *J. Amer. Chem. Soc.*, 1949, **71**, 4062.

<sup>16</sup> C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, 1965, **87**, 5404.

were carried out as described in (a) with water (10 mol per mol of sulphoxide) added to the reaction medium. Under these conditions the acid (XII) afforded a mixture of the sulphone (XIII) and  $\alpha$ -chloro-sulphoxide (XIV) in a ratio of 3:1 (80% overall yield); ester (XV) gave a mixture of the chloro-sulphoxide (XVI) and sulphone (XVII) in a ratio of 4:1 (82% overall yield). Methyl 3-ethylsulphonylbenzoate (XVII) had m.p. 40° (Found: C, 52.85; H, 5.35.  $C_{10}H_{12}O_4S$  requires C, 52.65; H, 5.3%). Sulphoxide (XX) afforded a mixture of the chloro-sulphoxide (XXI) and sulphone (XXII) in a ratio of 9:1 (overall yield 75%). Ethyl phenyl sulphone (XXII) had m.p. 42° (lit.,<sup>15</sup> 42°).

(c) *Reaction in the presence of water and benzoic acid.* Reaction of the sulphoxide (XX) (0.5 g) in anhydrous medium in the presence of benzoic acid (3 mol per mol of sulphoxide) gave, after the usual work-up, a mixture of (XXI) and (XX) in a 1:1 ratio (overall yield 55%), together with starting sulphoxide (40%). Benzoic anhydride (68 mg) was also isolated. When the reaction was repeated with benzoic acid (3 mol) and water (10 mol) the ratio (XXI):(XXII) was 3:7 (overall yield 65%). The use of 10% <sup>18</sup>O-enriched water and isotopically normal benzoic acid afforded sulphone (XXII) 1% <sup>18</sup>O-enriched (by mass spectrum). When isotopically normal water and 10% <sup>18</sup>O-enriched benzoic acid (from benzoyl chloride and 10% <sup>18</sup>O-enriched water) were utilized, sulphone (XXII) was 5% <sup>18</sup>O-enriched.

Reaction of benzyl *p*-tolyl and of dibenzyl sulphoxide in the presence of benzoic acid and water afforded the corresponding chloro-sulphoxides in 80% yield.

*Inversion of Methyl 3- $\alpha$ -Chloroethylsulphinylbenzoate (XVI).*—The  $\alpha$ -chloro-sulphoxide (XVIa) (221 mg) was converted into the corresponding alkoxy-sulphonium salt by the general method described by Johnson<sup>16</sup> using trimethylxonium fluoroborate. After 10 h anhydrous diethyl ether was added and the methoxy-sulphonium salt precipitated. After hydrolysis of the salt with sodium hydroxide<sup>16</sup> the inverted methyl 3- $\alpha$ -chloroethylsulphinylbenzoate (XVib) was obtained (130 mg, 40%) as an oil,  $n_D^{18} 1.5722$  (Found: C, 48.75; H, 4.4.  $C_{10}H_{11}ClO_2S$  requires C, 48.7; H, 4.5).

*Reduction of Methyl (–)-3- $\alpha$ -Bromoethylsulphinylbenzoate (XVIIIa).*—The reduction of (–)-(XVIIIa),  $[\alpha]_D^{25} -120^\circ$  ( $c$  1,  $CHCl_3$ ) (98 mg), with zinc dust in methanol at room temperature was carried out as previously described<sup>4</sup> with a reaction time of 20 min to afford the (–)-sulphoxide (XV),  $[\alpha]_D^{25} -155^\circ$  ( $c$  1,  $CHCl_3$ ) (42 mg, 59%).

*Reaction of Dibenzyl Sulphoxide with (Diacetoxyiodo)benzene.*—Dibenzyl sulphoxide (230 mg, 1 mmol) was treated at 100° for 48 h with (diacetoxyiodo)benzene (1 mol. equiv.) in anhydrous pyridine (40 ml). The mixture was diluted with chloroform and washed with aqueous sulphuric acid. After evaporation of the solvent the crude product was purified by column chromatography ( $SiO_2$ , diethyl ether–light petroleum 1:1) to afford dibenzyl sulphone (118 mg, 48%), m.p. 152° (lit.,<sup>1</sup> 151.9°), and unchanged sulphoxide (110 mg, 48%), m.p. 135–136° (lit.,<sup>18</sup> 136–137°).

[4/1321 Received, 1st July, 1974]

<sup>17</sup> H. Rheinboldt and E. Giesbrecht, *J. Amer. Chem. Soc.*, 1947, **69**, 644.

<sup>18</sup> W. Tagaki, S. Kiso, and S. Oae, *Bull. Chem. Soc. Japan*, 1965, **38**, 414.