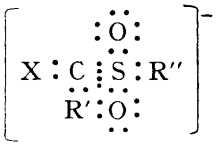
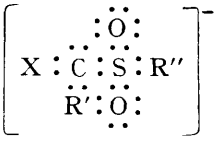
356. *The Attempted Resolution of Some Substituted Disulphonylmethanes and the Resolution of α-p-Carboxyphenylsulphonyl-α-p-tolylthioethane.*

By F. Barry Kipping.

Of the two formulæ for the acidic ion of the salt of a disulphone, $R{\cdot}SO_2{\cdot}CHR'{\cdot}SO_2{\cdot}R''$, formula (A) is discarded by Shriner, Struck, and Jorison (*J. Amer. Chem. Soc.*, 1930, **52**, 2060) on the ground that the sulphur atom cannot share ten electrons, and a similar conclusion as to the non-enolisation of the sulphone group is drawn by Arndt and Martius (*Annalen*, 1932, **499**, 223) from a consideration of the chemical properties of such compounds.

If, now, the sulphone contains a central asymmetric carbon group and is optically active, salt-formation leading to (A) must cause complete loss of optical activity: the ion (B), however, should retain its activity, at any rate to some extent.

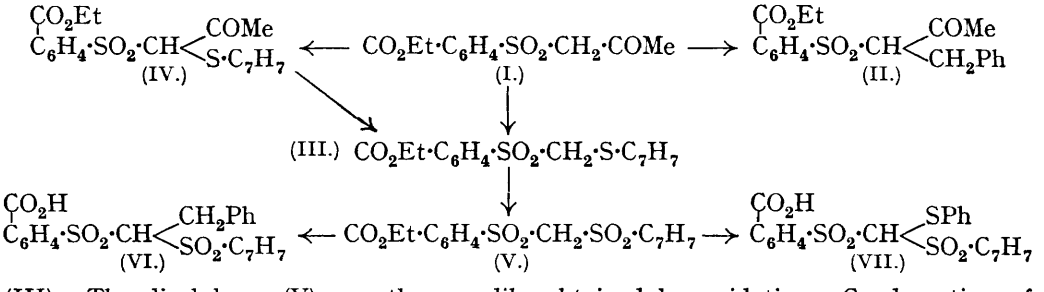
(A)   (B)

Attempts to resolve the acidic trisulphonylmethanes, $R{\cdot}SO_2{\cdot}CH(SO_2{\cdot}R'){\cdot}SO_2{\cdot}R''$, have been made by Gibson (J., 1931, 2637) without success, and Ashley and Shriner (*J. Amer. Chem. Soc.*, 1932, **54**, 4410) have shown that ethyl *l*-α-phenylsulphonylbutyrate, $Ph{\cdot}SO_2{\cdot}CHEt{\cdot}CO_2Et$, yields an optically inactive sodium salt: in the latter case, as the authors themselves point out, the evidence is inconclusive in that enolisation of the carbethoxy-group may occur.

It seemed essential, therefore, to prepare di- or tri-sulphones of the above type which satisfy two further conditions: (1) there must be no hydrogen atoms in the groups R and R″ which can account for salt-formation, that is to say, the hydrogen atom attached to the carbon atom between the two sulphone groups must be the only one which is capable of being displaced by an alkali metal; (2) as the disulphones are not strongly acidic, there must be a salt-forming group elsewhere in the molecule, which can be destroyed or rendered neutral after resolution has been effected. These conditions seem to be best satisfied by $R = p\text{-}C_6H_4{\cdot}CO_2H$ and R″ = phenyl or tolyl, the carboxyl group being used for the resolution and then esterified.

Two compounds of this type were therefore prepared by the following series of reactions. *Ethyl* p-*mercaptobenzoate* was condensed with chloroacetone, and the product oxidised: the resulting p-*carbethoxyphenylsulphonylacetone* (I) reacted easily with benzyl iodide and sodium ethoxide, giving (II), but the introduction of the *p*-tolylthio-group into this substance (Brooker and Smiles, J., 1926, 1723; Gibson, *loc. cit.*) with di-*p*-tolyl disulphoxide and sodium ethoxide could not be effected.

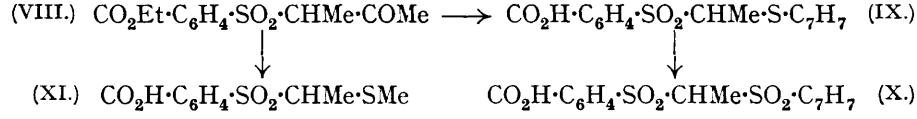
The sulphonylacetone (I), however, reacted easily with di-*p*-tolyl disulphoxide, giving a mixture of (III) and (IV), and under suitable conditions, a good yield of (III); alternatively, the mixture of (III) and (IV) could be hydrolysed to the acid corresponding to



(III). The disulphone (V) was then readily obtained by oxidation. Condensation of (V) with benzyl iodide in the presence of sodium ethoxide gave a good yield of the ester

of (VI), from which the acid was easily obtained. All attempts to resolve this acid failed, as those salts which were obtained crystalline could not be separated into diastereoisomeric forms. The disulphone (V) was therefore condensed with diphenyl disulphoxide, and the acid (VII) obtained by hydrolysis. Here again resolution could not be effected.

It seemed possible that the difficulty of obtaining an optically active substituted disulphonylmethane might be overcome by the resolution of a sulphonylarylthiomethane, $R{\cdot}SO_2{\cdot}CHR'{\cdot}SAr$, followed by the oxidation of it to the disulphone. Ethyl *p*-mercaptobenzoate was therefore condensed with bromoethyl methyl ketone and the product was oxidised without being isolated: a good yield of α-p-*carbethoxyphenylsulphonylethyl methyl ketone* (VIII) was thus obtained. Condensation of the sodium derivative of (VIII) with di-*p*-tolyl disulphoxide, followed by hydrolysis, furnished the required dl-α-p-*carboxyphenylsulphonyl*-α-p-*tolylthioethane* (IX), the acetyl group being eliminated during either condensation or hydrolysis:



The *dl*-acid (IX) was resolved into its optically active components by the crystallisation of its quinine or *l*-menthylamine salt, but the active forms were most easily obtained in quantity by the half-equivalent method using the latter base. The optically active acid was stable in the presence of acids, could be crystallised from acetic acid, and converted into its esters with the aid of hydrogen chloride: in faintly alkaline solution, however, fairly rapid racemisation occurred. The acid was therefore oxidised to the disulphone in acetic acid solution both with potassium permanganate and with hydrogen peroxide, but an optically inactive product was obtained: the optically active *methyl* ester also gave an inactive disulphonyl ester when oxidised in a similar manner.

The resolution of α-p-*carboxyphenylsulphonyl*-α-p-*tolylsulphonylethane* (X) failed in the case of five salts with optically active bases.

In view of the difficulty of obtaining crystalline salts of the disulphonyl acids with many alkaloids, it was considered possible that a decrease in the molecular weight of the acid might favour crystallisation. By the condensation of (VIII) with methyl *p*-toluenethiosulphonate, followed by hydrolysis, α-p-*carboxyphenylsulphonyl*-α-*methylthioethane* (XI) was obtained and, by oxidation, the corresponding disulphonyl compound. No improvement in crystallising power of the salts was, however, found and neither of the last two compounds could be resolved.

Experimental.

The disulphoxides were prepared by warming aqueous solutions of the corresponding sulphinic acids, obtained from the sulphonyl chlorides by reduction with sodium sulphite or zinc dust and water, with a few drops of sulphuric acid and hydriodic acid (Smiles and Gibson, J., **1924**, **125**, 179).

Ethyl p-*Mercaptobenzoate.*—*p*-Mercaptobenzoic acid (90 g.) (*p*-thiolbenzoic acid; J., **1922**, **121**, 2022) was esterified with boiling alcohol (600 c.c.) and hydrogen chloride until complete solution had occurred: most of the alcohol was removed, and the residue poured on ice. The oil produced was extracted and washed (sodium bicarbonate) in ether and distilled in an atmosphere of nitrogen. *Ethyl* p-*mercaptobenzoate* (68 g.) had b. p. 162—164°/22 mm. and 275° (slight decomp.)/atmospheric pressure (Found: C, 58·6; H, 5·2. $C_9H_{10}O_2S$ requires C, 59·3; H, 5·4%). In some preparations an ester, which crystallised from alcohol in colourless needles, m. p. 65—66°, was obtained (Found: C, 60·3; H, 4·6; S, 17·4. $C_{18}H_{18}O_4S_2$ requires C, 59·7; H, 5·0; S, 17·7%). The same ester was formed by the oxidation of ethyl *p*-mercaptobenzoate with iodine in alcoholic solution and it is therefore *bis*-p-*carbethoxyphenyl disulphide*: the corresponding acid is doubtless an impurity in the *p*-mercaptobenzoic acid. Hot alcoholic solutions of this ester are yellow, but the colour is lost on cooling.

p-*Carbethoxyphenylthioacetone*, $CO_2Et{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}COMe$.—Monochloroacetone (1 mol.) was gradually added to an alcoholic solution of the sodium derivative of ethyl *p*-mercaptobenzoate (1 mol.): sodium chloride separated at once, and, after pouring into water, the precipitated

solid was crystallised from alcohol. It had m. p. 53—54° (Found: C, 60·5; H, 5·9; S, 13·7. $C_{12}H_{14}O_3S$ requires C, 60·5; H, 5·9; S, 13·5%).

p-*Carbethoxyphenylsulphonylacetone* (I).—A solution of the thioacetone (54·5 g.) in carbon tetrachloride was shaken with dilute sulphuric acid (50 c.c. of concentrated acid) while potassium permanganate (42·5 g.) was gradually added; the product was poured into sulphurous acid to dissolve manganese dioxide. The *sulphone* crystallised from alcohol in colourless plates (46 g.), m. p. 88° (Found: C, 53·6; H, 5·5; S, 12·3. $C_{12}H_{14}O_5S$ requires C, 53·3; H, 5·2; S, 11·9%). It yielded a *sodium* salt with sodium ethoxide (Found: Na, 7·5. $C_{12}H_{13}O_5SNa$ requires Na, 7·9%). The methylation of this sulphone gave oily products which were probably mixtures.

α-p-*Carbethoxyphenylsulphonyl-α-benzylacetone* (II) was prepared by the condensation of the above sodium salt with benzyl iodide in alcoholic solution: after evaporation of the alcohol, addition of water gave an oil, which solidified after some days and then crystallised from alcohol in small needles, m. p. 104° (Found: C, 63·2; H, 5·65. $C_{19}H_{20}O_5S$ requires C, 63·3; H, 5·55%). This *ester* was hydrolysed with sodium hydroxide, and the acid, α-*p*-carboxyphenylsulphonyl-β-phenylethane, $CO_2H{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2Ph$, precipitated with hydrochloric acid; it crystallised from acetic acid in bunches of needles, m. p. 232—233°, and gave an *ethyl* ester, m. p. 77—78° (Found: C, 64·4; H, 5·9. $C_{17}H_{18}O_4S$ requires C, 64·2; H, 5·7%).

Condensation of p-*Carbethoxyphenylsulphonylacetone* (I) *with Di*-p-*tolyl Disulphoxide*.—The two substances (1 mol. of each) were boiled in alcohol with sodium ethoxide (1 mol.) until the solution was neutral: after evaporation of the alcohol, the oily residue was washed with water. The resulting p-*carbethoxyphenylsulphonyl*-p-*tolylthiomethane* (III) crystallised from alcohol in plates, m. p. 121° (Found: C, 58·1; H, 5·1; S, 18·0. $C_{17}H_{18}O_4S_2$ requires C, 58·3; H, 5·15; S, 18·3%). From the alcoholic mother-liquor a much more soluble compound, α-p-*carbethoxyphenylsulphonyl*-α-p-*tolylthioacetone* (IV), was isolated, which, after repeated crystallisations from alcohol and light petroleum, formed fine needles, m. p. 86—87° (Found: C, 57·9; H, 5·1; S, 16·25. $C_{19}H_{20}O_5S_2$ requires C, 58·1; H, 5·1; S, 16·3%). (III) and (IV) are difficult to separate and the yields are poor, but if the reactants are boiled for a longer time (7 hours) the amount of (III) produced is much increased and it separates at once from the cooled mixture and may be obtained in about 80% yield, or the whole of the oily reaction product, obtained by pouring into water, may be hydrolysed with alkali, and the acid (below) obtained. (IV) gave a transitory yellow colour with warm dilute sodium hydroxide solution and dissolved rapidly; (III), on the other hand, dissolved slowly with no colour: *p*-carboxyphenylsulphonyl-*p*-tolylthiomethane was precipitated from both solutions on acidification, and from the filtrate in the former case acetic acid was isolated.

p-*Carboxyphenylsulphonyl*-p-*tolylthiomethane* crystallises from glacial or dilute acetic acid in colourless needles, m. p. 205—206° (Found: C, 55·4; H, 4·4. $C_{15}H_{14}O_4S_2$ requires C, 55·8; H, 4·35%). The *sodium* salt crystallises from water in needles (Found: Na, 6·6. $C_{15}H_{13}O_4S_2Na$ requires Na, 6·7%). The ethyl ester, obtained with alcohol and hydrogen chloride, was identical with (III), thus providing the final proof of the constitutions of (III) and (IV).

p-*Carboxyphenylsulphonyl*-p-*tolylsulphonylmethane* (as V).—The preceding acid (1 mol.) was oxidised in acetic acid by the gradual addition of potassium permanganate (1·33 mols.) during about 8 hours, and the product poured into sulphurous acid. The precipitated *acid* crystallised from acetic acid in small prisms, m. p. 240—242° (Found: C, 50·6; H, 4·0. $C_{15}H_{14}O_6S_2$ requires C, 50·8; H, 4·0%). The *ethyl* ester (V), prepared in good yield in a similar manner from (III), or from the acid, crystallised from alcohol in small needles, m. p. 147·5° (Found: C, 53·3; H, 4·7. $C_{17}H_{18}O_6S_2$ requires C, 53·3; H, 4·7%), very easily soluble in acetone, sparingly in alcohol, and almost insoluble in light petroleum; it gave a solid sodium salt with sodium ethoxide.

p-*Carboxyphenylsulphonyl*-p-*tolylsulphonylbenzylmethane* (VI).—The ester (V) (1 mol.) was added to an alcoholic solution of sodium ethoxide (1 mol.). Immediate precipitation of the sodium salt took place, and a solution of benzyl iodide (1 mol.) in alcohol was then slowly added: the sodium salt dissolved rapidly and after being heated during ½ hour the solution was neutral. On cooling, crystals, m. p. 116—117°, separated, which after recrystallisation from alcohol proved to be the pure *ethyl* ester of (VI), m. p. 118—119° (yield, 80%) (Found: C, 61·3; H, 5·4; S, 14·0. $C_{24}H_{24}O_6S_2$ requires C, 61·0; H, 5·1; S, 13·6%).

The *acid* (VI), obtained by hydrolysis of the ester with alkali, crystallised from acetic acid in needles, m. p. 185—186° (Found: C, 59·3; H, 4·7; S, 14·5. $C_{22}H_{20}O_6S_2$ requires C, 59·4; H, 4·5; S, 14·4%).

Salts of the Acid (VI) *with Optically Active Bases*.—The final fraction of each salt was dissolved in acetic acid, and the acid (VI) precipitated by the addition of water and examined in chloroform solution: no activity was detected in any case. The following salts were examined: quinine, m. p. 215°, $[\alpha]_{5780}$ — 115°, $[\alpha]_{5461}$ — 132° in chloroform (c = 1·3); nor-*d*-ψ-ephedrine, m. p. 115—118°; l-*menthylamine*, m. p. 214—215° (Found: C, 64·4; H, 7·1. $C_{22}H_{20}O_6S_2,C_{10}H_{21}N$ requires C, 64·2; H, 6·85%); *d*-sec.-butylamine, m. p. 205—207°; cinchonidine, $[\alpha]_{5780}$ — 66°, $[\alpha]_{5461}$ — 75° in chloroform (c = 1·0); *l*-phenylethylamine, m. p. 186°. Salts with brucine, cinchonine, strychnine, and morphine could not be obtained crystalline.

p-*Carboxyphenylsulphonyl*-p-*tolylsulphonylphenylthiomethane* (VII).—The disulphone (V), sodium ethoxide, and diphenyl disulphoxide in equimolecular proportions were boiled in alcoholic solution: after evaporation of the alcohol, the semi-solid residue was washed with water and warmed with alkali, and the *acid* precipitated with hydrochloric acid. It crystallised from acetic acid in prisms, m. p. 212° (Found: C, 54·5; H, 4·2; S, 20·8. $C_{21}H_{18}O_6S_3$ requires C, 54·6; H, 3·9; S, 20·8%). The ethyl ester had m. p. 126—127°.

The quinine salt, m. p. 209—210°, $[\alpha]_{5780}$ — 111·5°, $[\alpha]_{5461}$ — 127° in chloroform (c = 1·2), and the *l*-menthylamine salt, m. p. 184—185°, $[\alpha]_{5461}$ = — 10·7° in chloroform (c = 1·07), both appeared homogeneous and the recovered acid was optically inactive. The *l*-phenylethylamine, brucine, cinchonine, morphine, and strychnine salts could not be obtained crystalline.

α-p-*Carbethoxyphenylsulphonylethyl Methyl Ketone* (VIII).—To a solution of ethyl *p*-mercaptobenzoate (38 g.) in an alcoholic solution of sodium ethoxide (1 mol.), α-bromoethyl methyl ketone (31·5 g.) was slowly added: sodium bromide separated at once. After evaporation of most of the alcohol, the residual oil was washed with water, dissolved in carbon tetrachloride, and shaken with dilute sulphuric acid (40 c.c. of concentrated acid) during the gradual addition of permanganate (45 g.). The precipitated manganese dioxide was destroyed with sulphurous acid, the carbon tetrachloride layer separated and dried, and the solvent evaporated. The residual oil crystallised from alcohol; m. p. 66—67° (45·5 g.; 77% of the theoretical) (Found: C, 54·6, 55·2; H, 5·8, 5·9. $C_{13}H_{16}O_5S$ requires C, 54·9; H, 5·65%).

dl-α-p-*Carboxyphenylsulphonyl*-α-p-*tolylthioethane* (IX).—The sulphonyl ketone (VIII) gave with a solution of sodium ethoxide (1 mol.) a yellow colour which was almost instantly destroyed by the addition of di-*p*-tolyl disulphoxide (1 mol.), giving a neutral solution: after evaporation of most of the solvent, the residual oil was washed with water, dissolved in alcohol, and boiled for a few minutes with rather more than 1 mol. of dilute aqueous alkali. The alkaline solution was poured into excess of dilute acid; the precipitated solid crystallised from acetic acid in prisms, m. p. 168—169° (Found: C, 56·9, 57·5, 57·0; H, 4·9, 4·5, 4·9. $C_{16}H_{16}O_4S_2$ requires C, 57·2; H, 4·75%); yield, 85%. The dl-*ethyl* ester of (IX) crystallised from alcohol in small prisms, m. p. 72° (Found: C, 59·75; H, 5·5. $C_{18}H_{20}O_4S_2$ requires C, 59·4; H, 5·5%), and the *dl*-methyl ester from methyl alcohol in prisms, m. p. 112—113°. The dl-*acid chloride* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 83—84° (Found: C, 54·35; H, 4·3. $C_{16}H_{15}O_3ClS_2$ requires C, 54·2; H, 4·2%).

Resolution of dl-α-p-*Carboxyphenylsulphonyl*-α-p-*tolylthioethane* (IX).—The l-*menthylamine* salt was precipitated when aqueous solutions of equivalent proportions of the sodium salt of the acid and the hydrochloride of the base were mixed. After one recrystallisation from 50% alcohol, it had m. p. 175—185° (Found: C, 63·7, 63·9; H, 6·5, 7·1. $C_{16}H_{16}O_4S_2,C_{10}H_{21}N$ requires C, 63·7; H, 7·5%). $[\alpha]_{5461}$ — 2·21° in chloroform (c = 0·9). The salt was then crystallised five times from aqueous alcohol and four times from alcohol, from which it finally separated in long fine needles, m. p. 199—202° (Found: C, 63·8, 64·2; H, 7·3, 7·5%). $[\alpha]_{5461}$ + 57·0° in chloroform (c = 1·2).

The acid liberated from the last fraction by solution of the salt in acetic acid and addition of water had m. p. 160°, and $[\alpha]_{5461}$ + 130° in chloroform (c = 0·55).

The resolution can be simplified by dissolving *l*-menthylamine hydrochloride (1 equiv.) and the sodium salt of the acid (2 equivs.) in 50% aqueous alcohol and seeding the solution with the pure *l*B*d*A salt described above. When crystallisation is complete, the deposit is recrystallised once from alcohol, and the acid isolated from it. The crude *d*-acid is dissolved in acetic acid, the solution seeded with the *dl*-acid and kept until no further crystallisation occurs. After filtration, the filtrate is precipitated with water, and the *d*-acid collected, $[\alpha]_{5461}$ = + 130°. From the original mother-liquor the crude *l*-acid is liberated, and purified with acetic acid, $[\alpha]_{5461}$ = — 126°. The *dl*-acid is practically insoluble in cold acetic acid, but the active isomerides are moderately readily soluble.

The active acid racemises in faintly alkaline solution: a sample ($[\alpha]_{5461}$ + 122° in chloroform), dissolved in sodium hydroxide solution (1 equiv.), showed a half-life period of about 10 hours,

whereas a similar sample in aqueous ammonia had a half-life period of about 60 hours at the ordinary temperature. The acid can also be resolved with the aid of its quinine salt, which after repeated crystallisation from alcohol finally separates in prisms, m. p. 180—181°, $[\alpha]_{5461}$ — 100° in chloroform ($c = 0{\cdot}6$). The acid from this salt gave $[\alpha]_{5461}$ + 112° in chloroform.

The d- and the l-*methyl* ester, prepared by the hydrogen chloride method, crystallised from methyl alcohol in long stout needles or elongated prisms, m. p. 131—132° (Found: C, 58·7, 58·6; H, 5·0, 5·35; S, 18·0, 17·9. $C_{17}H_{18}O_4S_2$ requires C, 58·4; H, 5·15; S, 18·3%). These esters are much less soluble in methyl alcohol than the *dl*-ester and may be readily separated from small quantities of the latter. $[\alpha]_{5780}$ + 114°, $[\alpha]_{5461}$ + 134°, and $[\alpha]_{5461}$ — 132° in chloroform ($c = 1{\cdot}025$). The *d*-ethyl ester had m. p. 44—45°. The d-*acid chloride* crystallised from petroleum (b. p. 80—100°) in plates, m. p. 101—102° (Found: C, 54·6; H, 4·4. $C_{16}H_{15}O_3ClS_2$ requires C, 54·2; H, 4·2%), $[\alpha]_{5461}$ + 145° in chloroform ($c = 1{\cdot}31$).

α-p-*Carboxyphenylsulphonyl*-α-p-*tolylsulphonylethane* (X).—The *dl*-acid (IX) was oxidised in acetic acid solution with 100-volume hydrogen peroxide at 50—60° during 3½ hours. The *disulphonyl-ethane* (X), crystallised from acetic acid, had m. p. 233—234° (Found: C, 52·2, 52·4; H, 4·7, 4·6. $C_{16}H_{16}O_6S_2$ requires C, 52·2; H, 4·4%).

The *ethyl* ester, prepared both from the acid and by the oxidation of the ester of (IX) with permanganate in acetic acid solution during 7 hours, crystallised from alcohol in small needles, m. p. 120—121° (Found: C, 54·9; H, 4·9. $C_{18}H_{20}O_6S_2$ requires C, 54·5; H, 5·0%). It was also isolated in small yield by the fractionation from alcohol of the product of methylation of (V). The methyl ester crystallised from methyl alcohol in small prisms, m. p. 141°.

Oxidation of the optically active acid and its methyl ester in acetic acid solution with permanganate or hydrogen peroxide gave inactive products in all cases.

Salts of the Acid (X) *with Optically Active Bases.*—In all the following cases the acid obtained from the final fraction of each salt was inactive. The quinine salt had m. p. 211—212° and was so sparingly soluble in cold solvents that rotations could not be determined. The *l*-menthylamine salt had m. p. 187—191°, $[\alpha]_{5461}$ — 18·6° in alcohol ($c = 1{\cdot}5$); the cinchonidine salt, m. p. 177—178°, $[\alpha]_{5461}$ — 85·5° in chloroform ($c = 1{\cdot}08$); *l*-hydroxyhydrindamine salt, m. p. 208—210°, $[\alpha]_{5461}$ — 72° in acetone ($c = 0{\cdot}84$); *l*-phenylethylamine salt, m. p. 214—215°. Salts with brucine, cinchonine, morphine, *d*-sec.-butylamine, and nor-*d*-ψ-ephedrine could not be obtained crystalline.

α-p-*Carboxyphenylsulphonyl*-α-*methylthioethane* (XI).—An alcoholic solution of the sodium derivative of (VIII) (1 mol.) was warmed with methyl *p*-toluenethiosulphonate (J., 1931, 2640) (1 mol.) until it was neutral (5 mins.): aqueous sodium hydroxide (1·25 mols.) was then added, and boiling continued until dilution with water produced no precipitate. The *acid* (XI), isolated by pouring the solution into dilute hydrochloric acid, crystallised from alcohol in needles, m. p. 185° (decomp.) (Found: C, 46·3; H, 4·8. $C_{10}H_{12}O_4S_2$ requires C, 46·2; H, 4·6%).

α-p-*Carboxyphenylsulphonyl*-α-*methylsulphonylethane* was readily prepared by the oxidation of (XI) in acetic acid with permanganate at 30°. Crystallised from alcohol, it had m. p. 273° (Found: C, 41·4; H, 4·4. $C_{10}H_{12}O_6S_2$ requires C, 41·1; H, 4·1%).

Salts of (XI).—The recovered acid was invariably optically inactive. The *l*-hydroxyhydrindamine salt had m. p. 194° (decomp.), $[\alpha]_{5461}$ — 91° in acetone ($c = 0{\cdot}6$); strychnine salt, m. p. 234° (decomp.), $[\alpha]_{5461}$ — 10·3° in chloroform ($c = 0{\cdot}63$); *l*-menthylamine salt, m. p. 174—177°, $[\alpha]_{5461}$ — 21·0° in alcohol ($c = 0{\cdot}76$); quinine salt, m. p. 217°, $[\alpha]_{5461}$ — 160° in chloroform ($c = 1{\cdot}3$). Salts with brucine, cinchonine, and cinchonidine could not be obtained crystalline.

Salts of α-p-*Carboxyphenylsulphonyl*-α-*methylsulphonylethane.*—The acid recovered from the final fraction was inactive in each case. The *d*-hydroxyhydrindamine salt had m. p. 186—187°, $[\alpha]_{5461}$ + 85° in acetone ($c = 0{\cdot}7$); quinine salt, m. p. 165—167°, $[\alpha]_{5461}$ — 94·5° in chloroform ($c = 0{\cdot}51$); *l*-phenylethylamine salt, m. p. 195—198°; cinchonidine salt, m. p. 183—184°, $[\alpha]_{5461}$ — 78·7° in alcohol ($c = 1{\cdot}53$); *l*-menthylamine salt, m. p. 189—190°, $[\alpha]_{5461}$ — 18·3° in alcohol ($c = 2{\cdot}26$). Salts with brucine, morphine, nor-*d*-ψ-ephedrine, and quinidine could not be crystallised.

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