CCLXXIX.—*The Dependence of Rotatory Power on Chemical Constitution. Part XXIX. The Resolution of Sulphoxides into their Optically Active Forms.*

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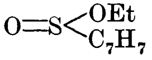
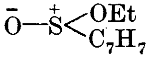
THE preparation of ethyl *p*-toluenesulphinate in an optically active state (Phillips, J., 1925, **127**, 2552) provided substantial experimental evidence that the constitution of this ester was not accurately represented by the usually accepted formula (I).

(I.)



$$\mathrm{O{=}S}<\begin{matrix}\mathrm{OEt}\\ \mathrm{C_7H_7}\end{matrix}$$



$$\overset{-}{\mathrm{O}}-\overset{+}{\mathrm{S}}<\begin{matrix}\mathrm{OEt}\\ \mathrm{C_7H_7}\end{matrix}$$

(II.)

This formula is also in conflict with the postulates of the newer electronic theories of valency, since the presence of a true double bond between the sulphur and the sulphoxyl oxygen atom would create a surplus of valency electrons (10 instead of 8) in the valency shell of the sulphur atom. According to these theories of valency

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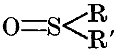
* In this and each of the following analyses the three weights recorded are respectively the quantity of substance taken and the quantities of mixed silver halides found and calculated.

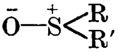
the sulphur atom contributes the two electrons that make up the duplet by which its union with the sulphoxyl oxygen atom is denoted, and Lowry has suggested (*Trans. Faraday Soc.*, 1923, **18**, 385) that in such cases the union should be indicated by an electrovalency and a covalency, *i. e.*, by a semipolar double bond. Experimental support for this suggestion has been obtained by Sugden, Reed, and Wilkins (J., 1925, **127**, 1525), who determined the molecular parachors (Sugden, J., 1924, **125**, 1177) of compounds containing sulphur linked to oxygen and deduced that the parachor of this linking (a semipolar double bond) was — 1·6 instead of 23·2 (the parachor of a true double bond). Since the determination of the molecular parachor of ethyl *dl-p*-toluenesulphinate (Phillips, *loc. cit.*, p. 2570) revealed that the sulphur and the sulphoxyl oxygen atom were linked by a semipolar double bond, formula (II) was adopted as more accurately representing the constitution of this ester. The newly discovered asymmetric ester molecule could then be considered to assume a tetrahedral configuration in which the apex was occupied by the positively charged sulphur atom, two other corners by the *p*-tolyl and ethoxy-groups respectively, whilst the remaining corner was occupied by the oxygen atom united to the sulphur atom by the semipolar double bond.

From such considerations it was at once evident that an alteration in the accepted formula of sulphoxides (III) could be suggested, and the new formula (IV) carries with it the implication that, like the *n*-alkyl esters of *p*-toluenesulphinic acid, mixed sulphoxides should be capable of existing in an optically active state.

(III.)



$\mathrm{O{=}S}<\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}$,

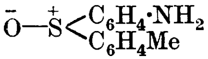


$\overset{-}{\mathrm{O}}-\overset{+}{\mathrm{S}}<\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}$,

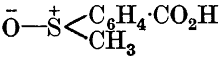
(IV.)

4′-*Amino*-4-*methyldiphenyl sulphoxide* (V) and m-*carboxyphenyl methyl sulphoxide* (VI) were therefore prepared and examined, and it was found that they were resolvable into enantiomorphous modifications.

(V.)



$\overset{-}{\mathrm{O}}-\overset{+}{\mathrm{S}}<\begin{matrix}\mathrm{C_6H_4{\cdot}NH_2}\\ \mathrm{C_6H_4Me}\end{matrix}$



$\overset{-}{\mathrm{O}}-\overset{+}{\mathrm{S}}<\begin{matrix}\mathrm{C_6H_4{\cdot}CO_2H}\\ \mathrm{CH_3}\end{matrix}$

(VI.)

Therefore it can now be regarded as definitely established that the fourth valency of quadrivalent sulphur differs from the three other valencies. This experimental fact is in agreement with the electronic theories of valency, according to which sulphur, when quadrivalent, is linked to other atoms by three covalencies and one electrovalency, a conclusion which re-states in other terms the suggestion of Werner (" Lehrbuch der Stereochemie," 1904, p. 317) that one of the four valency units of quadrivalent sulphur is co-ordinated.

4′-*Amino*-4-*methyldiphenyl Sulphoxide.*

dl-4′-Amino-4-methyldiphenyl sulphoxide (V) was prepared by the interaction of aniline and *p*-toluenesulphinic acid, a method by which Hinsberg (*Ber.*, 1908, **41**, 113), using benzenesulphinic acid and aniline, prepared *dl*-*p*-aminodiphenyl sulphoxide.*

dl-4′-Amino-4-methyldiphenyl sulphoxide readily combined with *d*-camphorsulphonic acid to give a salt which could be recrystallised, without the obvious occurrence of hydrolysis, from water containing a small quantity of that acid. The d-*camphorsulphonate* thus obtained was not optically pure, but nevertheless it gave on decomposition a dextrorotatory *sulphoxide* with $[\alpha]_{5461}$ + 60·1° in chloroform solution. This sulphoxide, on repeated recrystallisation from aqueous ethyl alcohol, rapidly reached a constant rotatory power in ethyl-alcoholic solution of $[\alpha]_{5461}^{25^\circ}$ + 123°. The lævorotatory sulphoxide recovered from the mother-liquors of the recrystallisations of the *d*-camphorsulphonate was combined with *l*-camphorsulphonic acid. The l-*camphorsulphonate* obtained, after recrystallisation from dilute aqueous solutions of l-camphorsulphonic acid until its rotatory power remained unchanged by further recrystallisation, gave on decomposition l-4′-*amino*-4-*methyldiphenyl sulphoxide* with $[\alpha]_{5461}^{25^\circ}$ − 122° in ethyl alcohol, a value equal in magnitude to that obtained for the dextrorotatory isomeride. Other determinations of the specific rotatory power of the lævorotatory sulphoxide are recorded in Table I.

m-*Carboxyphenyl Methyl Sulphoxide.*

dl-*m*-Carboxyphenyl methyl sulphoxide (VI), m. p. 171—172°, was prepared by the oxidation with hydrogen peroxide of the potassium salt of the corresponding sulphide (Smiles and Stewart, J., 1921, **119**, 1792) dissolved in water. Its *brucine* salt, after

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* That during such interactions the R·SO· group enters the aniline nucleus in the *p*-position was proved by Hinsberg (*loc. cit.*), who showed that the aminodiphenyl sulphoxide produced from aniline and benzenesulphinic acid gave an aminodiphenyl sulphide, m. p. 95° (acetyl derivative, m. p. 148°), on reduction. Kehrmann and Bauer (*Ber.*, 1896, **29**, 2364) obtained *p*-aminodiphenyl sulphide, m. p. 93° (acetyl derivative, m. p. 146°), by the following series of reactions, which leave no doubt as to the correct orientation of this sulphide : 4 : 4′-dinitrodiphenyl sulphide, obtained by the interaction of sodium sulphide and *p*-chloronitrobenzene, gave, on reduction with ammonium sulphide, 4-nitro-4′-aminodiphenyl sulphide; elimination of the amino-group from this sulphide and reduction of the *p*-nitrodiphenyl sulphide obtained gave the required *p*-aminodiphenyl sulphide.

TABLE I.

Observed Rotatory Powers of 4'-Amino-4-methyldiphenyl Sulphoxide in Solvents.

c = g. of *l*-sulphoxide in 100 c.c. of solution. $l = 2$. $\alpha = 0{\cdot}02\,c\,[\alpha]$.

		$\alpha_{\lambda}^{25^\circ}$.			
Solvent.	*c*.	λ 6708.	λ 5893.	λ 5461.	λ 4359.
Chloroform	1·2580	−1·30°	−1·76°	−2·23°	−4·71°
Ethyl alcohol	1·2110	1·83	2·35	2·95	6·17
Pyridine	1·3375	2·52	3·37	4·21	8·97
1·04*N*-Hydrochloric acid	1·2430	+0·69	+0·86	+1·16	+2·19

recrystallisation from methyl alcohol until no further increase in its rotatory power occurred, gave on decomposition d-m-*carboxyphenyl methyl sulphoxide* with $[\alpha]_{5461}$ + 125° in methyl alcohol. This dextrorotatory sulphoxide was, however, optically impure, since by fractional recrystallisation from mixtures of chloroform and light petroleum it was separated into fractions with slightly different rotatory powers. It was therefore combined with *l*-menthylamine, and the *salt* obtained ($[\alpha]_{5461}$ + 66°) recrystallised from acetone until its rotatory power was unaltered by subsequent recrystallisation. It then had $[\alpha]_{5461}$ + 69°. On the decomposition of this *l*-menthylamine salt, *d*-*m*-carboxyphenyl methyl sulphoxide was obtained with m. p. 134°, and with $[\alpha]_{5461}$ + 137° in methyl-alcoholic solution.

The more soluble *brucine* salt recovered from the first mother-liquor was decomposed with *N*-sodium hydroxide solution, a concentrated solution of the sodium salt of the lævorotatory sulphoxide being eventually obtained and acidified. This solution was then extracted with chloroform insufficient in amount to dissolve completely the sulphoxide which had separated. The sulphoxide which remained undissolved had m. p. 170° and $[\alpha]_{5461}$ − 8° in methyl alcohol, whilst the *sulphoxide* recovered from the chloroform extract by the addition of light petroleum had m. p. 133° and $[\alpha]_{5461}$ − 122°. Partial solution of the sulphoxide ($[\alpha]_{5461}$ − 122°) in chloroform did not lead to any further separation, since the sulphoxide which dissolved was recovered with the same rotatory power. The chloroform did not therefore cause the separation previously observed and it thus appeared that the precipitation of an optically impure sulphoxide from its solution in aqueous sodium hydroxide, by the addition of acids, favoured the formation of the *dl*-sulphoxide, which is sparingly soluble in chloroform. That this explanation is substantially correct was proved by subjecting the sulphoxide with $[\alpha]_{5461}$ − 122° twice to such treatment; it was then recovered from the final chloroform extract with $[\alpha]_{5461}$ − 133·5°. This value (within the limits of experimental error) is almost equal in magnitude to the value obtained for the rotatory power of the dextrorotatory isomeride and it is therefore not surprising that a further repetition of the above process (using the sulphoxide with $[\alpha]_{5461}$ − 133·5°) did not result in any increase in its rotatory power.

Other determinations of the specific rotatory power of the *d*-sulphoxide and of its sodium salt are recorded in Table II.

Table II.

Observed Rotatory Powers of d-m-*Carboxyphenyl Methyl Sulphoxide in Solvents.*

c = g. of *d*-sulphoxide in 100 c.c. of solution. $l = 1$. $\alpha = 0{\cdot}01\, c\, [\alpha]$.

		$\alpha_\lambda^{25^\circ}$.			
Solvent.	c.	λ 6708.	λ 5893.	λ 5461.	λ 4359.
Methyl alcohol	2·515	+2·17°	+2·87°	+3·46°	+6·95°
Ethyl alcohol	2·515	2·24	3·09	3·77	7·68
Chloroform *	1·265	2·92	4·07	5·02	10·11
Pyridine	2·515	2·44	3·25	4·04	8·34

* $l = 2$.

The Specific Rotatory Power of the Sodium Salt of d-m-*Carboxyphenyl Methyl Sulphoxide.*

Water †	2·830	+1·70	+2·42	+3·00	+5·98

† This solution was prepared by diluting to the required volume a solution of a known weight of the *d*-sulphoxide in the calculated quantity of standard sodium hydroxide.

Some Properties of the Optically Active Sulphoxides.

Certain notable characteristics of the optically active sulphoxides described are worthy of brief comment. In both the examples studied, the *dl*-sulphoxides are racemic compounds with physical properties widely different from those of the optically active enantiomorphs. For example, when chloroform solutions containing equal quantities of the optically active modifications are mixed, the sparingly soluble *dl*-sulphoxide of much higher melting point crystallises out. This marked racemic character of the *dl*-sulphoxides can be contrasted with the apparently unimolecular character of the liquid ethyl *dl*-*p*-toluenesulphinate as shown by measurements of its surface tension (Phillips, *loc. cit.*, p. 2570).

The asymmetric complex contained in the optically active sulphoxides is destroyed on oxidation, the sulphones thus produced being optically inactive. In the same way optically active ethyl *p*-toluenesulphinate on oxidation (*loc. cit.*, p. 2579) gave optically inactive ethyl *p*-toluenesulphonate.

It was also shown (*loc. cit.*, p. 2560) that esters of *p*-toluenesulphinic acid which contained the newly discovered asymmetric complex in an optically active state exhibited a marked mutarotation. It was suggested that this might be ascribed to an alteration in the normal linking of the sulphur atom, giving rise to a labile form of these esters which was capable of yielding either stereoisomeride by the reverse isomeric change. An analogous isomeric change has not been detected in the optically active sulphoxides now described; the experiments so far attempted, however, have not been of a sufficiently searching character to reveal a possible slow mutarotation such as was typical of the sulphinic esters. Certain experimental difficulties encountered during the attempts made to find a satisfactory method of decomposing the brucine salt of *d*-*m*-carboxyphenyl methyl sulphoxide without loss of the sulphoxide, suggest, however, that this sulphoxide may readily undergo isomerisation leading to decomposition which may be the counterpart in this compound of the observed mutarotation of the sulphinic esters. In this connexion the study of the dynamic isomerism of benzyl sulphoxide by Smythe (J., 1909, **95**, 349) is of interest, as is also the discovery by Pummerer (*Ber.*, 1909, **42**, 2282) that both *p*-tolyl- and phenyl-sulphoxyacetic acids are readily decomposed by traces of mineral acids into the corresponding aromatic thiols and glyoxylic acid.

Under the experimental conditions employed, *l*-4′-amino-4-methyldiphenyl sulphoxide and its acetyl derivative and also *d*-*m*-carboxyphenyl methyl sulphoxide exhibit complex rotatory dispersion, since curves are obtained when $1/\alpha$ for these compounds is plotted against λ^2. Owing to the relatively complex constitutions of these sulphoxides it is difficult to ascribe this phenomenon to any particular factor. It is possible, however, that it may be connected with their aromatic character * and also with solvent action accentuated by the presence of the semipolar double bond.

Lastly, it is noteworthy that, as in the case of many optically active carbon compounds containing an amino-group, the sign of the rotatory power of *l*-4′-amino-4-methyldiphenyl sulphoxide is reversed in hydrochloric acid solution.

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* Optically active secondary alcohols which contain an aromatic nucleus often exhibit complex rotatory dispersion, a phenomenon which is rarely encountered amongst purely aliphatic alcohols (see Part XXV, J., 1925, **127**, 1094).

EXPERIMENTAL.

Preparation and Resolution of dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*

dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*—A mixture of *p*-toluenesulphinic acid (1 part) and aniline (4 parts) was heated at 110—115° for 30 hours. The excess of aniline was removed in a current of steam, and the non-volatile residue dissolved in ether. The ethereal solution was washed several times with dilute hydrochloric acid, and the *dl*-sulphoxide precipitated from the acid solution by the addition of sodium carbonate. dl-4′-*Amino*-4-*methyldiphenyl sulphoxide* crystallised from ethyl alcohol, after treatment of the hot solution with "norit," in colourless needles, m. p. 169—170°. Yield about 27% (Found: C, 67·6; H, 6·0; N, 6·0. $C_{13}H_{13}ONS$ requires C, 67·5; H, 5·6; N, 6·1%).

On removal of the ether from the washed and dried ethereal solution a non-basic residue remained which slowly crystallised and after crystallisation from ethyl alcohol had m. p. 78°. It was proved to be di-*p*-tolyl disulphoxide by comparison with an authentic specimen prepared from *p*-toluenesulphinic acid by Hilditch's method (J., 1910, **97**, 1096).

Resolution of dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*—The *dl*-sulphoxide (55 g.) was dissolved in a hot solution of *d*-camphorsulphonic acid (60 g.) * in water (100 c.c.). The optically impure *d*-4′-amino-4-methyldiphenyl sulphoxide *d*-camphorsulphonate deposited on cooling was recrystallised from water (100 c.c.) containing *d*-camphorsulphonic acid (2 g.).

l-4′-*Amino*-4-*methyldiphenyl sulphoxide.* By the addition of ammonia to the combined mother-liquors from the two crystallisations described above, a lævorotatory sulphoxide (26 g.) was obtained with $[\alpha]_{5461}$ − 37° ($c = 1{\cdot}0$, $l = 2{\cdot}0$) in chloroform solution. It crystallised from hot ethyl alcohol on cooling and then weighed 20 g., had m. p. 162—166°, and $[\alpha]_{5461}$ − 24° in chloroform ($c = 1{\cdot}32, l = 2{\cdot}0$). The more soluble lævorotatory sulphoxide was recovered from the concentrated alcoholic mother-liquor by the addition of water and was obtained as a bulky crop of fine, hair-like needles (6 g.) with $[\alpha]_{5461}$ − 81·5° in chloroform solution ($c = 1{\cdot}0$, $l = 2{\cdot}0$). This lævorotatory sulphoxide was dissolved in a hot solution of *l*-camphorsulphonic acid (6·5 g.) in water (25 c.c.), and on cooling, an optically impure *l*-4′-amino-4-methyldiphenylsulphoxide *l*-camphorsulphonate was deposited as rosettes of fine needles. By the addition of water to the filtrate from this

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* The theoretical quantity is 55 g. The camphorsulphonates of this sulphoxide were readily hydrolysed, but crystallised uncontaminated by free sulphoxide from dilute aqueous solutions of the camphorsulphonic acids.

salt a lævorotatory sulphoxide was obtained with $[\alpha]_{5461}$ — 10·7° in chloroform solution, showing that the separation was proceeding rapidly. After six recrystallisations from water (containing small quantities of *l*-camphorsulphonic acid) the salt was considered to be optically pure, since the *l*-sulphoxides recovered from a portion of the final crop and from the final mother-liquor had identical specific rotatory powers.

Thus isolated, l-4′-*amino*-4-*methyldiphenyl sulphoxide* l-*camphorsulphonate* had m. p. 133—134°, and $[\alpha]_{5461}^{25°}$ — 18·1° in ethyl-alcoholic solution ($c = 3·75$, $l = 2·0$).

l-4′-*Amino*-4-*methyldiphenyl sulphoxide* obtained by the decomposition of this salt crystallised from aqueous ethyl alcohol in long, slender, hair-like needles, m. p. 151°. (Found : C, 67·2; H, 5·9; S, 14·3%). Its specific rotatory powers in various solvents are recorded in Table I.

d-4′-*Amino*-4-*methyldiphenyl sulphoxide.* The optically impure salt of this sulphoxide with *d*-camphorsulphonic acid obtained from the *dl*-sulphoxide as previously described (p. 2085) was recrystallised fifteen times from dilute aqueous solutions of *d*-camphorsulphonic acid. On decomposition of a portion of the final crop a dextrorotatory sulphoxide was obtained with $[\alpha]_{5461}$ + 60° in chloroform ($c = 1·25$, $l = 2·0$), a value identical with the rotatory power of the dextrorotatory sulphoxide obtained from the final mother-liquor. Since five additional crystallisations of the salt produced no further resolution,* it was decomposed and the sulphoxide obtained was twice crystallised from ethyl alcohol. d-4′-*Amino*-4-*methyldiphenyl sulphoxide* was thus obtained, m. p. 151°, with $[\alpha]_{5461}$ + 89·9° in chloroform solution ($c = 1·279$, $l = 2·0$) and $[\alpha]_{5461}^{25°}$ + 123° in ethyl-alcoholic solution ($c = 1·209$, $l = 2·0$), values equal in magnitude, within the limits of experimental error, to those possessed by the *l*-sulphoxide obtained, as described, from *l*-4′-amino-4-methyldiphenyl sulphoxide *l*-camphorsulphonate (Found : C, 67·6; H, 5·8; S, 13·8%).

d-4′-*Amino*-4-*methyldiphenyl sulphoxide* d-*camphorsulphonate* prepared from this sulphoxide had m. p. 133—134° and $[\alpha]_{5461}^{25°}$ + 17·2° in ethyl alcohol ($c = 3·75$, $l = 2·0$).

Recombination of d- *and* l-4′-*Amino*-4-*methyldiphenyl Sulphoxides.*—A solution of the *d*-sulphoxide, m. p. 151° (0·2 g.), in warm ethyl alcohol (1·5 c.c.) was added to a similar solution of the *l*-sulphoxide, m. p. 151°. The needles obtained (0·33 g.) had m. p. 169—170° alone and when mixed with the *dl*-sulphoxide.

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* This result was unexpected, since the resolution of an optically impure *l*-4′-amino-4-methyldiphenyl sulphoxide *l*-camphorsulphonate prepared from a lævorotatory sulphoxide with $[\alpha]_{5461}$ —42° proceeded quite normally.

dl-4′-*Acetylamino-4-methyldiphenyl Sulphoxide.* — This sulphoxide crystallised from a solution of the *dl*-4′-amino-4-methyldiphenyl sulphoxide (7 g.) in acetic anhydride (7 c.c.). It was obtained after recrystallisation from aqueous ethyl alcohol as bulky, feathery needles, m. p. 183—184° (Found: C, 65·3; H, 5·6. $C_{15}H_{15}ONS$ requires C, 65·9; H, 5·5%).

l-4′-*Acetylamino-4-methyldiphenyl Sulphoxide.*—This sulphoxide was prepared as described above from the *l*-sulphoxide and crystallised from aqueous ethyl alcohol in small prisms, m. p. 173—174°. 0·2490 G. was made up to 20 c.c. with ethyl alcohol, and the rotatory power of the solution obtained was determined in a 200 mm. tube at 25°:

	λ 6708.	λ 5893.	λ 5461.	λ 4359.
$\alpha_\lambda^{25°}$	−1·07°	−1·34°	−1·68°	−3·92°
$[\alpha]^{25°}$	−43·0	−53·8	−66·2	−157·0

d-4′-*Acetylamino-4-methyldiphenyl sulphoxide* prepared from the *d*-sulphoxide was repeatedly crystallised from ethyl alcohol and aqueous acetic acid, but its specific rotatory power in ethyl-alcoholic solution ($c = 1·25$, $l = 2·0$) remained unchanged at $[\alpha]_{6708}^{25°}$ + 42·0°, $[\alpha]_{5893}^{25°}$ + 52·4°, $[\alpha]_{5461}^{25°}$ + 66·4°, values in close agreement with those obtained for the lævorotatory isomeride.

4′-*Acetylamino-4-methyldiphenyl Sulphone.*—To a solution of *dl*-4′-amino-4-methyldiphenyl sulphoxide (1·36 g.) in warm acetic acid (50 c.c.), finely ground potassium permanganate (1 g.) was added. The mixture was gently heated and agitated during ½ hour and the solution was then diluted with water and decolorised with sulphur dioxide. The sulphone produced, after recrystallisation from aqueous ethyl alcohol, had m. p. 194° (Found: C, 62·2; H, 5·2. $C_{15}H_{15}O_2NS$ requires C, 62·3; H, 5·2%).

Oxidation of d-4′-*Acetylamino-4-methyldiphenyl Sulphoxide.*—1 G. of the *d*-sulphoxide was oxidised as described above. The sulphone obtained had m. p. 192° alone and when mixed with the sulphone obtained by the oxidation of the *dl*-sulphoxide. 0·5 G. made up to 20 c.c. with pyridine was optically inactive to light of λ 5461 and of λ 4359.

Preparation and Resolution of m-*Carboxyphenyl Methyl Sulphoxide.*

m-Chlorosulphonylbenzoic acid (Smiles and Stewart, *loc. cit.*) was reduced in acetic acid solution with zinc and concentrated hydrochloric acid to *m*-thiolbenzoic acid (compare the reduction of *p*-chlorosulphonylbenzoic acid, Smiles and Harrison, J., 1922, **121**, 2024), which was converted into *m*-methylthiolbenzoic acid by treatment of its solution in aqueous sodium hydroxide with methyl sulphate (Smiles and Stewart, *loc. cit.*).

dl-m-*Carboxyphenyl Methyl Sulphoxide.*—The oxidation of *m*-methylthiolbenzoic acid in acetone solution by means of 30% hydrogen peroxide led to the formation of a considerable proportion of *m*-carboxyphenylmethylsulphone (compare Gadzar and Smiles, J., 1908, **93**, 1833). The following procedure was therefore adopted. Hydrogen peroxide (30% ; 40 g.) was gradually added with stirring to a solution at 40° of *m*-methylthiolbenzoic acid (30 g.) in water (250 c.c.) containing potassium carbonate (37 g.). The solution obtained was evaporated to a small bulk, cooled, and acidified; impure *m*-carboxyphenyl methyl sulphoxide, m. p. 169—170°, was then precipitated. The crude sulphoxide was dissolved in concentrated hydrochloric acid (4 parts), the insoluble sulphone filtered off, and the filtrate diluted with water; the dl-m-*carboxyphenyl methyl sulphoxide*, m. p. 170—172°, slowly crystallised (Found : C, 51·9; H, 4·5. $C_8H_8O_3S$ requires C, 52·2; H, 4·4%. 0·3182 G. neutralised 0·0685 g. of sodium hydroxide. Theory, 0·0691 g.). *dl-m*-Carboxyphenyl methyl sulphoxide is sparingly soluble in water, ethyl alcohol, benzene, chloroform, and acetone, and it cannot be purified (when contaminated with traces of the corresponding sulphone) by recrystallisation from these solvents.

d-m-*Carboxyphenyl Methyl Sulphoxide.*—*Brucine salt.* When a filtered solution of brucine (207 g.) and the *dl*-sulphoxide (97 g.) in hot acetone (3 litres) was cooled, the *brucine* salt (245 g.) crystallised; it had m. p. 115° and $[\alpha]_{5461}$ — 13·2° in chloroform ($c = 3{\cdot}95$, $l = 2{\cdot}0$). Since it had $[\alpha]_{5461}$ — 14° after crystallisation from acetone (6 litres), it was crystallised, together with the salt which was recovered from the mother-liquors, from methyl alcohol (500 c.c.). The salt thus obtained (130 g.) had m. p. 128—130° and $[\alpha]_{5461} + 8{\cdot}5°$ in chloroform ($c = 3{\cdot}96$, $l = 2{\cdot}0$). After twelve further recrystallisations from methyl alcohol subsequent recrystallisation from this solvent and also from water produced no further change in the rotatory power of the salt, which then had m. p. 136—137°, and $[\alpha]_{5461} + 40{\cdot}3°$ in chloroform ($c = 2{\cdot}00$, $l = 2{\cdot}0$) (Found : C, 64·2 ; H, 6·2. $C_{31}H_{34}O_7N_2S$ requires C, 64·3 ; H, 5·9%).

Decomposition of the brucine salt in aqueous solution by an excess or a theoretical quantity of either ammonia, potassium hydroxide, or hydrochloric acid gave much less than the theoretical quantity of dextrorotatory sulphoxide. Titration of aqueous solutions of the salt with *N*/10-sodium hydroxide and phenolphthalein showed that under such conditions the salt was incapable of neutralising the expected quantity of alkali; it was capable of so doing (as a subsequent experiment showed) when dissolved in 50% aqueous ethyl alcohol.

A solution of the final fraction of the brucine salt ($[\alpha]_{5461} + 40{\cdot}3°$;

25 g.) in ethyl alcohol (100 c.c.) was therefore diluted with water (55 c.c.), and *N*-sodium hydroxide solution added until the mixture was alkaline. It was then extracted seven times with chloroform to remove the liberated brucine, and the aqueous solution of the sodium salt of the sulphoxide remaining was evaporated to 30 c.c. The ice-cold concentrated solution of this salt was carefully acidified and extracted repeatedly with chloroform. The chloroform extract was dried with anhydrous sodium sulphate and then gave on dilution with light petroleum a crystalline dextrorotatory sulphoxide (6 g.), m. p. 130—131°, $[\alpha]_{5461} + 125°$ in methyl alcohol ($c = 2{\cdot}04$, $l = 2{\cdot}0$). Subsequent crystallisation of this dextrorotatory sulphoxide from mixtures of chloroform and light petroleum indicated that it was not optically pure, since by such means it was divided into fractions with $[\alpha]_{5461} + 128°$ and $[\alpha]_{5461} + 103°$ respectively. The fraction with $[\alpha]_{5461} + 128°$ recrystallised unchanged in rotatory power from chloroform–light petroleum, and in order to test its optical purity its salt with *l*-menthylamine was prepared and recrystallised.

l-*Menthylamine salt.* To a hot solution of the dextrorotatory sulphoxide (4·2 g.; $[\alpha]_{5461} + 128°$) in acetone (30 c.c.) *l*-menthylamine (3·5 g.) in acetone (15 c.c.) was added. On cooling the filtered solution, the l-*menthylamine* salt crystallised; it had $[\alpha]_{5461} + 66{\cdot}4°$ in ethyl alcohol ($c = 2{\cdot}50$, $l = 1{\cdot}0$). After recrystallisation from acetone (500 c.c.) this salt was obtained with m. p. 171° and $[\alpha]_{5461} + 68{\cdot}9°$, a value which remained unchanged after recrystallisation of the salt from acetone. The *l*-menthylamine salt of *d*-*m*-carboxyphenyl methyl sulphoxide thus obtained was dissolved in 50% ethyl alcohol (130 c.c.), and the solution made alkaline with *N*-sodium hydroxide. The liberated *l*-menthylamine was removed by extraction with ether, and the aqueous solution of the sodium salt of the sulphoxide concentrated, cooled, and carefully acidified. The sulphoxide was extracted with chloroform, which was then dried and diluted with light petroleum. The d-m-*carboxyphenyl methyl sulphoxide* thus precipitated (Found: C, 52·2; H, 4·4%) had m. p. 134°, and $[\alpha]_{5461} + 137{\cdot}6°$ in methyl alcohol ($c = 2{\cdot}515$, $l = 1{\cdot}0$). Other determinations of its rotatory power are recorded in Table II.

l-m-*Carboxyphenyl Methyl Sulphoxide.*—A portion of the brucine salt (60 g.) (with approximately $[\alpha]_{5461} - 50°$ in chloroform solution) was dissolved in 50% ethyl alcohol, decomposed by the addition of *N*-sodium hydroxide, and a concentrated solution of the sodium salt of the lævorotatory sulphoxide was obtained from this reaction mixture as previously described. This concentrated solution was then acidified, and the solution and precipitated sulphoxide were extracted with chloroform. The sulphoxide (5·5 g.) which remained undissolved was removed from the aqueous solution and the chloroform extract. It had m. p. 170—171° and $[\alpha]_{5461}$ − 8·0° in methyl alcohol ($c = 2{\cdot}5$, $l = 1{\cdot}0$). From the dried chloroform extract light petroleum precipitated a lævorotatory sulphoxide (10 g.), m. p. 133°, $[\alpha]_{5461}$ − 122° in methyl alcohol ($c = 2{\cdot}5$, $l = 1{\cdot}0$). To test whether this sulphoxide could be further resolved by means of chloroform alone, 2 g. were warmed with chloroform (10 c.c.). From the cold chloroform solution, on addition of light petroleum, 0·65 g. of sulphoxide was recovered with $[\alpha]_{5893}$ − 102° in methyl alcohol ($c = 2{\cdot}52$, $l = 1{\cdot}0$), whilst the sulphoxide (1·3 g.) which had remained undissolved had $[\alpha]_{5893}$ − 103° under the same experimental conditions. As no separation had occurred, the whole of the lævorotatory sulphoxide ($[\alpha]_{5461}$ − 122°) was dissolved in dilute sodium hydroxide, and the solution obtained acidified and then extracted with chloroform as before. The sulphoxide recovered from this chloroform extract was again submitted to the same process, being finally obtained with $[\alpha]_{5461}$ − 133·5° in methyl alcohol ($c = 2{\cdot}5$, $l = 1{\cdot}0$). Repetition of the above process failed to produce any further increase in the rotatory power of this sulphoxide. The *l*-*m*-carboxyphenyl methyl sulphoxide thus obtained had m. p. 133° (Found : C, 52·0; H, 4·4%).

Recombination of the d- *and* l-m-*Carboxyphenyl Methyl Sulphoxides.*—Cold solutions of the *d*- and *l*-sulphoxides in chloroform (0·1 g. in 1·3 c.c.) were mixed. The crystals (0·17 g.), which were precipitated immediately, had m. p. 170°, alone, and when mixed with the *dl*-sulphoxide.

Oxidation of d-m-*Carboxyphenyl Methyl Sulphoxide.*—The *d*-sulphoxide (0·5 g.) in aqueous acetic acid (25 c.c.) was oxidised with potassium permanganate (0·35 g.). Sulphur dioxide was passed through the diluted reaction mixture, from which *m*-carboxyphenylmethylsulphone (0·26 g.) then slowly crystallised in glistening plates, m. p. 230°. 0·201 G. made up to 10 c.c. with 0·1*N*-potassium hydroxide was optically inactive.

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