XXX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXI. The Resolution of* m-*Carboxyphenylmethylsulphine-*p-*toluenesulphonylimine.*

By Sydney George Clarke, Joseph Kenyon, and Henry Phillips.

Raper discovered that the condensation of chloramine-T with dialkyl sulphides gave rise to compounds of a new type containing a quadrivalent sulphur atom linked to nitrogen. Such compounds were named sulphilimines by Mann and Pope (J., 1922, **121**, 1052), who expressed by the general formula $C_6H_4Me{\cdot}SO_2{\cdot}N{:}SXY$ the constitution of those sulphilimines arising by the use of chloramine-T. These authors (J., 1924, **125**, 911) also pointed out that "the sulphilimines might be expected to exist in enantiomorphously related forms owing to the operation of a trihedral disposition of the three valency directions of the doubly-linked nitrogen atom." It would appear from this statement that they considered that, in a sulphilimine of the above type, the *p*-toluenesulphonyl group was not in the same plane as the groups X and Y, a space arrangement which need not necessarily be similar (as Mann and Pope suggested it should be) to that existing in *cyclo*hexylene dithiocarbonate 2-pyridylhydrazone, which was resolved by Mills and Schindler (J., 1923, **123**, 312). This is true even if the $>S{:}N-$ group of the sulphilimine can produce a similar space arrangement as the $>C{:}N-$ group of the hydrazone. The problem involved was also considered by Mann and Pope to have a bearing on the question whether the four valencies of quadrivalent sulphur are identical or whether one is co-ordinated as was indicated by Werner ("Lehrbuch der Stereochemie," 1904, p. 316).

Mann and Pope prepared and examined *d*- and *l*-camphorylidenemethylethylsulphine-*p*-toluenesulphonylimine

$$(C_{10}H_{14}O{:}CH{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_6H_4Me)$$

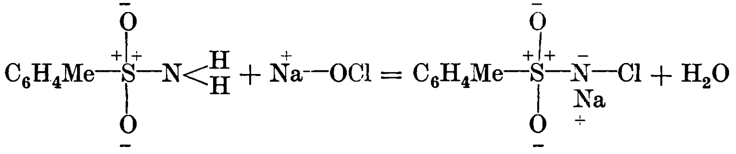
and stated that neither of these compounds furnished any indication of stereoisomerism of the type *d*-C,*d*-S and *d*-C,*l*-S and that therefore they proposed to investigate other methods for realising this type of isomerism.

In this communication, however, it is suggested that the sulphilimines contain the group $>\overset{+}{S}-\overset{-}{N}-$. Any question as to the disposition in space of the three valency directions of the nitrogen atom, which is now linked by two covalencies and one electrovalency, must therefore be left in abeyance. It is nevertheless suggested that sulphilimines of the type $C_6H_4Me{\cdot}SO_2{\cdot}\overset{-}{N}{\cdot}\overset{+}{S}XY$ should be capable of existing in enantiomorphously-related forms, since the quadrivalent sulphur atoms which they contain are in a state of combination analogous to that of the quadrivalent sulphur atoms of the esters of *p*-toluenesulphinic acid and of mixed sulphoxides the optically active forms of which have been described (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079). In other words, the positively charged sulphur atom of the sulphilimine molecule can be considered to occupy the apex of a tetrahedron at the other three corners of which lie the groups X and Y and the *p*-toluenesulphonamido-group the nitrogen atom of which bears a negative charge.

To support these suggestions, it is necessary to review the constitution of chloramine-T and its reactions with thio-ethers in the light of the newer electronic theories of valency and the investigations to which those theories have given rise.

The Constitution of Chloramine-T.

Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) have shown, by measurements of the molecular parachors of compounds containing a sexavalent sulphur atom linked to two oxygen atoms (*e.g.*, ethyl ethanesulphonate), that in such compounds the sulphur and oxygen atoms are linked by semipolar double bonds as had been suggested by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285). Hence the constitution of *p*-toluenesulphonamide, the parent substance of chloramine-T, is doubtless more accurately represented by the formula given in the equation below than by the structural formula by which it is usually indicated. The reaction which occurs when *p*-toluenesulphonamide is converted into chloramine-T by the action of sodium hypochlorite (Dakin, Cohen, Daufresne, and Kenyon, *Proc. Roy. Soc.*, 1916, *B*, **89**, 236) can then be represented by the following equation :

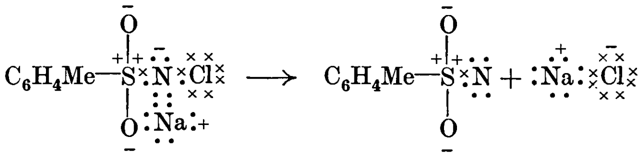


$$C_6H_4Me-\overset{\overset{\overset{-}{O}}{|}}{\underset{\underset{\underset{-}{O}}{|}}{\overset{+\,+}{S}}}-N<^{H}_{H}+\overset{+}{Na}-OCl=C_6H_4Me-\overset{\overset{\overset{-}{O}}{|}}{\underset{\underset{\underset{-}{O}}{|}}{\overset{+\,+}{S}}}-\underset{\underset{+}{Na}}{\overset{-}{N}}-Cl+H_2O$$

Thus it is suggested that the valencies of the tervalent nitrogen atom which chloramine-T contains are made up of two covalencies and one electrovalency. If, therefore, the sodium ion is considered to be closely attracted to the nitrogen atom, then this atom possesses the same type of tricovalency as that of the nitrogen atom of sodium phthalimide. It should be noticed, however, that the sodium ion can become attracted to either of the negatively charged sulphoxy-oxygen atoms in the molecule without causing any change in the mode of linking of the nitrogen atom. Hence it would appear that the formulation of chloramine-T as a derivative of *iso*chloramine with the constitution $C_6H_4Me{\cdot}SO(ONa){:}NCl$ (compare Chattaway, J., 1905, **87**, 146, 153; Dakin, Cohen, Daufresne, and Kenyon, *loc. cit.*; Mann and Pope, *loc. cit.*) is not only unnecessary but misleading, since it requires that the sexavalent sulphur atom should be surrounded by twelve valency electrons instead of the normal octet the presence of which around the sulphur atom in such compounds agrees with the experimental results of Sugden, Reed, and Wilkins (*loc. cit.*).

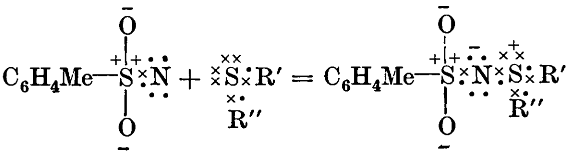
The Condensation of Chloramine-T with Thio-ethers.

The constitutional formula of a sulphilimine is more easily deduced if the condensation of the chloramine-T with the thio-ether is assumed to occur in two stages. Under the experimental conditions employed, during the first stage of the reaction the chloramine-T can be considered to decompose into sodium chloride and an active radical:



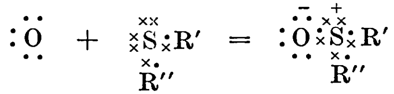
$$C_6H_4Me-\underset{\underset{\bar{O}\,:Na:^{+}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\times}{\times}\overset{-}{N}\overset{\times}{:}Cl \longrightarrow C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\times}{:}N + :\overset{+}{Na}:\overset{-}{Cl}$$

In the above formulæ the electrons represented by crosses in the valency octet of the nitrogen atom are contributed to that octet by the sulphur and chlorine atoms to which the nitrogen atom is united by covalencies. When chloramine-T decomposes as indicated above, it loses the chlorine atom as *an ion* and hence the active radical produced contains a nitrogen atom surrounded by a sextet of valency electrons. It can then be assumed that during the second stage of the condensation this nitrogen atom completes its octet at the expense of one of the two lone pairs of electrons present in the valency shell of the sulphur atom which the thio-ether contains.



$$C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\times}{:}N + \underset{R''}{\overset{\times\times}{S}}{:}R' = C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\times}{:}\overset{-}{N}\overset{\times}{:}\underset{R''}{\overset{+}{S}}\overset{\times}{}R'$$

These electronic formulæ reveal two points of interest. First, the nitrogen and sulphur atoms cannot become united by a true double bond (non-polar double bond), since such a linking would create a surplus of electrons (10 instead of 8) in the valency shells of both atoms. Secondly, the sulphur atom contributes both electrons to form the covalency by which it is subsequently united to the nitrogen atom, and after the union one of these electrons functions as though it had been contributed originally by the nitrogen atom. Hence the nitrogen atom acquires a negative charge (having gained an electron or, alternatively, gained a half share of two electrons), whilst the sulphur atom (having lost an electron, or, alternatively, lost a half share in two electrons) acquires a positive charge. The nitrogen and sulphur atoms thus become united by a semipolar double bond. When viewed from this standpoint, the formation of the sulphilimine becomes strictly analogous to the oxidation of a sulphide to a sulphoxide.



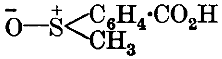
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \; + \; {}^{\times}_{\times}\underset{\underset{R''}{\times\cdot}}{\overset{\times\times}{S}}{}^{\times}_{\times}R' \; = \; :\underset{\cdot\cdot}{\overset{\overset{-}{\cdot\cdot}}{O}}{}^{\times}_{\times}\underset{\underset{R''}{\times\cdot}}{\overset{\overset{+}{\times\times}}{S}}{}^{\times}_{\times}R'$$

In this instance, the neutral oxygen atom with a sextet of valency electrons completes its octet, as did the nitrogen atom of the *p*-toluenesulphonamido-radical, at the expense of the valency electrons of the sulphur atom.

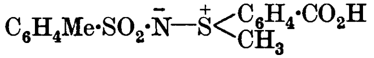
Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine.*

Since *dl*-*m*-carboxyphenyl methyl sulphoxide (I) was successfully resolved into its optically active forms by Harrison, Kenyon, and Phillips (*loc. cit.*), there appeared to be no reason, if the above arguments are valid, why the corresponding sulphilimine (II) should not also be capable of existing in enantiomorphously related forms.

(I.)



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



$$C_6H_4Me\cdot SO_2\cdot\overset{-}{N}-\overset{+}{S}<\begin{matrix}C_6H_4\cdot CO_2H\\ CH_3\end{matrix}$$

(II.)

dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was therefore prepared and examined. It was readily obtained by the condensation of chloramine-T with *m*-carboxyphenyl methyl sulphide. Its *brucine* salt, on recrystallisation from acetone, changed rapidly in rotatory power, and when optically pure the *l*-B, *l*-A salt had $[\alpha]_{5461}$ $-144°$ in ethyl-alcoholic solution. On decomposition of this salt with dilute hydrochloric acid the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was obtained with $[\alpha]_{5461}$ $-338°$, $[\alpha]_{4359}$ $-627°$ in ethyl-alcoholic solution. The more soluble brucine salt was recovered from the mother-liquors from the crystallisations of the *l*-B, *l*-A salt, and on decomposition gave a sulphilimine with $[\alpha]_{5461}$ +145°. This sulphilimine was combined with cinchonidine and the *cinchonidine* salt obtained was repeatedly crystallised from ethyl alcohol until its rotatory power was constant. It then had $[\alpha]_{5461}$ +48·3° in chloroform and on decomposition gave d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* with $[\alpha]_{5461}$ +337°, $[\alpha]_{4359}$ +627° in ethyl-alcoholic solution. The satisfactory agreement between the specific rotatory powers of the two enantiomorphs indicates that both were obtained optically pure. The specific rotatory powers of the optically pure sulphilimine in various solvents are in Table I.

TABLE I.

Specific Rotatory Powers of l-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine in Solvents.*

c = g. of l-sulphilimine in 100 c.c. of solution. $l = 2$. $a_{\lambda} = 0{\cdot}02c[a]_{\lambda}$.

Solvents.	c.	λ_{6708}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4359}.
Ethyl alcohol	3·0000	209°	276°	293°	338°	627°
Pyridine	3·0000	190	255	265	308	583
Chloroform	0·2505	216	272	288	332	609
Ethyl acetate	0·4146	190	260	267	306	570
Glacial acetic acid ...	2·0000	190	253	266	306	569

This table shows that the specific rotatory power of the optically active sulphilimine is but slightly influenced by solvents. Under the experimental conditions employed, the sulphilimine exhibits complex rotatory dispersion (except possibly when dissolved in ethyl acetate), since curves are obtained when $1/\alpha$ for this compound is plotted against λ^2. Unlike the optically active sulphoxides previously described (Harrison, Kenyon, and Phillips, *loc. cit.*), which differed considerably in physical properties from their racemic modifications, the optically active sulphilimine now described is closely similar to the optically inactive compound. The specific rotatory power of the sulphilimine in solvents remains unchanged on standing, and in this respect it resembles the optically active sulphoxides (*loc. cit.*) rather than the esters of *p*-toluenesulphinic acid (Phillips, *loc. cit.*, p. 2573), which exhibit marked mutarotation in solution.

dl-m-Carboxyphenylmethylsulphine-*p*-toluenesulphonylimine was converted by the action of dilute hydrochloric acid into a mixture of *p*-toluenesulphonamide, *m*-carboxyphenyl methyl sulphide and sulphoxide, whilst the sulphonamide and *m*-carboxyphenylmethylsulphone were the sole products of the action of hydrogen peroxide. Further experiments are under consideration with the object of converting the sulphilimine into an unsymmetrical compound containing sexavalent sulphur.

EXPERIMENTAL.

dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—To a solution of *m*-methylthiolbenzoic acid (100 g.) in warm alcohol (500 c.c.) made just alkaline by the addition of 3*N*-sodium hydroxide, chloramine-T (190 g.; 1·1 mols.) in warm water (550 c.c.) was added, and the mixture heated on a steam-bath for 2 hours. Dilute hydrochloric acid was added to the resulting solution after cooling and dl-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* then separated, m. p. 160—164°. Yield 150 g. (75%). By recrystallisation from aqueous ethyl alcohol it was obtained as small needles, m. p. 173—175° (Found: C, 53·6; H, 4·5; N, 4·2. $C_{15}H_{15}O_4NS_2$ requires C, 53·4; H, 4·5; N, 4·2%. 0·3370 required 0·0404 of sodium hydroxide; theory requires 0·0400).

Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—(a) *By means of brucine.* To *dl-m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (105 g.) in acetone (500 c.c.), brucine (124 g.) was added, and the mixture was warmed until solution was complete. After cooling, the brucine salt (m. p. 95—105°) which crystallised was removed and recrystallised from four successive quantities (about 1000 c.c. in each case) of acetone until constancy of rotatory power was reached.

l-*Brucine* l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had m. p. 123—125°, $[\alpha]_{5461}$ −144°, $[\alpha]_{4359}$ −279° in ethyl alcohol ($l = 2$; $c = 2{\cdot}500$).

The optically pure salt, dissolved in warm ethyl alcohol, was added to dilute hydrochloric acid. After 48 hours, the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had separated completely. It crystallised from aqueous ethyl alcohol in prismatic needles, m. p. 172—173°. Its specific rotatory power in various solvents is recorded in Table I.

(b) *By means of cinchonidine.* The acetone mother-liquor from the first crystallisation of the brucine salt described above was added to dilute hydrochloric acid. The *d* + *dl-m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (18·5 g.; with $[\alpha]_{5461}$ +145°) which was precipitated was dissolved in ethyl alcohol (70 c.c.) and to the warm solution cinchonidine was added (16·1 g.). After standing over-night, the cinchonidine salt, m. p. 193—194°, was removed by filtration and repeatedly crystallised from the minimum of ethyl alcohol (about 200 c.c.) until its rotatory power remained unchanged. The l-*cinchonidine* d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* thus obtained had m. p. 204°, and $[\alpha]_{6708}^{17{\cdot}5^\circ}$ +29·42°, $[\alpha]_{5893}^{17{\cdot}5^\circ}$ +38·47°, $[\alpha]_{5780}^{17{\cdot}5^\circ}$ +46·76°, $[\alpha]_{5461}^{17{\cdot}5^\circ}$ + 48·27°, $[\alpha]_{4359}^{17{\cdot}5^\circ}$ + 102·6°, in chloroform solution ($c = 1{\cdot}326$, $l = 2{\cdot}0$). On decomposition, as previously described, it gave d-*carboxyphenyl-*

methylsulphine-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ $+ 337°$, $[\alpha]_{4359}$ $+627°$ in ethyl alcohol ($c = 2{\cdot}59$, $l = 1{\cdot}0$).

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrochloric Acid.*—A clear deep red solution was obtained by heating the *dl*-sulphilimine (6·74 g.) with concentrated hydrochloric acid (18 c.c.) on a steam-bath for 5 minutes. From the solution, neutralised by means of sodium carbonate, *p*-toluenesulphonamide (1·62 g.), m. p. 137°, was precipitated, whilst the products which remained dissolved consisted of two acids which were obtained after acidification of the concentrated solution, and were separated by fractional crystallisation from aqueous ethyl alcohol into *m*-carboxyphenyl methyl sulphoxide (1·4 g.), m. p. 171°, and *m*-methylthiolbenzoic acid (1·45 g.), m. p. 127—128°. The overall yield of hydrolytic products was therefore 66%.

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrogen Peroxide.*—A mixture of the sulphilimine (2 g.) and perhydrol (20 c.c.) was heated on a steam-bath with occasional shaking; a clear solution resulted after 15 minutes. The crystalline material (1·6 g.), m. p. 130—180°, which separated on cooling, was crystallised from a small bulk of ethyl alcohol, glistening leaflets (0·7 g.) of *m*-carboxyphenylmethylsulphone (m. p. 229—230° either alone or mixed with an authentic specimen) being obtained. After dilution, the filtrate yielded a second crop of crystals (0·9 g.) which proved to be *p*-toluenesulphonamide, m. p. 135—136°. The original hydrogen peroxide filtrate was evaporated to small bulk; a further quantity (0·29 g.) of *m*-carboxyphenylmethylsulphone was then obtained.

BATTERSEA POLYTECHNIC,
LONDON, S.W. 11.

[*Received, December 7th,* 1926.]