246. *The Mobility of Groups containing a Sulphur Atom.*

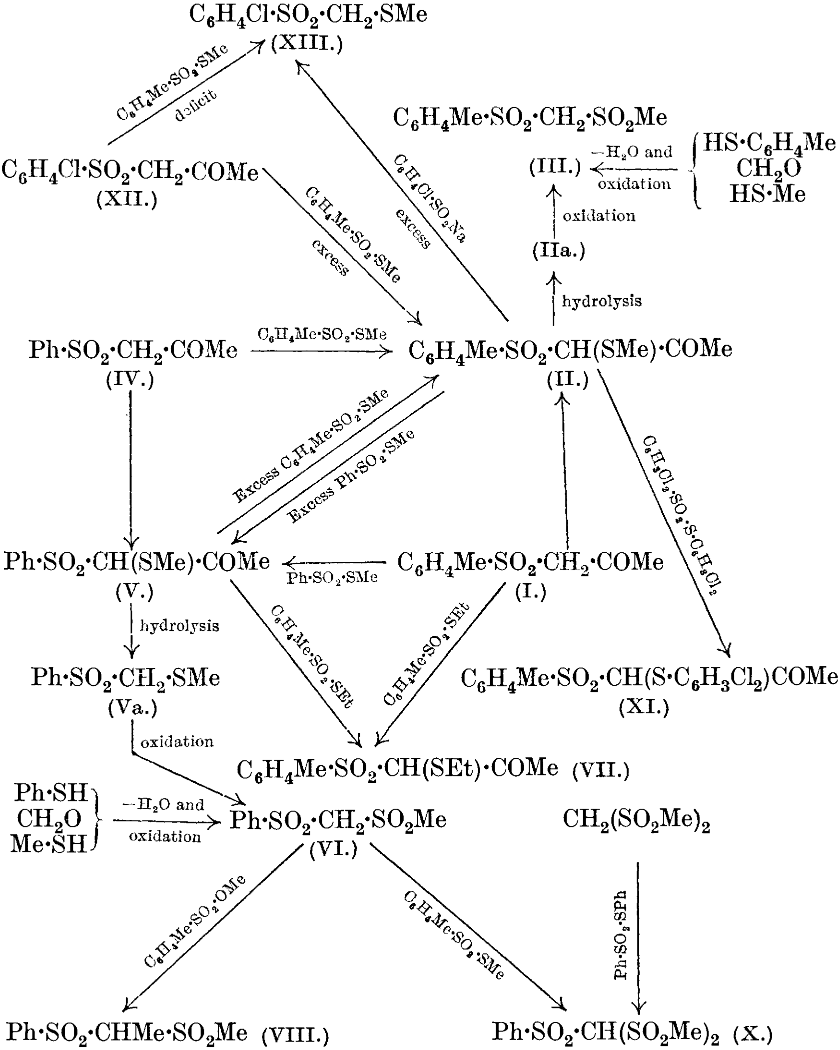
By DAVID T. GIBSON.

THE reaction between phenylsulphonylacetone (IV) and methyl *p*-toluenethiolsulphonate, giving *p*-tolylsulphonylmethylthioacetone (II) instead of the expected phenyl derivative (V) (J., 1931, 2641), has now been found to take place in two stages, for the direct substitution product (V) can be isolated by using a considerable excess of phenylsulphonylacetone and then converted by further action of methyl *p*-toluenethiolsulphonate into the tolyl derivative (II) : this can be reconverted into (V) by treatment with excess of *methyl benzenethiolsulphonate.*

The constitution of (V) was confirmed by its preparation from phenylsulphonylacetone and methyl benzenethiolsulphonate (the possibility of exchange thus being eliminated) and by the fact that on hydrolysis and oxidation it gave the same disulphonylmethane (VI) as is obtained by oxidation of the condensation product of phenyl mercaptan, formaldehyde, and methyl mercaptan.

p-Toluenesulphonylmethylthioacetone (II) was similarly correlated with the corresponding *p*-toluene derivative (III).

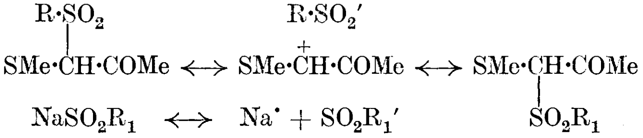
Similar exchanges were observed when methyl *p*-toluenesulphonate reacted with phenacylsulphone and, rather more slowly, with ethyl phenylsulphonylacetate.



From 4-*chlorophenylsulphonylacetone* and excess of methyl *p*-toluenethiolsulphonate, (II) and 4-chlorobenzenesulphinic acid were isolated; with a deficit of the thiolsulphonate, 4-*chlorophenylsulphonylmethylthiomethane* (XIII).

Mixtures may well have been formed in all these cases, but by using a fivefold excess of one reactant the principal component was readily purified.

The work of Otto (*J. pr. Chem.*, 1884, **30**, 171) and of Ingold (J., 1930, 705) on the decomposition of sulphones, and especially that of Kenyon and Phillips (J., 1930, 1680; equations iii, iv, and v) suggests that the interconversion of these phenyl and *p*-tolyl derivatives is due, not to exchange of phenyl for *p*-tolyl, but rather to the phenylsulphonyl group separating as an anion and its place being taken by a *p*-toluenesulphonyl ion. If we may assume the methylthio-group would direct ortho–para in aromatic substitution as Hammick and Illingworth's rule (J., 1930, 2358) indicates, then in an alkaline alcoholic solution of $SMe\cdot CH(SO_2R)\cdot COMe$ all the conditions (compare *Ann. Reports*, 1928, **26**, 127) are present for the separation of $R\cdot SO_2{}'$, and the exchanges described above may be compared with Burton's observation (J., 1928, 1653) that, in presence of tetramethylammonium acetate, phenylallyl nitrobenzoate is largely converted into cinnamyl acetate; and also with the rearrangement of 2-naphtholsulphone, which Smiles (J., 1931, 3264) considers is facilitated by the strongly positive character of the carbon atom. This explanation receives support from the observation that *p*-toluenesulphonylmethylthioacetone (II) is largely converted (with hydrolysis of the acetyl group) into the corresponding 4-chlorobenzene derivative (XIII) by warming in alcohol with sodium 4-chlorobenzenesulphinate:



$$\begin{array}{ccccc} R\cdot SO_2 & & R\cdot SO_2{}' & & \\ | & & + & & \\ SMe\cdot CH\cdot COMe & \longleftrightarrow & SMe\cdot CH\cdot COMe & \longleftrightarrow & SMe\cdot CH\cdot COMe \\ & & & & | \\ NaSO_2R_1 & \longleftrightarrow & Na^{\cdot} + SO_2R_1{}' & & SO_2R_1 \end{array}$$

In the experiments described below, the excess or deficit of the attacking ions has determined the main course of the reaction. Various unsuccessful attempts to convert phenylsulphonylacetone into *p*-tolylsulphonylacetone by treatment with excess of sodium *p*-toluenesulphinate confirm the view that the methylthio-group is essential to the exchange. It has indeed long been known (Otto, *loc. cit.*) that the sulphonylacetones and sulphonylacetic acids decompose in alkaline media readily to yield sulphones:

$$R\cdot SO_2\cdot CH_2 \,|\, COR \longrightarrow R\cdot SO_2\cdot CH_3 + HO\cdot COR.$$

On the other hand, Stuffer (*Ber.*, 1890, **23**, 3226) showed that the disulphonylmethanes (*e.g.*, VI) are very much more stable to alkalis than the sulphonylacetones. Although they react readily with methyl *p*-toluenethiolsulphonate, forming disulphonylmethylthiomethanes, no indication of exchange of RSO_2 groups has been observed even by using a tenfold excess of the thiolsulphonic ester.

This indicates that the enolisation of phenylsulphonylmethylthioacetone plays a part in the exchange, for this factor is absent in disulphonylmethylthiomethanes (compare Bell, J., 1931, 2346), but it fails to explain why even with sulphonylacetones no exchange should occur when the thiolsulphonic ester is purely aromatic (*e.g.*, $Ph·SO_2·SPh$).

In investigating this point, a further complication was revealed, for it was found that the alkylthio-groups were also susceptible to exchange; *e.g.*, phenylsulphonylmethylthioacetone was readily converted by ethyl *p*-toluenethiolsulphonate into p-*tolylsulphonylethylthioacetone* (VII). Further, the replacement of the alkylthio-group is not necessarily accompanied by that of the arylsulphonyl group, for 2 : 5-dichlorophenyl 2′ : 5′-dichlorobenzenethiolsulphonate converted *p*-tolylsulphonylmethylthioacetone into p-*tolylsulphonyl*-2 : 5-*dichlorophenylthioacetone* (XI). The acid formed was practically pure 2 : 5-dichlorobenzenesulphinic acid, m. p. 119—120°, indicating that no exchange of the sulphonyl radicals had occurred.

Now, Posner (*Ber.*, 1905, **38**, 646; 1907, **40**, 4788) assumed that his oxidised condensation product of thiophenol with acrylic acid, m. p. 56°, must be either $X·CH_2·CH(SO_2Ph)·CO_2H$ or $X·CH(SO_2Ph)·CH_2·CO_2H$. He preferred the latter ($X = H$), apparently overlooking the fact that both compounds had been synthesised by Otto (*J. pr. Chem.*, 1889, **40**, 5418; m. p. 115° : *Ber.*, 1888, **21**, 95; m. p. 124°). Similarly, Posner's oxidised thiophenol–cinnamic acid condensate (m. p. 172°; ethyl ester, m. p. 54°) cannot have had either formula ($X = Ph$), for the former (ethyl ester, m. p. 95°) was prepared by Michael and Comey (*Amer. Chem. J.*, 1883, **5**, 118), and the latter (m. p. 173°; ethyl ester, m. p. 139°) by Kohler and Reimer (*ibid.*, 1904, **31**, 163). The experiments described in the present paper suggest that Posner's discrepancies are to be explained by the (partial) migration of the sulphonyl group, giving rise to mixtures. The uncertainty of deducing the constitution of such sulphide condensation products from their oxidation products is illustrated by several examples recorded by Ashworth and Burkhardt (J., 1928, 1797).

EXPERIMENTAL.

Methyl benzenethiolsulphonate, b. p. 123°/1 mm. (Found: C, 44·9; H, 4·6. $C_7H_8O_2S_2$ requires C, 44·7; H, 4·3%), was prepared by methylating (methyl sulphate) sodium benzenethiolsulphonate, obtained from crystalline benzenesulphonyl chloride and a 50% solution of sodium sulphide at 30°.

Ethyl *p*-toluenethiolsulphonate (described as an oil by Otto, *Ber.*, 1882, **15**, 129) was similarly prepared; it solidified after fractionation at 145—150°/1 mm. and had m. p. 32° after recrystallisation from alcohol.

Phenylsulphonylmethylthioacetone (V), m. p. 60° (Found : C, 49·6; H, 5·15. $C_{10}H_{12}O_3S_2$ requires C, 49·25; H, 4·9%), was prepared by heating an alcoholic solution of phenylsulphonylacetone (1 mol.) and methyl benzenethiolsulphonate (1 mol.) with sodium carbonate (1 mol.). On hydrolysis it gave *phenylsulphonylmethylthiomethane* (Va), m. p. 84° (water) (Found : C, 48·0; H, 4·95. $C_8H_{10}O_2S_2$ requires C, 47·5; H, 4·95%), oxidation of which with permanganate gave phenylsulphonylmethylsulphonylmethane (VI), m. p. 147° (compare J., 1931, 2641).

p-Tolylsulphonylmethylthioacetone (II), prepared similarly from *p*-tolylsulphonylacetone and methyl *p*-toluenethiolsulphonate, had m. p. 81° (alcohol). On hydrolysis it yielded *p*-tolylsulphonylmethylthiomethane (IIa), m. p. 80° (water), which on oxidation gave p-*tolylsulphonylmethylsulphonylmethane* (III), m. p. 158° (benzene) (Found : C, 43·8; H, 5·05. $C_9H_{12}O_4S_2$ requires C, 43·6; H, 4·85%). When (II) was heated for 4 hours with methyl benzenethiolsulphonate and a trace of sodium carbonate, and the product hydrolysed, crystals (ligroin), m. p. 80°, were obtained which depressed the m. p. of (IIa) but not that of (Va). The experiment was repeated, sodium carbonate being omitted : the product, m. p. 79°, depressed the m. p. of (V) but not that of (II).

Phenylsulphonylacetone (5 mols.) and methyl *p*-toluenethiolsulphonate (1 mol.) with sodium carbonate gave an alkali-soluble product. After hydrolysis, the fraction more soluble in water melted at 80—83°. Mixed melting-point determinations showed that it was identical with (Va) and different from (IIa).

p-Tolylsulphonylacetone (1 mol.) and methyl benzenethiolsulphonate (3 mols.) gave a product, m. p. 59° (unchanged by V), and, on hydrolysis, a product, m. p. 79° (unchanged by Va, depressed by IIa).

Replacement of the Methylthio-group.—Phenylsulphonylmethylthioacetone (V), heated for 2 hours in alcohol with sodium carbonate (1 mol.) and ethyl *p*-toluenethiolsulphonate (15 mols.), gave an alkali-soluble product, which was precipitated by acetic acid. Recrystallised from that solvent, it melted at 93—94° and was identified as p-*tolylsulphonylethylthioacetone* (VII) by the m. p. (94°) of a mixture with a specimen prepared from *p*-tolylsulphonylacetone and ethyl *p*-toluenethiolsulphonate (Found : C, 53·0; H, 6·2. $C_{12}H_{16}O_3S_2$ requires C, 53·0; H, 5·9%). An attempt to convert it with excess of methyl toluenethiolsulphonate into (II) was not wholly successful, for only a small fraction of the reaction product melted at 78°. The difficulty is probably due to the incomplete conversion of ethylthio ⟶ methylthio, and as the latter is the more soluble, any unchanged ethylthio-compound separates first and the methylthio-compound must be sought in the mother-liquors. It was always easier to obtain pure *p*-tolyl derivatives from phenyl than vice versa, for the latter are usually the more soluble.

p-Tolylsulphonylmethylthioacetone, 2 : 5-dichlorophenyl 2′ : 5′-dichlorobenzenethiolsulphonate, and sodium ethoxide gave (4 hours) 2 : 5 : 2′ : 5′-tetrachlorodiphenyl disulphide (m. p. 79—81°), 2 : 5-dichlorobenzenesulphinic acid (m. p. 119°), and a product, m. p. 104°, soluble in sodium hydroxide but insoluble in sodium acetate. After recrystallisation from alcohol, p-*tolylsulphonyl-2 : 5-dichlorophenylthioacetone* (XI) melted at 111° (Found : C, 49·7; H, 3·8; S, 16·7. $C_{16}H_{14}O_3Cl_2S_2$ requires C, 49·4; H, 3·6; S, 16·4%).

Ethyl phenylsulphonylacetate, methyl benzenethiolsulphonate, and sodium carbonate (1 mol. of each) gave *ethyl phenylsulphonylmethylthioacetate*, m. p. 84° (Found : C, 48·3; H, 5·2. $C_{11}H_{14}O_4S_2$ requires C, 48·2; H, 5·1%), hydrolysis of which gave (Va), m. p. 84°.

Ethyl phenylsulphonylacetate (1 mol.) and methyl *p*-toluenethiolsulphonate (3 mols.) gave, after 20 hours, an alkali-soluble oil, which on hydrolysis gave crystals, m. p. 78—79° (unchanged by IIa, depressed by Va). The corresponding product after 3 hours' reaction melted at about 65° and was evidently a mixture of phenyl and tolyl compounds.

Phenylsulphonylacetone and diphenyl disulphoxide (equal mols.) with sodium ethoxide gave *phenylsulphonylphenylthioacetone* (VIII), m. p. 69—70° (Found : C, 58·6; H, 4·4. $C_{15}H_{14}O_3S_2$ requires C, 58·8; H, 4·6%).

p-Tolylsulphonylacetone and di-*p*-tolyl disulphoxide gave p-*tolylsulphonyl*-p-*tolylthioacetone* (IX), m. p. 98° (Found : C, 61·1; H, 5·3. $C_{17}H_{18}O_3S_2$ requires C, 61·1; H, 5·4%). It was different from phenylsulphonyl-*p*-tolylthioacetone, m. p. 99° (J., 1931, 2641). The latter was also obtained by the action of phenylsulphonylacetone (1 mol.) on di-*p*-tolyl disulphoxide (4 mols.); m. p. 94—95°, alone or mixed with the old specimen; m. p. 70—80° when mixed with (IX). This indicates that exchange of sulphonyl radicals takes place very slowly, if at all, with purely aromatic disulphoxides. This is confirmed by the observation that *p*-tolylsulphonylacetone (1 mol.) and diphenyl disulphoxide (5 mols.) give p-*tolylsulphonylphenylthioacetone*, m. p. 83°, which is different from the other three compounds (Found : C, 60·0; H, 5·2. $C_{16}H_{16}O_3S_2$ requires C, 59·8; H, 5·0%).

Phenylsulphonylacetophenone (1 mol.), methyl *p*-toluenethiolsulphonate (5 mols.), and sodium carbonate gave a solution, saturation of which with carbon dioxide precipitated a *double salt*, $C_6H_4Me{\cdot}SO_2{\cdot}CH(SMe){\cdot}COPh,Na_2CO_3$, which was recrystallised from alcohol (Found: Na, 10·4. $C_{16}H_{16}O_3S_2,Na_2CO_3$ requires Na, 10·8%). On hydrolysis it gave crystals, m. p. 80°, unchanged by admixture with (IIa).

No Exchange of Groups in Disulphonylmethanes.—Phenylsulphonylbis(methylsulphonyl)methane (X), m. p. 225°, was obtained either by condensation of (VI) with methyl *p*-toluenethiolsulphonate (10 mols.) and subsequent oxidation, or by condensation of bis(methylsulphonyl)methane and diphenyl disulphoxide (Found: S, 31·2; equiv., 328. $C_9H_{12}O_6S_3$ requires S, 30·8%; equiv., 312).

Similarly (interchanging "phenyl" and "*p*-tolyl" above), the two samples of p-*tolylsulphonylbis(methylsulphonyl)methane* melted at 185° either separately or together (Found: C, 36·6; H, 4·4. $C_{10}H_{14}O_6S_3$ requires C, 36·8; H, 4·3%).

Phenylsulphonylmethylsulphonylmethane (1 mol.) and di-*p*-tolyl disulphone (Kohler and McDonald, *Amer. Chem. J.*, 1899, **22**, 219) with sodium ethoxide did not give the expected trisulphone. A small amount of the alkali-soluble product was insoluble in hot water, and was identified as phenylsulphonylmethylsulphonyl-*p*-tolylthiomethane (m. p. 169°) by comparison with the sample previously prepared.

Phenylsulphonylmethylsulphonylmethane (1 mol.) and methyl *p*-toluenesulphonate with sodium ethoxide gave the corresponding sulphonyl-ethane (VIII), m. p. 101°, identified by mixed melting point with a specimen prepared from acetaldehyde (compare Peacock and Tha, J., 1928, 2303).

4-*Chlorophenylsulphonylacetone*, from sodium 4-chlorobenzenesulphinate and chloroacetone, melted at 79° (alcohol) (Found: C, 46·7; H, 3·97; S, 13·8. $C_9H_9O_3ClS$ requires C, 46·5; H, 3·85; S, 13·8%). When it was treated with methyl *p*-toluenethiolsulphonate (5 mols.) in alcohol (sodium carbonate), *p*-tolylsulphonylmethylthioacetone, m. p. 80° (not depressed by II) and 4-chlorobenzenesulphinic acid (qualitative) were obtained. When, however, the proportions of the reactants were reversed, and the alkali-soluble reaction product was precipitated with acetic acid and hydrolysed with dilute soda solution, 4-*chlorophenylsulphonylmethylthiomethane*, m. p. 93° (dil. acetic acid), was obtained (Found: C, 40·4; H, 4·2. $C_8H_9O_2ClS$ requires C, 40·6; H, 3·8%).

The same compound was also obtained by heating *p*-toluenesulphonylmethylthioacetone in alcohol with a fourfold excess of sodium 4-chlorobenzenesulphinate and a trace of sodium carbonate.

The residue, insoluble in alkali, melted at 93° and gave no depression with the previous specimen.

With anisole in concentrated sulphuric acid, (II), (V), (IIa), and (Va) gave reddish to purple colours; (I) and (IV), pale yellow; (III), (VIII), and (X), nil.

The author is indebted to the Chemical Society for a grant towards materials, to the Carnegie Trustees for a Teaching Fellowship, and to Dr. Cuthbertson for facilities in carrying out microanalyses in the Biochemical Laboratory of the Royal Infirmary.

UNIVERSITY OF GLASGOW. [*Received, March* 30*th*, 1932.]