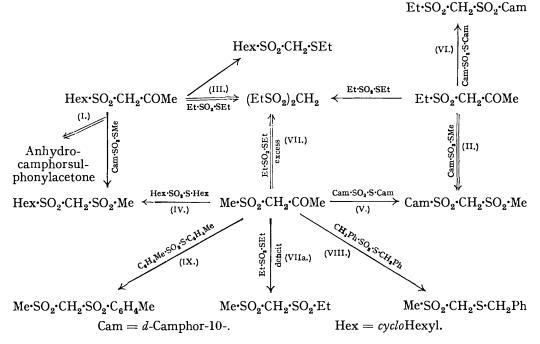
## **13.** The Mobility of Groups containing a Sulphur Atom. Part III. By Douglas W. Cowie and David T. Gibson.

THE study of the exchange reaction has been extended to competition between two nonaromatic sulphonyl radicals :

(E) 
$$R_1 \cdot SO_2 \cdot CH \cdot COMe \xleftarrow{\text{exchange}} R \cdot SO_2 \cdot CH_2 \cdot COMe + R_1 \cdot SO_2 \cdot SMe \xrightarrow{\text{normal}} R \cdot SO_2 \cdot CH \cdot COMe$$
 (N)  
SMe

Exchange occurs only when an alkylthio-group is entering. In Part I (J., 1932, 1819) this was related to its para-directing influence. As, however, the bromination of thioanisole proceeds (Bourgeois and Abraham, *Rec. trav. chim.*, 1911, **30**, 407) *via* an unstable dibromide, the prediction by Hammick and Illingworth's rule (J., 1930, 2358) is not reliable and in view of the adverse criticism of another part of Bourgeois and Abraham's paper (Twist and Smiles, J., 1925, **127**, 1248; Baldwin and Robinson, J., 1930, 2554) we repeated the bromination of thioanisole and confirmed that the methylthio-group is para-directing.

In the following table exchange reactions are indicated by double-lined arrows. The product in each case was finally identified as a bissulphonyl-methane, and the ease with which a sharply melting product (except in VII) was obtained is evidence that no considerable amount of other product was overlooked. The behaviour of dibenzyl disulphoxide may be compared with von Braun and Englebert's results (*Ber.*, 1923, 56, 1574).



As the low melting point of many of these products makes exact quantitative measurement difficult, we have carried out a reaction between equimolecular amounts of methyl p-toluenethiolsulphonate and 4-chlorophenylsulphonylacetone. We recovered about 70% of the products of reaction and, by estimating the halogen content of each, found (taking into account the lesser solubility of the halogenated derivatives) that the product was a 50 : 50 mixture of exchanged and normal material.

m-Nitrophenylsulphonyl-acetic ester and -acetophenone could not be prepared by the usual method (interaction of the sodium sulphinate with chloroacetic ester and bromo-

acetophenone respectively). A similar failure to prepare o-nitrophenylsulphonylacetic ester is recorded by Claasz (*Ber.*, 1912, **45**, 748). This cannot be attributed to the intrinsic instability of the ester, for Claasz obtained it subsequently by oxidising the product from o-nitrophenylthiol and chloroacetic ester. This led us to try the action of alkaline phenylthiol on sodium o-nitrophenylsulphonylacetate; but instead of the expected sodium phenylthioacetate we obtained quickly in the cold o-nitrodiphenyl sulphide : other mercaptans gave corresponding sulphides.

$$NO_2 \cdot C_6H_4 \cdot SO_2 \cdot CH_2 \cdot CO_2Na + PhSNa \longrightarrow NO_2 \cdot C_6H_4 \cdot SPh$$

The replacement was much smoother than in similar experiments with phenol or aniline recorded by Levi and Smiles (J., 1932, 1491).

In the light of these experiments we were inclined to doubt the structure (XI) assigned by Steinkopf and Jaeger (*J. pr. Chem.*, 1930, **128**, 66) to the "tertiare sulfonsäure,"  $C_{13}H_{14}O_4S_2$ , m. p. 123—124°, which they obtained from methylmagnesium iodide and benzenesulphonyl fluoride. They found that it formed an easily hydrolysed potassium

(XI.) 
$$C_6H_5 \cdot SO_2 - S - C_6H_5$$
  
O OH  $C_6H_5 \cdot SO_2 - C - SO_2 \cdot C_6H_5$  (XII.)

salt and a methyl ester (OMe for OH). Taking advantage of Davies and Dick's excellent route to sulphonyl fluorides (J., 1931, 2104), we repeated Steinkopf's experiment and obtained his substance, m. p. 121–122°. It gave no depression in melting point (121–122°) when mixed with the oxidised condensate (XII;  $R = R_1 = H$ ) of phenylthiol and formaldehyde (bisphenylsulphonylmethane).

Methylation produced not only Steinkopf's "methyl ester" (which we identified as bisphenylsulphonylethane; XII; R = H,  $R_1 = Me$ ) but also a substance, m. p. 186°, which is evidently  $\beta\beta$ -bisphenylsulphonylpropane (XII;  $R = R_1 = Me$ ) (Shriner, Struck, and Jorison, J. Amer. Chem. Soc., 1930, 52, 2060). The isolation of a dimethyl derivative is scarcely possible on Steinkopf's formulation. On the other hand it is not difficult to understand the formation of bisphenylsulphonylmethane, especially as Steinkopf's analyses are actually in better accord with a bisphenylsulphonyl-methane (C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub>) and -ethane (C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>) than with the formulæ he put forward.

Ethylmagnesium iodide and benzenesulphonyl fluoride gave bisphenylsulphonylethane.

## EXPERIMENTAL.

Bromination of Thioanisole.—Thioanisole was brominated as described by Bourgeois and Abraham (*loc. cit.*), and the resulting bromophenyl methyl sulphide converted into a sulphone, m. p. 103°, identical with authentic 4-bromophenylmethylsulphone (for which we are indebted to Professor Smiles) and different from 3-bromophenylmethylsulphone, m. p. 103° also, prepared by direct bromination of phenylmethylsulphone.

(I) cycloHexylsulphonylacetone (2 g.), methyl d-camphorylthiolsulphonate (5 g. or 10 g.), and sodium carbonate (0.5 g.) gave anhydrocamphorsulphonylacetone (0.05 g.) and an oil which after hydrolysis and oxidation gave cyclohexylsulphonylmethylsulphonylmethane, m. p. 119° (Found : S, 26.6.  $C_8H_{16}O_4S_2$  requires S, 26.7%).

(II) Ethylsulphonylacetone (3 g.), methyl *d*-camphorylthiolsulphonate (5 g.), and sodium carbonate (1 g.) gave *d*-camphorsulphonic acid (0.7 g. as bromide), anhydrocamphorsulphonylacetone (0.1 g.), and an oil (0.5 g.) which after hydrolysis and oxidation gave *camphorsulphonylmethylsulphonylmethane*, m. p. 123° (different from I above, 119°) (Found : C, 46.4; H. 6.6; S, 20.4.  $C_{12}H_{20}O_5S_2$  requires C, 46.7; H, 6.5; S, 20.75%).

(III) cycloHexylsulphonylacetone (7 g.), ethyl ethanethiolsulphonate (15·4 g.), and sodium carbonate (1·75 g.) gave a sulphide and an alkaline extract. The former gave methylethyl-sulphone on oxidation; the latter, on acidification, an oil which was separated into three fractions: (a) 1·5 g., b. p.  $106^{\circ}/0.2 \text{ mm.}$ ,  $n_D^{10}$  1·5050 (Found : S.  $30\cdot5^{\circ}$ ); (b) 2 g., b. p.  $115^{\circ}/0.2 \text{ mm.}$ ; and (c) 1 g., b. p.  $132^{\circ}/0.2 \text{ mm.}$  The lowest fraction was identified as  $\alpha$ -ethylsulphonyl-

 $\alpha$ -ethylthioacetone (b. p. 105—106°/0·2 mm.,  $n_{15}^{16*}$  1·5040. Calc.: S, 30·4%), and both were readily converted into bisethylsulphonylmethane. The highest fraction was identified as  $\alpha$ -cyclohexylsulphonyl- $\alpha$ -ethylthioacetone (Found : S, 24·7. C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub> requires S, 24·2%). It was converted into cyclohexylsulphonylethylthiomethane, m. p. 38°, on hydrolysis (Found : S, 28·5. C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> requires S, 28·8%).

(IV) cycloHexyl cyclohexanethiolsulphonate was described by von Braun and Weissbach (Ber., 1930, 63, 2842) as an oil, b. p.  $184^{\circ}/0.1$  mm.; it melts at  $38^{\circ}$  (Found : S, 24.5. Calc. for  $C_{12}H_{22}O_2S_2$ : S, 24.4%). With methylsulphonylacetone and sodium ethoxide it gave, by hydrolysis and oxidation of the alkali-soluble product, cyclohexylsulphonylmethylsulphonylmethane, m. p.  $119-120^{\circ}$ , identical with (I N). Threefold excess of the thiolsulphonic ester gave the same product.

(V) The alkali-soluble product obtained from camphor disulphoxide, methylsulphonylacetone, and sodium ethoxide gave, after hydrolysis and oxidation, camphorsulphonylmethylsulphonylmethane, m. p. 122°, identical with (II E).

*Methylsulphonylacetone* was prepared from sodium methanesulphinate and chloroacetone. On removal of the excess of solvent, the residue solidified; m. p. 54° (Found : S, 23.4.  $C_4H_8O_3S$  requires S, 23.5%).

(VI) "Camphor disulphoxide" (13 g.), ethylsulphonylacetone (4 g.), and sodium carbonate (1·3 g.) gave an alkali-soluble oil which after hydrolysis and oxidation gave camphorsulphonyl-ethylsulphonylmethane, m. p. 85° (Found : S, 19·7.  $C_{13}H_{22}O_5S_2$  requires S, 19·8%).

(VII) Methylsulphonylacetone (0.65 g.), ethyl ethanethiolsulphonate (6 g.), and sodium carbonate (0.25 g.) gave, on hydrolysis and oxidation of the alkali-soluble product, a sulphone, m. p.  $95-100^{\circ}$ , which, recrystallised, melted at  $102^{\circ}$  alone or mixed with authentic bisethyl-sulphonylmethane.

(VIIa) When equimolecular proportions of the same reagents were used, the *sulphone* obtained melted at 95° and depressed the m. p. of bisethylsulphonylmethane (Found : S, 34.0.  $C_4H_{10}O_4S_2$  requires S, 34.4%).

(VIII) Benzyl benzylthiolsulphonate (2.7 g.), methylsulphonylacetone (1.4 g.), and sodium carbonate (0.5 g.) gave a practically entirely alkali-soluble product. The fraction precipitated by acetic acid gave on hydrolysis crystals, m. p. 54° (depressed by admixture with methyl-sulphonylacetone) (Found : S, 29.9, 29.7.  $C_9H_{12}O_2S_2$  requires S, 29.6%).

(IX) The alkali-soluble product from methylsulphonylacetone, *p*-tolyl *p*-toluenethiolsulphonate, and sodium ethoxide gave *methylsulphonyl*-p-tolylthioacetone, m. p. 50° (Found : S, 24·7.  $C_{11}H_{14}O_{3}S_{2}$  requires S, 24·8%), which after hydrolysis and oxidation gave *p*-tolylsulphonylmethylsulphonylmethane, m. p. 155°, identical with a previous specimen (J., 1931, 2461).

(X) Benzoylacetonitrile, dissolved in the calculated amount of sodium hydroxide solution, gave with an alcoholic solution of methyl *p*-toluenethiolsulphonate  $\omega$ -cyano- $\omega$ -methylthio-acetophenone, m. p. 50° (ligroin) (yield, 30%) (Found : C, 62.9; H, 5.3. C<sub>10</sub>H<sub>9</sub>ONS requires C, 62.8; H, 4.7%). No cyanide ion was detected when it was boiled with sodium benzene-sulphinate.

o-Nitrophenylsulphonylacetic acid with phenylthiol gave o-nitrodiphenyl sulphide, m. p. 80° (Levi and Smiles, J., 1932, 1490), and with methylthiourea gave o-nitrothioanisole, m. p. 58—59° (Claasz, *Ber.*, 1912, **45**, 1022).

4-Chlorophenylsulphonylacetone (1 mol.), methyl p-toluenethiolsulphonate (1 mol.), and potassium acetate (1 mol.) were kept in alcoholic solution for 5 days. The alcohol, removed below 30°, contained no volatile sulphur compounds. The residue was dissolved in ether (D), washed with water, and extracted with dilute sodium carbonate solution (unchanged initial materials thereby being eliminated). The alkaline solution was boiled to hydrolyse the mixture of R·SO<sub>2</sub>·CH(SMe)·CO·CH<sub>3</sub>, and the resulting mixture of R·SO<sub>2</sub>·CH<sub>2</sub>·SMe was obtained as a crystalline solid [Found : Cl, 7·1. R·SO<sub>2</sub>·CH<sub>2</sub>·SMe requires (R = p-tolyl) Cl, 0; (R = 4-chlorophenyl) Cl, 15·0%. Hence the ratio p-tolyl : 4-chlorophenyl is 53 : 47].

About 5% of R·SO<sub>2</sub>·CH(SMe)·CO·CH<sub>3</sub> underwent hydrolysis during the original reaction. It was recovered from the ether (D) and found to contain 7.0% Cl, indicating a similar ratio of *p*-tolyl : 4-chlorophenyl.

We are indebted to the Chemical Society for a grant.

UNIVERSITY OF GLASGOW.

[Received, November 3rd, 1933.]