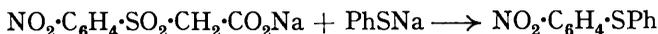
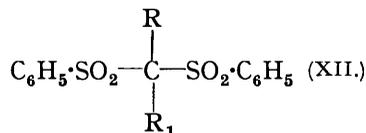
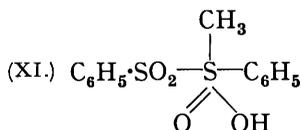


acetophenone respectively). A similar failure to prepare *o*-nitrophenylsulphonylacetic ester is recorded by Claasz (*Ber.*, 1912, **45**, 748). This cannot be attributed to the intrinsic instability of the ester, for Claasz obtained it subsequently by oxidising the product from *o*-nitrophenylthiol 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.



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," $\text{C}_{13}\text{H}_{14}\text{O}_4\text{S}_2$, m. p. 123—124°, which they obtained from methylmagnesium iodide and benzenesulphonyl fluoride. They found that it formed an easily hydrolysed potassium



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; $\text{R} = \text{R}_1 = \text{H}$) of phenylthiol and formaldehyde (bisphenylsulphonylmethane).

Methylation produced not only Steinkopf's "methyl ester" (which we identified as bisphenylsulphonyl ethane; XII; $\text{R} = \text{H}$, $\text{R}_1 = \text{Me}$) but also a substance, m. p. 186°, which is evidently $\beta\beta$ -bisphenylsulphonylpropane (XII; $\text{R} = \text{R}_1 = \text{Me}$) (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 found phenylmethylsulphone as a by-product of his reaction. Further, Steinkopf's analyses are actually in better accord with a bisphenylsulphonyl-methane ($\text{C}_{13}\text{H}_{12}\text{O}_4\text{S}_2$) and -ethane ($\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2$) than with the formulæ he put forward.

Ethylmagnesium iodide and benzenesulphonyl fluoride gave bisphenylsulphonyl ethane.

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) *cyclo*Hexylsulphonylacetone (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. $\text{C}_8\text{H}_{16}\text{O}_4\text{S}_2$ 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. $\text{C}_{12}\text{H}_{20}\text{O}_5\text{S}_2$ requires C, 46.7; H, 6.5; S, 20.75%).

(III) *cyclo*Hexylsulphonylacetone (7 g.), ethyl ethanethiolsulphonate (15.4 g.), and sodium carbonate (1.75 g.) gave a sulphide and an alkaline extract. The former gave methylethylsulphone on oxidation; the latter, on acidification, an oil which was separated into three fractions: (a) 1.5 g., b. p. 106°/0.2 mm., n_D^{20} 1.5050 (Found: S, 30.5%); (b) 2 g., b. p. 115°/0.2 mm.; and (c) 1 g., b. p. 132°/0.2 mm. The lowest fraction was identified as α -ethylsulphonyl-

α -ethylthioacetone (b. p. 105—106°/0.2 mm., n_D^{20} 1.5040. Calc.: S, 30.4%), and both were readily converted into bisethylsulphonylmethane. The highest fraction was identified as α -cyclohexylsulphonyl- α -ethylthioacetone (Found: S, 24.7. $C_{11}H_{20}O_3S_2$ requires S, 24.2%). It was converted into cyclohexylsulphonylethylthiomethane, m. p. 38°, on hydrolysis (Found: S, 28.5. $C_9H_{18}O_2S_2$ requires S, 28.8%).

(IV) *cyclo*Hexyl cyclohexanethiolsulphonate was described by von Braun and Weissbach (*Ber.*, 1930, **63**, 2842) as an oil, b. p. 184°/0.1 mm.; it melts at 38° (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°, 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 camphorsulphonylethylsulphonylmethane, m. p. 85° (Found: S, 19.7. $C_{13}H_{22}O_3S_2$ 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°, which, recrystallised, melted at 102° alone or mixed with authentic bisethylsulphonylmethane.

(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 methylsulphonylacetone) (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-tolylihoacetone*, m. p. 50° (Found: S, 24.7. $C_{11}H_{14}O_3S_2$ 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 ω -cyano- ω -methylthioacetophenone, m. p. 50° (ligroin) (yield, 30%) (Found: C, 62.9; H, 5.3. $C_{10}H_9ONS$ requires C, 62.8; H, 4.7%). No cyanide ion was detected when it was boiled with sodium benzenesulphinate.

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 $R \cdot SO_2 \cdot CH(SMe) \cdot CO \cdot CH_3$, and the resulting mixture of $R \cdot SO_2 \cdot CH_2 \cdot SMe$ was obtained as a crystalline solid [Found: Cl, 7.1. $R \cdot SO_2 \cdot CH_2 \cdot SMe$ 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 $R \cdot SO_2 \cdot CH(SMe) \cdot CO \cdot CH_3$ 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.

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