CXCIII.—*Aromatic Sulphonyl Disulphides.*

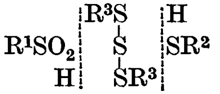
By LESLIE GEORGE SCOTT BROOKER, REGINALD CHILD, and SAMUEL SMILES.

THE relative stability of incompletely oxidised sulphur chains attached to aromatic nuclei has not yet been systematically examined. Facts available from various sources show that so far as the dithio-system is concerned the fully oxidised chain of the disulphones is more resistant to fission than the partly oxidised group in the thiolsulphonates or in the unoxidised chain of disulphides. These relations, considered together with the labile character of the disulphide group in the tetrathio-compounds, $ArSO_2{\cdot}S_2{\cdot}SO_2Ar$, which spontaneously lose sulphur, yielding the corresponding monosulphides (Otto and Troger, *Ber.*, 1891, **24**, 1125), led to attempts to devise a method of introducing the thiolsulphonate group similar to that recently devised for inserting the thioaryl group (J., 1926, 1723). The experiments hitherto made with this object have chiefly dealt with the fission of substances containing the partly oxidised system $ArSO_2{\cdot}S{\cdot}S$— and have been devised to determine the mode of fission of this sulphur chain. If, as appeared probable for reasons such as those stated, the dithio-linking proved to be the less stable point of the sulphur complex, an intact thiolsulphonate group might survive the attack of suitable agents. The present investigation deals mainly with the diaryl sulphonyl disulphides. Although the desired method of synthesis of disulphoxides has not yet been attained, the results are now described, since this class of substance has not been previously encountered and their reactions illustrate the labile character of this type of sulphur chain and the varying character of the decomposition products. The substances in question are readily obtained from the reaction of an aryl thiolsulphonate with a sulphur chloride,

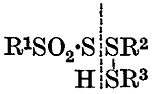
$$ArSO_2{\cdot}SNa + SClAr = NaCl + ArSO_2{\cdot}S{\cdot}SAr,$$

and are well-defined materials which may be purified by the usual methods but decompose near their temperatures of fusion. Attempts to obtain these substances by partial oxidation of the more stable of the aromatic trisulphides or by reaction of a sulphinate with a disulphur chloride have not yet been successful. The sulphur chain in the aryl sulphonyl disulphides is easily broken by mercaptans, the chief product being the trisulphide corresponding to the mercaptan used (I). At the same time, fission of the dithio-system takes place in the reverse manner with the result that, when the aryl group of the mercaptan used is different from those present in the sulphonyl disulphide, unsymmetrical disulphides are formed (II). These modes of fission are summarised as follows :

(I.)



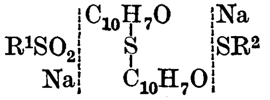
$$\begin{array}{r|c|l} & R^3S & H \\ R^1SO_2 & S & SR^2 \\ H & SR^3 & \end{array}$$



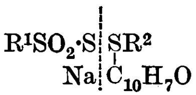
$$\begin{array}{r|l} & \\ R^1SO_2{\cdot}S & SR^2 \\ H & SR^3 \end{array}$$

(II.)

(III.)



$$\begin{array}{r|c|l} & C_{10}H_7O & Na \\ R^1SO_2 & S & SR^2 \\ Na & C_{10}H_7O & \end{array}$$



$$\begin{array}{r|l} & \\ R^1SO_2{\cdot}S & SR^2 \\ Na & C_{10}H_7O \end{array}$$

(IV.)

With sodium 2-naphthoxide or the sodium derivative of acetylacetone the unsymmetrical monosulphides are obtained (IV) together with 2-naphthol sulphide in the case of the first-named reagent (III), but since sodium mercaptide is liberated during these decompositions the symmetrical disulphide which is formed according to (II) is usually also encountered.

The behaviour of these reagents with the diarylsulphonyl monosulphides and trisulphides is similar. Thus ditoluenesulphonyl trisulphide was almost quantitatively decomposed by sodium 2-naphthoxide to 2-naphthol sulphide and toluenethiolsulphonate,

$$RSO_2{\cdot}S_3{\cdot}SO_2R \xrightarrow[C_{10}H_7{\cdot}ONa]{} 2RSO_2{\cdot}SNa + (C_{10}H_6{\cdot}OH)_2S,$$

and by sodium mercaptide to the trisulphide,

$$RSO_2{\cdot}S_3{\cdot}SO_2R \xrightarrow[R^1SNa]{} R^1{}_2S_3 + 2RSO_2{\cdot}SNa.$$

Ditoluenesulphonyl sulphide yielded 2-naphthol sulphide and the sulphinate

$$(RSO_2)_2S \xrightarrow[C_{10}H_7{\cdot}ONa]{O} 2RSO_2Na + (C_{10}H_6{\cdot}OH)_2S.$$

The trisulphides, sulphonyl disulphides and disulphonyl monosulphides form an interesting series in which the trithio-system occurs in successive stages of oxidation, but at present it is inadvisable to discuss the relative stability of these, since experience has shown that in each class this may vary with the nature of the substituents in the aromatic nuclei, and precise information concerning this factor is lacking.

EXPERIMENTAL.

The sulphonyl disulphides were prepared by shaking the finely powdered potassium thiolsulphonate with dry ether containing the theoretical amount of aryl sulphur chloride. Interaction was usually rapid and when it was complete the solid was collected and washed with water; the residue, containing the desired material, was then purified from a suitable solvent. A further quantity of the sulphonyl disulphide could in most cases be obtained from the ethereal solution. In this way, the following derivatives were obtained; they are numbered for the purpose of reference on a subsequent page.

I. 4-*Toluenesulphonyl* 2-*nitrophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

formed yellow plates, m. p. 141°, from acetic acid (Found: S, 28·3; *M*, 336. $C_{13}H_{11}O_4NS_3$ requires S, 28·2%; *M*, 341).

II. 4-*Acetamidobenzenesulphonyl* 2-*nitrophenyl disulphide*,

$$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

separated from acetone in yellow needles, m. p. 171° (decomp.) (Found: C, 43·8; H, 3·1; S, 24·9. $C_{14}H_{12}O_5N_2S_3$ requires C, 43·7; H, 3·1; S, 25·0%).

III. 4-*Toluenesulphonyl* 4-*chloro*-2-*nitrophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_3Cl{\cdot}NO_2,$$

was obtained from hot alcohol in yellow needles, m. p. 114° (Found: C, 41·6; H, 2·9; Cl, 9·3; S, 25·5. $C_{13}H_{10}O_4NClS_3$ requires C, 41·5; H, 2·9; Cl, 9·4; S, 25·6%).

IV. 4-*Toluenesulphonyl* 2 : 5-*dichlorophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_3Cl_2,$$

separated from benzene–light petroleum in prisms, m. p. 95—96° (Found: C, 42·7; H, 2·7; Cl, 19·3; S, 26·1. $C_{13}H_{10}O_2Cl_2S_3$ requires C, 42·7; H, 2·8; Cl, 19·4; S, 26·3%).

V. 4-*Methoxytoluene*-3-*sulphonyl* 2-*nitrophenyl disulphide*,

$$MeO{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

has m. p. 115—116° (Found: C, 45·2; H, 3·7; S, 25·4; *M*, 362. $C_{14}H_{13}O_5NS_3$ requires C, 45·2; H, 3·5; S, 25·9%; *M*, 371).

VI. 4-*Chlorobenzenesulphonyl* 2-*nitrophenyl disulphide*,

$$C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

formed yellow plates from acetic acid; m. p. 147° after softening at about 130° (Found: C, 39·9; H, 2·4; Cl, 9·9; *M*, 352. $C_{12}H_8O_4NClS_3$ requires C, 39·8; H, 2·2; Cl, 9·8%; *M*, 361·5).

The interaction of these substances with the reagents mentioned was effected in boiling alcohol which contained two molecular proportions of the mercaptan or sodium 2-naphthoxide and one of the sulphonyl disulphide. When the reaction was complete, the alcohol was evaporated and the residue was extracted with water. The further separation of the products varied according to the nature of the reactants. Identification of the products was effected by comparison with authentic specimens from other sources; when the substances had not been previously described, they were prepared for comparison by other methods. In the following summary the numerals refer to the sulphonyl disulphides described above.

I, with the sodium derivative of acetylacetone, yielded 2-nitrophenyl disulphide and 2-nitrophenyl acetylacetonyl sulphide, m. p. 136—137° (J., 1926, 1727). From the interaction with 2 : 5-dibromophenyl mercaptan the corresponding trisulphide and 2 : 5-dibromophenyl 2-nitrophenyl disulphide were isolated. 2 : 5-*Dibromophenyl trisulphide*, m. p. 167—168°, formed needles from benzene (Found: Br, 56·5. $C_{12}H_6Br_4S_3$ requires Br, 56·5%) and was also prepared from the mercaptan and sulphur dichloride in carbon tetrachloride. 2 : 5-*Dibromophenyl* 2-*nitrophenyl disulphide*, $C_6H_3Br_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, was also obtained from the dibromophenyl mercaptan and 2-nitrophenyl sulphur chloride. It formed yellow prisms, m. p. 138°, from acetic acid (Found: Br, 38·1. $C_{12}H_7O_2NBr_2S_2$ requires Br, 38·0%).

III, with sodium 2-naphthoxide, yielded 2-naphthol sulphide, toluenesulphinic acid, 4-chloro-2-nitrophenyl disulphide, and 4-chloro-2-nitrophenyl 2-naphthol sulphide (I) (Found: Cl, 10·3. Calc.: Cl, 10·7%).

IV, with 2-nitrophenyl mercaptan, gave 2-nitrophenyl trisulphide (Lecher, *Ber.*, 1922, **55**, 2423) and 2 : 5-*dichlorophenyl* 2-*nitrophenyl disulphide*, $C_6H_3Cl_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, which was also prepared from 2-nitrophenyl sulphur chloride and 2 : 5-dichlorophenyl mercaptan, and separated from hot acetic acid in yellow needles, m. p. 138° (Found: C, 43·3; H, 2·1. $C_{12}H_7O_2NCl_2S_2$ requires C, 43·2; H, 2·2%).

V, with 2 : 5-dichlorophenyl mercaptan, yielded 2 : 5-dichlorophenyl 2-nitrophenyl disulphide, 4-methoxytoluene-3-sulphinic acid, and 2 : 5-*dichlorophenyl trisulphide*, $(C_6H_3Cl_2)_2S_3$, which formed needles, m. p. 140°, from acetic acid (Found: Cl, 36·2. $C_{12}H_6Cl_4S_3$ requires Cl, 36·5%). This substance was also obtained from the mercaptan and sulphur chloride; by hydrogen peroxide in acetic acid at 100°, it was converted into 2 : 5-dichlorophenyl disulphoxide.

VI, with the sodium derivative of acetylacetone, yielded 2-nitrophenyl disulphide, 4-chlorobenzenesulphinic acid, and 2-nitrophenyl acetylacetonyl sulphide.

4-Toluenesulphonyl trisulphide or 4-toluenesulphonyl sulphide was decomposed in boiling alcohol by sodium 2-naphthoxide (2 mols.). The products were as stated in the theoretical part. Sodium 4-toluenethiolsulphonate, formed from the first-named sulphide, was identified by conversion into 4-toluenesulphonyl 4-chloro-2-nitrophenyl disulphide.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us (L. G. S. B.) to take part in these experiments.

King's College, London.

[*Received, April* 28*th*, 1927.]