XCIV.—*Derivatives of* 1 : 3-*Dithiolan and of* 1 : 3-*Dithian.*

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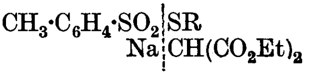
IN a previous communication (J., 1926, 1723) it was shown that the reaction of aromatic disulphoxides with substances of the type of ethyl malonate, deoxybenzoin, phloroglucinol, and the naphthols in presence of alkali affords a means of inserting the thioaryl group in these substances. Subsequent experiments, which are now described, have been directed to the behaviour under similar conditions of the substances obtained (Otto, *Ber.*, 1882, **15**, 121; 1886, **19**, 1235; 1887, **20**, 2074; 1892, **25**, 1477) from alkyl halides and aromatic thiolsulphonates. The known reactions of these products (Otto, *loc. cit.*) are similar to those of the aromatic disulphoxides and clearly indicate the presence of the thiolsulphonate structure (*e.g.*, I).

(I.) $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_2H_5$



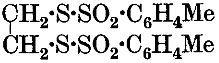
$$\begin{array}{r|l} CH_3{\cdot}C_6H_4{\cdot}SO_2 & SR \\ Na & CH(CO_2Et)_2 \end{array}$$

(II.)

It was therefore expected that these disulphoxides of mixed fatty aromatic character would provide a new method of obtaining alkylthiol derivatives of the naphthols, malonic acid, and similar compounds (II). Thioalkyl sulphonates are very easily decomposed by alkali hydroxide and it was found that with this reagent, which was successfully employed in dealing with aromatic thiolsulphonates, none of the required thioalkyl derivatives could be isolated from among the usual products of hydrolysis. When potassium acetate was used to provide the necessary alkaline medium, the desired substitution products were obtained; *e.g.*, dibenzyl disulphoxide yielded with deoxybenzoin the mercaptol of benzil (III), with ethyl malonate, after hydrolysis of the product, benzylthiolacetic acid (IV) was obtained, and β-naphthol and ethylene ditoluene-*p*-thiolsulphonate (V) yielded the ethylene ether of 1-thiol-2-naphthol (VI).

(III.) $(CH_2Ph\cdot S)_2CPh\cdot COPh$

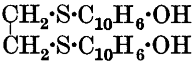
(IV.) $CH_2Ph\cdot S\cdot CH_2\cdot CO_2H$



$$\begin{array}{l} CH_2\cdot S\cdot SO_2\cdot C_6H_4Me \\ CH_2\cdot S\cdot SO_2\cdot C_6H_4Me \end{array}$$

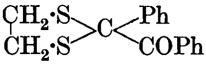
(V.)

These preliminary results led to the study of the formation of cyclic 1 : 3-dithio-systems from dithiolsulphonates derived from ethane, propane, and pentane (compare V). The behaviour of deoxybenzoin with dibenzyl disulphoxide and aromatic disulphoxides (*loc. cit.*) showed that the dithiol derivatives (*e.g.*, III) are formed even when excess of the ketone is present. Accordingly, this substance readily furnished the cyclic mercaptols of benzil (VII and VIII), but with the αε-pentanedithiolsulphonate no trace of the analogous 8-membered ring was isolated. With ethyl malonate and the aromatic disulphoxides or benzyl disulphoxide, only monosubstitution products (*e.g.*, IV) were encountered even when excess of the disulphoxide was present. It is therefore remarkable that the ethane and αγ-propane derivatives gave excellent yields of the cyclic compounds resulting from disubstitution of the malonic nucleus (IX and X), and when excess of malonate was present only very small quantities of the monosubstituted type (XI) could be detected in the product. On the other hand, in the case of the αε-pentanedithiolsulphonate no cyclic derivative was formed and only small yields of the open-chain acid (type XI) were isolated. These results



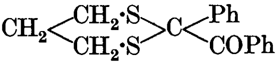
$$\begin{array}{l} CH_2\cdot S\cdot C_{10}H_6\cdot OH \\ CH_2\cdot S\cdot C_{10}H_6\cdot OH \end{array}$$

(VI.)



$$\begin{array}{l} CH_2\cdot S \\ CH_2\cdot S \end{array}\!>C<\!\begin{array}{l} Ph \\ COPh \end{array}$$

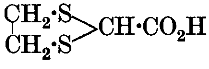
(VII.)



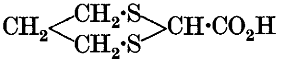
$$CH_2\!<\!\begin{array}{l} CH_2\cdot S \\ CH_2\cdot S \end{array}\!>C<\!\begin{array}{l} Ph \\ COPh \end{array}$$

(VIII.)

(IX.)



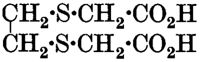
$$\begin{array}{l} CH_2\cdot S \\ CH_2\cdot S \end{array}\!>CH\cdot CO_2H$$



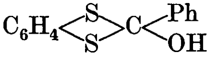
$$CH_2\!<\!\begin{array}{l} CH_2\cdot S \\ CH_2\cdot S \end{array}\!>CH\cdot CO_2H$$

(X.)

(XI.)



$$\begin{array}{l} CH_2\cdot S\cdot CH_2\cdot CO_2H \\ CH_2\cdot S\cdot CH_2\cdot CO_2H \end{array}$$



$$C_6H_4\!<\!\begin{array}{l} S \\ S \end{array}\!>C<\!\begin{array}{l} Ph \\ OH \end{array}$$

(XII.)

clearly indicate the favourable configurations of the 5- and 6-membered rings contained by the 1 : 3-dithiolan and 1 : 3-dithian systems. Although these systems resist fission by mild oxidising agents, being then converted into disulphones (compare Fasbender, *Ber.*, 1888, **21**, 1473; Autenrieth, *Ber.*, 1899, **32**, 1239), they are remarkably sensitive to halogens. In cold acetic acid bromine expels the 2-carbon atom with its substituents and liberates a polymeric sulphide derived from ethane or propane. It seems that this characteristic decomposition is preceded by the formation of an additive product, since the unstable *dibromide* of 1 : 3-*dithiolan*-2-*carboxylic acid* could be isolated under special conditions and the *di-iodides* of this acid and of 1 : 3-*dithian*-2-*carboxylic acid* were also obtained. Oxidation of these acids with hydrogen peroxide led to the unsubstituted disulphones and loss of carbon dioxide; but they were destroyed by cold nitric acid. In the 2-phenyl-1 : 3-benzdithiole series, bromine and nitric acid yield salts (J., 1926, 1823) derived from a pseudo-base (XII), but similar derivatives could not be obtained from the saturated ring-systems now investigated, and no evidence even of their transitory existence during the action of these reagents could be discovered.

EXPERIMENTAL.

Reactions of Benzyl Disulphoxide.—(a) *With deoxybenzoin.* After a solution of the disulphoxide (2 mols.), deoxybenzoin (1 mol.), and potassium acetate (5—6 mols.) in alcohol had been boiled for 6 hours, the solvent was evaporated and the residue rendered alkaline with aqueous sodium carbonate. An ethereal extract of the product contained benzyl disulphide and the monomercaptol of benzil, which could not be satisfactorily separated by the usual means. The latter substance was isolated as the dioxide by treating the crude product with hydrogen peroxide in warm acetic acid. The *dioxide* of the benzyl mercaptol of benzil separated from the cooled reaction mixture in needles, which were purified from alcohol; m. p. 167° (Found: C, 70·7; H, 5·1; *M*, 494. $C_{28}H_{24}O_3S_2$ requires C, 71·1; H, 5·1%; *M*, 472).

(b) *With ethyl malonate.* Interaction of the disulphoxide (1 mol.) and the ester (1·5 mols.) was conducted under conditions similar to those already described. The residue from the ethereal extract was boiled with concentrated hydrochloric acid until hydrolysis was complete. Evaporation of the aqueous acid yielded benzylthiolacetic acid, m. p. 60° (Gabriel, *Ber.*, 1879, **12**, 1641) (Found: C, 59·5; H, 5·4. Calc.: C, 59·3; H, 5·5%).

*Reactions of Ethane-*αβ*-di-*p*-toluenethiolsulphonate* (V).—(a) *With deoxybenzoin.* The interaction of the ketone (2·6 g.) and thiolsulphonate (5 g.) in presence of potassium acetate (6 g.) was conducted in boiling alcohol as usual. The residue from the solvent was purified from alcohol; the 2-benzoyl-2-phenyl-1 : 3-dithiolan, m. p. 94—95°, then isolated was identical with the product obtained from αβ-dithiolethane and benzil (Hurtley and Smiles, J., 1926, 2267).

(b) *With ethyl malonate.* Interaction of this ester (5 g.) with the thiolsulphonate (12 g.) in presence of potassium carbonate (8 g.) was effected in boiling alcohol (6 hours). The solvent was removed, and the residue rendered alkaline with sodium carbonate. The portion soluble in ether was boiled with concentrated hydrochloric acid for 8 hours and when the solution obtained was concentrated and cooled, 1 : 3-*dithiolan*-2-*carboxylic acid* (IX) separated in the crystalline state. From benzene this substance was obtained in prisms, m. p. 90° (Found: C, 32·3; H, 4·3; *M*, 154. $C_4H_6O_2S_2$ requires C, 32·0; H, 4·0%; *M*, 150). The solution from which this material separated after hydrolysis of the ester yielded a small quantity of ethylenedithiolacetic acid (m. p. 107°), showing the characteristic behaviour with cuprous oxide described by Ramberg and Tiberg (*Ber.*, 1914, **47**, 733). When the reaction was carried out in presence of excess of ethyl malonate, the amount of this acid formed was somewhat greater but was always less than that of the cyclic compound. 1 : 3-*Dithiolan*-2-*carboxylic acid dibromide* was obtained in the crystalline state by cautiously adding bromine to a solution of the acid in low-boiling petroleum. The substance rapidly decomposed, yielding hydrogen bromide, carbon dioxide, and the insoluble ethylene polysulphide, but immediate analysis showed the composition (Found : Br, 50·3. $C_4H_6O_2Br_2S_2$ requires Br, 51·7%). The corresponding *di-iodide* was isolated by adding a little bromine to a solution of the acid (1 mol.) and iodine (2 mols.) in low-boiling petroleum. It was more stable than the bromine derivative, but could not be purified without decomposition (Found : I, 62·3. $C_4H_6O_2I_2S_2$ requires I, 62·8%).

Oxidation of 1 : 3-dithiolan-2-carboxylic acid was effected by excess of hydrogen peroxide in warm acetic acid. After the evolution of carbon dioxide had subsided, the 1 : 3-dithiolan tetroxide separated (yield 50%) from the cooled liquid. It was identified (m. p. 203—204°) in the usual manner and by conversion into the dibromo-derivative (m. p. 271—272°) (Baumann and Walter, *Ber.*, 1893, **26**, 1129).

Propane-αγ-*di*-p-*toluenethiolsulphonate* (compare V) was prepared from the interaction of αγ-dibromopropane and potassium *p*-tolylthiolsulphonate in boiling alcohol. The viscous material obtained after removal of the solvent solidified when dried and kept in a vacuum. The required substance separated from a cooled mixture of ethyl acetate and alcohol in needles, m. p. 65—67° (Found: C, 48·6; H, 4·9. $C_{17}H_{20}O_4S_4$ requires C, 49·0; H, 4·8%).

(a) *Reaction with deoxybenzoin.* Interaction of this ketone (4·6 g.) and the thiolsulphonate (12 g.) was conducted as usual in presence of potassium acetate (8 g.). The crude material was purified from alcohol, 2-*benzoyl*-2-*phenyl*-1 : 3-*dithian* (VIII) being obtained in needles, m. p. 99—100° (Found: S, 21·6; *M*, 296. $C_{17}H_{16}OS_2$ requires S, 21·4; *M*, 300).

(b) *Reaction with ethyl malonate.* Reaction of the ester with the thiolsulphonate was effected in presence of potassium acetate in boiling alcohol. The crystalline material obtained after hydrolysis of the crude product with hydrochloric acid was purified from hot water. The resulting 1 : 3-*dithian*-2-*carboxylic acid* (X) had m. p. 115—116° (Found: C, 36·5; H, 4·8; *M*, 171. $C_5H_8O_2S_2$ requires C, 36·6; H, 4·8%; *M*, 164).

When it was treated with hydrogen peroxide in warm acetic acid, the cyclic disulphone (m. p. 287°) described by Autenrieth and Wolff (*Ber.*, 1899, **32**, 1375) was obtained; it was further identified by conversion into the dibromo-derivative described by these authors. The additive product of this acid with bromine could not be isolated owing to its instability, but the *di-iodo*-derivative was readily obtained in the crystalline state (Found: I, 60·8. $C_5H_8O_2S_2I_2$ requires I, 60·8%).

Pentane-$\alpha\varepsilon$-*di*-p-*toluenethiolsulphonate*.—The material obtained in the usual manner from $\alpha\varepsilon$-dibromopentane and potassium *p*-tolylthiolsulphonate solidified after remaining 3 weeks in a vacuum. The substance separated from various solvents as a clear, viscous liquid, considered unfit for analysis; it showed the usual reactions of the ethane and propane derivatives already described. Reaction with ethyl malonate was conducted as usual in presence of potassium acetate. After hydrolysis of the product a small amount of *pentane*-$\alpha\varepsilon$-*dithiolacetic acid* (compare XI) was isolated, m. p. 91—92° (Found: C, 42·9; H, 6·6. $C_9H_{16}O_4S_2$ requires C, 42·8; H, 6·3%). This substance was further identified by preparation from $\alpha\varepsilon$-dibromopentane and thiolacetic acid. The dibromide (11·5 g.) was slowly added to a boiling solution of thiolacetic acid (9·2 g.) and potassium hydroxide (12 g.) in water (50 c.c.). After 3 hours the solution was cooled and filtered. When 50% sulphuric acid was added to the clear liquid, an almost theoretical yield of the required acid was obtained. This was identical with the product isolated from the interaction of the thiolsulphonate with ethyl malonate; it separated from benzene in fine needles.

In conclusion, we desire to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

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