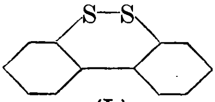
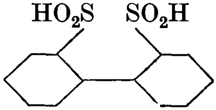
CXLV.—*Cyclic Disulphides derived from Diphenyl.*

By HARRY JAMES BARBER and SAMUEL SMILES.

THE mild treatment by which the dithio-group is formed from thiols seemed to offer favourable conditions for comparing the behaviour of the 4 : 4′-, 3 : 3′-, and 2 : 2′-dithioldiphenyls and their capacity to form cyclic disulphides. The experiments now described were originally planned for this purpose and with the object of providing information concerning the configuration of the diphenyl nucleus. In the meantime the supposed existence of the ring-compounds of benzidine has been clearly contradicted (Le Fèvre and Turner, J., 1926, 2476) and the stereochemistry of the diphenyl nucleus has been further developed on other lines. The results now obtained accord with the evidence collected from these sources. Simple ring-formation has not been observed with the 4 : 4′- and 3 : 3′-dithiols; the products obtained by the mild oxidation of these mercaptans are insoluble materials, evidently of high molecular weight, formed by the inclusion of more than one dithio-group. On the other hand, simple ring closure of the 2 : 2′-dithiol is readily effected, the cyclic disulphide (I) being formed by oxidation. Also the 2 : 2′-disulphinic acid (II) has not been isolated owing to the ease with which it yields the cyclic *thiolsulphonate* (III). In comparison, the 4 : 4′-disulphinic acid is relatively stable.



(I.)



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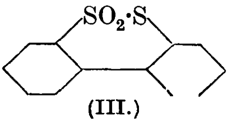
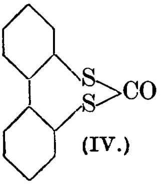


(III.)

2 : 2′-*Dithioldiphenyl* was obtained by the usual methods from the corresponding 2 : 2′-disulphonic acid, which in preliminary experiments was prepared from benzidine-2 : 2′-disulphonic acid (compare Limpricht, *Annalen*, 1891, **261**, 327), but subsequently sodium 2-iodobenzenesulphonate was used as a more convenient source. When a boiling aqueous solution of this substance was treated with copper, a good yield of the desired diphenyl derivative was obtained. *Sodium* 4-*iodotoluene*-3-*sulphonate* behaved similarly, but attempts to prepare the diphenyl-4 : 4′- and -3 : 3′-disulphonates from sodium 4- and 3-iodobenzenesulphonates, respectively, and the di-*o*-tolyl-4 : 4′-disulphonate from *sodium* 2-*iodotoluene*-5-*sulphonate* by this method were unsuccessful.

The formation of simple ring-systems from the 2 : 2′-dithiol is not confined to the six-membered disulphide (I); the *dithiolcarbonate* (IV), the *mercaptal* of benzaldehyde (V), and the *mercaptols* of acetone and benzil (VI) containing the seven-membered ring being obtained by the usual methods.



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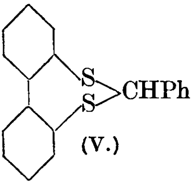

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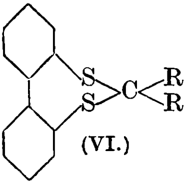
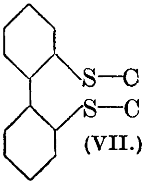


(VI.)

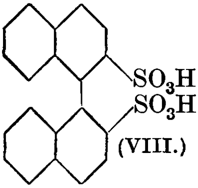


(VII.)

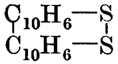
The production of the eight-membered ring (VII) from the dithiol and ethylene dibromide or oxalyl chloride was attempted without success.

In the 1 : 1′-dinaphthyl series similar ring-formation has been observed. When *sodium* 1-*iodonaphthalene*-2-*sulphonate* in boiling aqueous solution was submitted to the action of copper the 1 : 1′-*dinaphthyl*-2 : 2′-*disulphonate* (VIII) was obtained, but conversion of the chloride of this acid directly into the dithiol by reduction could not be effected owing to rupture of the dinaphthyl group; hence the required 1 : 1′-*dinaphthylene* 2 : 2′-*disulphide* (IX) was reached through the disulphoxide which resulted from the spontaneous decomposition of the unstable disulphinic acid.

When these disulphides are heated with copper their ring systems suffer contraction by loss of sulphur; *e.g.*, *diphenylene* 2 : 2′-*disulphide* (I) yielded dibenzthiophen, and 1 : 1′-dinaphthylene 2 : 2′-disulphide (IX) gave a dinaphthathiophen which must be regarded as 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*. This substance (m. p. 202°) is evidently different from that (m. p. 250°) obtained by Lanfry (*Compt. rend.*, 1911, **152**, 1254) from the interaction of sulphur and naphthalene; the constitution of the latter therefore remains uncertain.

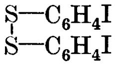


(VIII.)



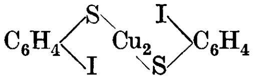
$$\begin{array}{l} C_{10}H_6-S \\ \,| \qquad\quad\;\; | \\ C_{10}H_6-S \end{array}$$

(IX.)



$$\begin{array}{l} S-C_6H_4I \\ | \\ S-C_6H_4I \end{array}$$

(X.)



(XI.)

A further point of interest was encountered in an attempt to obtain the cyclic disulphides by removing halogen from the *o*-iododisulphides (*e.g.*, X) with copper. Instead of the desired products, the corresponding thianthrens were isolated in good yield. Here the removal of iodine is evidently preceded by formation of the copper mercaptides (*e.g.*, XI), which subsequently lose cuprous iodide; this obvious interpretation was justified by the behaviour of the copper derivative of 2-iodophenyl mercaptan. This method of synthesis of thianthrens was realised in three cases, but it appears to be capable of wide application.

EXPERIMENTAL.

Sodium 2-*Iodobenzenesulphonate*.—The following improvement of the methods recorded (*e.g.*, Langmuir, *Ber.*, 1895, **28**, 95) for the preparation of this substance was used. A diazotised solution (500 c.c.) of aniline-*o*-sulphonic acid (32 g.) containing an excess of sulphuric acid was stirred and warmed with potassium iodide (42 g.). When decomposition was complete the solution was concentrated by evaporation, sulphurous acid being added at intervals to remove liberated iodine. The sulphonic acid which finally separated from the cooled liquid was converted into the sodium salt (yield, *ca.* 80%). *Di-2-iodophenyl disulphide*, m. p. 133°, was obtained by usual methods (Found : C, 30·6; H, 1·7. $C_{12}H_8I_2S_2$ requires C, 30·6; H, 1·7%). 2-*Iodophenylmethylsulphone*, m. p. 109°, was obtained from the *sulphinic acid*, m. p. 108°, by alkaline methylation (Found : C, 29·8; H, 2·5. $C_7H_7O_2IS$ requires C, 29·8; H, 2·4%).

2-*Iodotoluene*-5-*sulphonic Acid.*—The moist diazo-compound resulting from 2-aminotoluene-5-sulphonic acid (10 g.) was added to potassium iodide dissolved in dilute sulphuric acid. The solution was gradually heated until it boiled and on cooling the required material separated. The *barium* salt was sparingly soluble in cold water [Found in air-dried sample : H_2O, 3·8. $(C_7H_6O_3IS)_2Ba,1\frac{1}{2}H_2O$ requires H_2O, 3·6%. Found in anhydrous sample : Ba, 18·8. $(C_7H_6O_3IS)_2Ba$ requires Ba, 18·7%]. The *chloride* of this acid had m. p. 61—62° (Found : C, 26·9; H, 2·0. $C_7H_6O_2ClIS$ requires C, 26·5; H, 1·9%) and the *amide* separated from alcohol in leaflets, m. p. 135°.

4-*Iodotoluene*-3-*sulphonic Acid.*—The moist diazo-compound resulting from 4-aminotoluene-3-sulphonic acid (20 g.) was added to a saturated solution of potassium iodide (20 g.) in dilute sulphuric acid. After the usual decomposition had been effected, the *potassium* salt of the required acid separated from the cooled liquid (Found in air-dried sample : H_2O, 5·1. $C_7H_6O_3ISK,H_2O$ requires H_2O, 5·1%. Found in anhydrous material : K, 11·4. $C_7H_6O_3ISK$ requires K, 11·6%). 4-*Iodotoluene*-3-*sulphonyl chloride* formed flat needles, m. p. 68°, from acetic acid (Found : C, 26·6; H, 1·9. $C_7H_6O_2ClIS$ requires C, 26·5; H, 1·9%) and the *amide* had m. p. 161—162°.

Di-4-*iodo*-m-*tolyl Disulphide*, $(C_6H_3MeI{\cdot}S{\cdot})_2$.—When the sulphonyl chloride was reduced with zinc dust and mineral acid, iodine was removed. The *disulphide* was therefore prepared by reducing the crude sulphinic acid with hydrogen iodide in warm alcohol in presence of sulphurous acid. It was purified from acetone and had m. p. 104—105° (Found : I, 51·2; S, 12·7. $C_{14}H_{12}I_2S_2$ requires I, 51·0; S, 12·9%).

1-*Iodonaphthalene*-2-*sulphonic Acid.*—A cooled solution (2·5 l.) of sodium nitrite (12·6 g.) and sodium 1-aminonaphthalene-2-sulphonate (44·5 g.) was mixed with 60% sulphuric acid (50 c.c.). The sparingly soluble diazo-compound was collected and added to a cold solution of potassium iodide (40 g.) in dilute sulphuric acid; the mixture was then gradually heated. The required sulphonic acid, mixed with some alkali sulphonate, separated from the cooled solution (yield, about 50%). Further material obtained by evaporating the liquors was generally very impure owing to extensive separation of iodine during the process. The *barium* salt separated from hot water in needles [Found : Ba, 17·2. $(C_{10}H_6O_3IS)_2Ba$ requires Ba, 17·1%].

1-*Iodonaphthalene*-2-*sulphonyl chloride*, m. p. 94°, formed needles from acetic acid (Found : C, 33·9; H, 1·8. $C_{10}H_6O_2ClIS$ requires C, 34·0; H, 1·7%) and was converted by alkaline sulphite into the sparingly soluble 1-*iodonaphthalene*-2-*sulphinic acid*, m. p. 143° (Found : C, 37·7; H, 2·5. $C_{10}H_7O_2SI$ requires C, 37·7; H, 2·2%). When a solution of the latter substance in hot alcohol was mixed with sulphurous acid and a few drops of hydriodic acid, *di*-1-*iodo*-2-*naphthyl disulphide* rapidly separated. This substance formed plates, m. p. 154°, from benzene (Found : C, 42·4; H, 2·3; I, 44·5; *M*, 575. $C_{20}H_{12}I_2S_2$ requires C, 42·1; H, 2·1; I, 44·5%; *M*, 570).

Derivatives of Diphenyl and Dinaphthyl.

Diphenyl-2 : 2′-*disulphonyl Chloride*.—A concentrated aqueous solution of sodium 2-iodobenzenesulphonate (20 g.) was boiled with finely divided copper (12 g.) and a small quantity of copper sulphate solution (1 c.c.). The progress of the removal of halogen was followed by the change in appearance or increase in weight of the copper powder; usually the process was complete in about 2 hours. The solution, after being freed from copper by hydrogen sulphide, was evaporated on the water-bath; the residue was dried at 150° and treated with phosphorus pentachloride (20 g.), giving the crude disulphonyl chloride (yield, about 75%). The purified material, m. p. 138° (Found : Cl, 20·5. Calc. : Cl, 20·2%), was identified with a sample prepared by the method of Limpricht (*loc. cit.*) from benzidine-2 : 2′-disulphonic acid. The dianilide, m. p. 186°, was obtained by heating the chloride with excess of aniline (Found : N, 6·2. Calc. : N, 6·0%).

Diphenylene 2 : 2′-*Disulphide* (I).—The crude diphenyldisulphonyl chloride contained a small quantity of the iodobenzenesulphonyl chloride, but since this impurity was easily removed during conversion into the thiol further purification of the chloride was not necessary. In the reduction of this dichloride the use of tin was avoided because of the formation of a very stable tin derivative of the dithiol; zinc dust and hydrochloric acid gave the best results, the procedure being that used by Zincke (*Ber.*, 1909, **42**, 3367). The required product was isolated by treating the reduction liquor with a current of steam, in which the dithiol was moderately volatile; any 2-iodophenyl mercaptan present was rapidly removed with the alcohol in the first portion of the distillate. The yields (50—60%) varied somewhat according to the amount under treatment. In this way, 2 : 2′-*dithioldiphenyl* was obtained in needles of agreeable odour and m. p. 78—79° (Found : C, 66·0; H, 4·8; S, 29·7. $C_{12}H_{10}S_2$ requires C, 66·1; H, 4·6; S, 29·4%). Methylation in alkaline media yielded 2 : 2′-dimethylthioldiphenyl (m. p. 155°), which had been previously obtained by Brand (*J. pr. Chem.*, 1924, **107**, 358) from 2-iodophenyl methyl sulphide and copper.

2 : 2′-*Dicarboxymethylthioldiphenyl*, $(CO_2H{\cdot}CH_2{\cdot}S{\cdot}C_6H_4{\cdot})_2$, was obtained from the thiol and sodium chloroacetate in alkaline media. It separated from alcohol and water in plates, m. p. 201—202° (Found : C, 57·5; H, 4·3. $C_{16}H_{14}O_4S_2$ requires C, 57·5; H, 4·2%).

When a solution of the dithiol in warm alcohol was mixed with an excess of alcoholic ferric chloride *diphenylene* 2 : 2′-*disulphide* immediately separated in almost theoretical yield. It formed yellow needles, m. p. 113°, from hot acetic acid (Found : C, 66·4; H, 3·8; S, 29·1; *M*, 208. $C_{12}H_8S_2$ requires C, 66·6; H, 3·7; S, 29·6%; *M*, 216). When this substance was kept for 2 hours at 250° in presence of finely divided copper, dibenzthiophen was formed. This was extracted from the reaction mixture with hot alcohol, purified, and identified with an authentic sample in the usual manner.

Diphenylene 2 : 2′-*Disulphoxide* (III).—(*a*) When a warm solution of diphenylene 2 : 2′-disulphide (1 g.) in acetic acid (50 c.c.) was slowly mixed with nitric acid (10 c.c.), oxidation took place and the required disulphoxide later separated in the crystalline state. (*b*) The solution obtained from the interaction of the disulphonyl chloride and hot aqueous alkaline sulphite was mixed with excess of dilute mineral acid. The sulphinic acid which separated changed spontaneously in the course of a few minutes to the cyclic *disulphoxide* (III). This crystallised from hot alcohol in needles, m. p. 128° (Found : C, 57·9; H, 3·7; *M*, 237. $C_{12}H_8O_2S_2$ requires C, 58·1; H, 3·2%; *M*, 248), and yielded the disulphide when reduced with hydriodic acid in warm acetic acid.

Diphenylene 2 : 2′-*Dithiolcarbonate* (IV).—A toluene solution of carbonyl chloride was gradually added to a stirred alkaline solution of the dithiol until the latter was removed from the aqueous portion of the mixture. Evaporation of the toluene yielded the product which, after crystallising from alcohol (charcoal), had m. p. 101·5° (Found : C, 63·8; H, 3·4; *M*, 235. $C_{13}H_8OS_2$ requires C, 63·9; H, 3·2%; *M*, 244).

The diphenyl-2 : 2′-mercaptals and -mercaptols were prepared from the dithiol and the requisite aldehyde or ketone in alcohol with the aid of hydrogen chloride. Separation of the required products was usually complete in about 12 hours (yields, 70—90%). In this way were obtained the *diphenylene*-2 : 2′-*mercaptal* of benzaldehyde (V), m. p. 105—106° (Found: C, 74·2; H, 4·7; S, 20·8; *M*, 305. $C_{19}H_{14}S_2$ requires C, 74·5; H, 4·6; S, 20·9%; *M*, 306), the *diphenylene*-2 : 2′-*mercaptol* of acetone (VI), m. p. 95° (Found: C, 69·5; H, 5·8; *M*, 277. $C_{15}H_{14}S_2$ requires C, 69·7; H, 5·4%; *M*, 258), and the *diphenylene*-2 : 2′-*mercaptol* of benzil (VI), m. p. 198° (Found: C, 75·8; H, 4·6. $C_{26}H_{18}OS_2$ requires C, 76·1; H, 4·4%).

4 : 4′-*Dimethyldiphenyl*-2 : 2′-*disulphonyl Chloride.*—When sodium 4-iodotoluene-3-sulphonate was treated with copper and copper sulphate as described in the case of the 2-iodobenzenesulphonate, the halogen was removed. The crude product yielded the required *sulphonyl chloride* after the usual treatment. This substance formed needles, m. p. 117—118°, from acetic acid (Found: C, 44·0; H, 3·2; *M*, 387. $C_{14}H_{12}O_4Cl_2S_2$ requires C, 44·3; H, 3·2%; *M*, 379) and when it was treated with zinc and hydrochloric acid the ditolyl nucleus apparently suffered fission, since a 60% yield of *m*-tolyl mercaptan was isolated as the product. The latter substance was identified by comparing its *p*-nitrobenzoyl derivative with m-*tolyl* p-*nitrothiolbenzoate*, prepared from *m*-tolyl mercaptan and *p*-nitrobenzoyl chloride in quinoline, which crystallised from alcohol in pale yellow needles, m. p. 96° (Found: N, 5·3; *M*, 266. $C_{14}H_{11}O_3NS$ requires N, 5·1%; *M*, 273). The conversion of the disulphonyl chloride into the cyclic disulphide was not further pursued.

3 : 3′-*Dimethylthioldiphenyl.*—Benzidine-3 : 3′-disulphonic acid was converted into diphenyl-3 : 3′-disulphonyl chloride by Borsche's method (*Ber.*, 1917, **50**, 827). When this material was reduced with zinc dust and acid, the required dithiol was obtained as a pale yellow, viscous liquid which was not volatile in steam and was not obtained sufficiently pure for analysis. It was characterised by conversion into the *dimethylthiol*, which formed needles, m. p. 50°, from alcohol (Found: C, 67·7; H, 5·8. $C_{14}H_{14}S_2$ requires C, 68·2; H, 5·7%). The usual oxidising agents converted the dithiol into an amorphous material which was insoluble in organic solvents.

4 : 4′-*Dichlorodiphenyl*-3 : 3′-*disulphonyl Chloride.*—Replacement of the amino-groups in benzidine-3 : 3′-disulphonic acid was effected in the usual manner. After hydrochloric acid and copper had been removed from the solution of the chloro-acid, the solvent was removed and the residue was treated with phosphorus pentachloride. The crude *sulphonyl chloride* was purified from acetone and subsequently from acetic acid; it then melted at 179° (Found: Cl, 33·4. $C_{12}H_6O_4Cl_4S_2$ requires Cl, 33·8%). The dithiol obtained by the usual methods was a liquid and was characterised by conversion into 4 : 4′-*dichloro*-3 : 3′-*dimethylthioldiphenyl*, which crystallised

from alcohol in needles, m. p. 130° (Found: C, 53·8; H, 4·7; *M*, 308. $C_{14}H_{12}Cl_2S_2$ requires C, 53·3; H, 3·8%; *M*, 315). Treatment of the dithiol with ferric chloride or hydrogen peroxide gave an amorphous intractable material which was insoluble in organic solvents.

Diphenyl-4 : 4′-*disulphinic acid* was obtained (60% yield) by reduction of the 4 : 4′-disulphonyl chloride with boiling alkaline sulphite; it separated from hot water in needles, m. p. 143° (decomp.) (Found: C, 50·7; H, 3·8. $C_{12}H_{10}O_4S_2$ requires C, 51·0; H, 3·5%). In presence of mineral acid the substance was slowly converted into an amorphous material, presumably a disulphoxide of high molecular weight, which was insoluble in fused naphthalene or diphenyl. 4 : 4′-Dithioldiphenyl was prepared from the corresponding disulphonyl chloride; the formation of an amorphous insoluble material by oxidation of this according to Zincke (*Ber.*, 1912, **45**, 3466) was confirmed.

1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonic Acid* (VIII).—The potassium salt of this acid was obtained by the action of copper powder on a boiling aqueous solution of potassium 1-iodonaphthalene-2-sulphonate in presence of a little copper sulphate. It separated from water in nacreous leaflets (Found: K, 15·5. $C_{20}H_{12}O_6S_2K_2$ requires K, 15·9%). The corresponding disulphonyl chloride was purified from acetic acid and had m. p. 202—203° (Found: C, 53·1; H, 2·7; Cl, 15·7%; *M*, 452. $C_{20}H_{12}O_4Cl_2S_2$ requires C, 53·2; H, 2·6; Cl, 15·7; *M*, 451). Reduction of this chloride with zinc dust and hydrochloric acid in the usual manner yielded 2-naphthyl mercaptan, which was identified as disulphide.

1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide* (IX).—The chloride slowly dissolved in hot alkaline sulphite, but when this solution was acidified a colourless material separated which was insoluble in dilute alkali. This, by analogy with the diphenyl derivative, was the disulphoxide; it was not further investigated, but was submitted to the action of hydriodic acid in warm acetic acid. The required cyclic *disulphide* was then obtained in bright yellow needles, m. p. 214°, which were purified from hot acetic acid (Found: C, 75·2; H, 4·0; *M*, 307. $C_{20}H_{12}S_2$ requires C, 75·9; H, 3·8%; *M*, 316). When this substance (0·5 g.) was kept at 250° for an hour with finely divided copper (0·15 g.) the sulphide of the metal was formed; from the product, hot benzene extracted 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*, which, on purification, formed leaflets, m. p. 202° (Found: C, 84·4; S, 10·7. $C_{20}H_{12}S$ requires C, 84·5; S, 11·2%).

Thianthren derivatives were prepared from *o*-iodo-disulphides by the action of copper powder as in the following typical experiment. A mixture of di-*o*-iodophenyl disulphide (13 g.) and finely divided copper (8 g.) was heated at about 180° for ¼ hour and the mass was cooled and extracted with chloroform; the crude material (yield, about 60%) was purified and then identified with an authentic sample of thianthren. In this way di-4-iodotolyl 3-disulphide yielded 2 : 6-dimethylthianthren (Fries and Volk, *Ber.*, 1909, **42**, 1175), identified as the disulphone, and di-1-iodonaphthyl 2-disulphide gave dinaphthathianthren (Fries and Volk, *loc. cit.*).

In conclusion, we desire to thank Dr. Child for a supply of iodonaphthyl sulphide and Mr. Wright for data concerning iodophenyl mercaptan. We also wish to thank 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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