

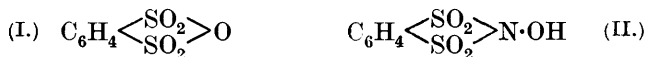
CCXLI.—*ortho*-Dithiolbenzene.

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FOR the preparation of *o*-dithiolbenzene and the study of its properties a considerable quantity of potassium benzene-*o*-disulphonate was required. Holleman's method of obtaining this salt from aniline-*o*-sulphonic acid (*Rec. trav. chim.*, 1910, **29**, 416) gave poor and variable yields (see also Pollak, *Monatsh.*, 1913, **34**, 1673) and his later modification of it (*Rec. trav. chim.*, 1921, **40**, 446) is scarcely suitable for the preparation of large quantities of material. The method described below is suitable for the rapid preparation of several hundred grams of the desired salt.

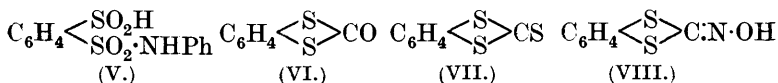
Pollak's method of reducing benzene-*o*-disulphonic acid to the *o*-dithiol (*loc. cit.*) has been improved and the properties assigned by him to the latter substance have been confirmed. This group of substances is remarkable for the ease with which five-membered ring systems containing oxygen, nitrogen or carbon may be formed

from them. This characteristic is seen in the action of ammonia on the *o*-disulphonyl chloride, when the ammonium salt of the disulphonimide (III) is formed (Holleman, *loc. cit.*). Moreover, the *anhydride* (I) has now been isolated from the disulphonate and chlorosulphonic acid, whilst the *hydroxyimide* (II) was obtained from the interaction of nitrous acid with the disulphinic acid, and when this was reduced with sulphurous acid the imide (III) was obtained. Also the *N-phenylimide* (IV) was easily formed by oxidising the *o*-sulphinylnbenzenesulphonanilide (V) with hypochlorite.



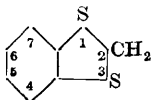
Benzene-*o*-disulphinic acid, in common with others of similar type which are being investigated, is unstable and has not been isolated in a pure condition; it has been characterised by conversion into the *o*-dimethylsulphone.

Preliminary investigation has been made of the simple derivatives of the five-membered ring containing carbon. This cyclic system is easily formed from the dithiol in several ways; for example, carbonyl chloride or carbon disulphide in presence of alkali yields *o*-phenylene dithiolcarbonate [1:3-benzdithiole-2-one] (VI) or the trithiocarbonate [2-thio-1:3-benzdithiole] (VII).* The parent ethylene derivatives of these substances are already known, the trithiocarbonate having been obtained by Husemann (*Annalen*, 1862, 123, 83) from ethylene bromide and alkali trithiocarbonate. Since Autenrieth and Hefner (*Ber.*, 1925, 58, 2151) have recorded the failure to obtain ethylene trithiocarbonate from ethylene dimercaptide and thiocarbonyl chloride, the smooth formation of this

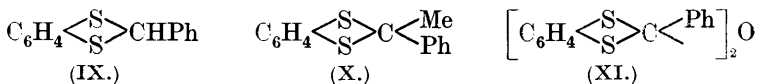


phenylene derivative seemed remarkable, but it has been found that ethylene trithiocarbonate also is easily formed from carbon disulphide and sodium ethylene dimercaptide. The thion sulphur in the phenylene derivative (VII) is not easily withdrawn by metals such as copper, but it may be replaced by reaction with hydroxylamine, when the *oximino*-derivative (VIII) is formed.

* To obtain a uniform nomenclature for this group it has been found necessary to adopt the name 1:3-benzdithiole for the annexed system. This plan is followed in the experimental part of this paper, where the substances are more precisely named.



o-Dithiolbenzene is attacked by aldehydes and ketones in presence of hydrogen chloride (compare Fasbender, *Ber.*, 1888, **21**, 1473); the mercaptols which are formed contain the singly or *gem*-disubstituted ring system and are typified by those derived from benzaldehyde (IX) and acetophenone (X). Interesting results have been obtained in the study of the action of oxidising agents on these substances.



With the usual reagents, the ring system of the dithiolcarbonate (VI) either resists attack or is ruptured, although with nitric acid nitration of the aromatic nucleus may ensue. With nitric acid, *phenylbenzodithiole* (IX) is converted into a bright yellow *nitrate*, and this on hydrolysis yields the corresponding base as a colourless material from which the *oxide* (XI) is obtained after treatment with warm solvents. This interesting substance behaves as the oxide of a pseudo-base similarly to those derived from xanthenol (R. Meyer, *Ber.*, 1893, **26**, 1276; Hewitt, *Ber.*, 1901, **34**, 3820; Werner, *Ber.*, 1901, **34**, 3301), thioxanthenol (Hilditch and Smiles, *J.*, 1911, **99**, 160), and analogous substances; it is converted by mineral acid into a series of orange or bright yellow, crystalline salts to which the sulphonium structure (XII) must be ascribed. These salts are more stable and more easily isolated than those of the thioxanthonium series, but the similarity between the two series is striking. In presence of excess of hydrogen chloride, an acid salt is formed and this when kept loses excess of mineral acid, yielding the *chloride* (XII). The crystalline *chloroplatinate* has the normal composition, and the parent substance (IX) is converted by bromine into the *perbromide* (XIII).



Phenylmethylbenzodithiole (X) does not exhibit the characteristic behaviour with nitric acid observed in the case of the phenyl derivative (IX).

The investigation of this group of substances is proceeding.

EXPERIMENTAL.

Potassium Benzene-o-disulphonate.—The aniline-*o*-sulphonic acid used was prepared from the *o*-nitro-sulphonate by reduction with zinc dust by Wohlfahrt's method (*J. pr. Chem.*, 1902, **66**, 551). The quality of the product and the yield (90% of the theoretical) are

much improved by the addition of copper sulphate to the reacting mixture.

A cooled saturated solution of sodium nitrite (16 g.) was slowly added to a mixture of aniline-*o*-sulphonic acid (40 g.) and crushed ice (40 g.). After a brief interval 250 c.c. of concentrated hydrochloric acid were added and the mixture was well stirred. The solid diazonium compound was washed and added to a solution of potassium xanthate (38 g. in 380 c.c. of water) at 60—70°. The residue obtained by evaporating this solution on the water-bath was dissolved in water (700 c.c.) and treated with a saturated solution of potassium permanganate (50—60 g.); the final portion of the latter was added at 100°, any excess being destroyed by alcohol. The aqueous solution obtained by extracting the oxides of manganese was added to the original filtrate, the whole evaporated to 600 c.c., and a boiling saturated solution of barium chloride (50 g.) added to the hot liquid. On cooling, the greater part of the required barium disulphonate separated; a further quantity was obtained by evaporating the liquid to about half its bulk in presence of hydrogen peroxide. The barium salt was converted into the potassium salt by treatment with aqueous potassium carbonate. In this way, 510 g. of potassium benzene-*o*-disulphonate (99% pure) were obtained from aniline-*o*-sulphonic acid in an average yield of 49—50%. The maximum yield in one operation was 61%.

o-Ethylsulphonylbenzenesulphonic acid, $C_6H_4(SO_2Et) \cdot SO_3H$, is evidently formed during this process, for the sulphonyl chloride prepared from the soluble material remaining after the barium disulphonate had been removed yielded *o*-ethylsulphonylbenzenesulphonamide, $C_6H_4(SO_2Et) \cdot SO_2 \cdot NH_2$, which separated from acetone and water in colourless plates, m. p. 190° (Found : N, 6.0; S, 25.2. $C_8H_{11}O_4NS_2$ requires N, 5.6; S, 25.7%).

Benzene-*o*-disulphonyl chloride was obtained in excellent yield by heating the potassium salt (50 g.) with phosphorus pentachloride (100 g.) for 25 minutes, the temperature, initially 110°, being finally raised to 170°.

Benzene-o-disulphonic anhydride (I) was obtained by keeping a mixture of 5 g. of the potassium salt and 35 g. of chlorosulphonic acid at 120° for 1 hour. After the usual treatment 2.5 g. of the *anhydride* were obtained. It separated from benzene in flat needles, m. p. 180°, which are slowly attacked by cold water (Found : S, 28.8; equiv., 111.2. $C_6H_4O_5S_2$ requires S, 29.1%; equiv., 110).

Benzene-o-disulphonhydroxyimide (II).—A solution of 6 g. of the sulphonyl chloride in a cold alkaline solution of sodium sulphite (36 g. in 50 c.c.) was acidified with cooled dilute sulphuric acid and after the excess of sulphur dioxide had been removed by a current

of air, aqueous sodium nitrite (1.3 g.) was added. The crude product (88% yield) was crystallised from hot water, the hydrated *hydroxyimide* being obtained in colourless plates, m. p. 90—91° (decomp.) (Found : N, 5.7; H₂O, 7.1. C₆H₅O₅NS₂·H₂O requires N, 5.5; H₂O, 7.1%). The substance is slowly decomposed by boiling water.

Benzene-*o*-disulphonimide (III) was prepared by treating an alcoholic solution of the crude oxime at 50—60° with sulphurous acid for 3 hours. The deliquescent mass remaining after the solvent had been evaporated was thoroughly dried, and crystallised from benzene, the imide being obtained in long needles, m. p. 186° (Found : N, 6.3. Calc. : N, 6.4%). Holleman (*loc. cit.*) gives m. p. 192° for a specimen which apparently was not recrystallised; other properties assigned by him to the substance have been confirmed. Determinations of freezing points of solutions showed that the substance is extensively ionised in dilute aqueous solution. The *silver salt* separates from water in large plates (Found : Ag, 31.6; H₂O, 5.3. C₆H₄O₄NS₂Ag·H₂O requires Ag, 31.4; H₂O, 5.2%).

Benzene-o-disulphonphenylimide (IV).—(a) The sulphonyl chloride was treated in boiling alcohol with aniline and fused sodium acetate. When the liquid cooled, the required material separated in almost theoretical yield. (b) The diazo-compound obtained from aniline-*o*-sulphonanilide (Ullmann, *Ber.*, 1910, **43**, 2700) was treated with sulphurous acid according to the method of Gattermann for the replacement of the amino- by the sulphinyl group (*Ber.*, 1899, **32**, 1136). The resulting *o*-sulphinylbenzenesulphonanilide (V) was collected with ether, but it was not further purified. An aqueous solution of the sodium salt was mixed with sodium hypochlorite; the required imide then separated in the crystalline state. The substance was purified from hot alcohol (m. p. 195°) (Found : N, 5.0; S, 21.5. C₁₂H₉O₄NS₂ requires N, 4.75; S, 21.7%).

Benzene-o-disulphinic Acid, C₆H₄(SO₂H)₂.—A solution of the alkali sulphinate was obtained by reducing the chloride with sulphite in the usual manner, but a purer product was furnished by the method of Suzuki (*J. Coll. Sci. Tokyo*, 1908, **25**, xiv, 1) applied to the hydroxyimide. These solutions having been made acid, the sulphinic acid was removed by repeated treatment with ether, but the crystalline product was unstable and could not be obtained in a state fit for analysis; when kept for a short time, the acid was converted into an insoluble material which appeared to be a complex disulphoxide. *Benzene-o-dimethylsulphone*, C₆H₄(SO₂Me)₂, was therefore prepared from the solution of the ammonium sulphinate furnished by Suzuki's method; this, after evaporation to expel the excess of ammonia, was mixed with an excess of aqueous silver nitrate, and

the sparingly soluble silver sulphinate treated with warm methyl iodide, the sulphone being thus obtained in prisms, m. p. 225° (Found: C, 40.8; H, 4.5. $C_8H_{10}O_4S_2$ requires C, 41.0; H, 4.3%).

o-Dithiolbenzene.—Reduction of the sulphonyl chloride with tin and hydrochloric acid should be avoided; the difficulties recorded by Pollak (*loc. cit.*) were encountered. Better yields (60–61%) were obtained by the use of zinc dust and the acid in presence of alcohol in a manner similar to that advocated by Zincke (*Ber.*, 1912, 45, 3472) in the case of the *m*-derivative. *o*-Phenylene dithiolbenzoate was obtained from benzene–ligroin in leaflets, m. p. 94 – 95° (Found: C, 68.6; H, 4.2. Calc. for $C_{20}H_{14}O_2S_2$: C, 68.6; H, 4.0%). Guha and Chakladar give the m. p. 77° for this substance; their dithiol had been prepared by reduction of the bromo-derivative (*J. Indian Chem. Soc.*, 1925, 2, 3).

1 : 3-Benzdithiole-2-one (VI).—This was prepared (80% yield) by shaking a solution of the dithiol in excess of alkali hydroxide with toluene containing carbonyl chloride. The product was isolated by evaporating the remaining toluene and crystallised from hot alcohol in long, colourless needles, m. p. 78 – 79° , which were volatile with a current of steam and had a pleasant characteristic odour (Found: C, 50.3; H, 2.5. $C_7H_4OS_2$ requires C, 50.0; H, 2.4%). The analogous ethylene derivative has been obtained by Huseman (*loc. cit.*) from nitric acid and the trithiocarbonate.

2-Thio-1 : 3-benzdithiole (VII).—A solution of the dithiol in aqueous sodium hydroxide was boiled with an excess of carbon disulphide for $1\frac{1}{2}$ hours. The product separated in almost quantitative yield and crystallised from hot acetic acid in yellow needles, m. p. 165° (Found: S, 52.1. $C_7H_4S_3$ requires S, 52.2%). Similar treatment of ethylene dimercaptan yielded ethylene trithiocarbonate, m. p. 37° (Found: C, 26.3; H, 3.0. Calc.: C, 26.5; H, 2.9%).

2-Oximino-1 : 3-benzdithiole (VIII).—A solution of the thiobenzdithiole (1 g.) in alcohol (60 c.c.) containing an excess of hydroxylamine hydrochloride (2 g.) and sodium acetate (2 g.) was boiled for about 10 hours or until the colour had faded. The precipitate obtained by diluting the solution with water was purified by reprecipitation from alkaline solution. The *oxime* was thus obtained in colourless needles, m. p. 129 – 130° , which were very soluble in alcohol or ether (Found: N, 7.7. $C_7H_5ONS_2$ requires N, 7.65%).

Nitro-1 : 3-benzdithiole-2-one, $O_2N \cdot C_6H_4 \cdot S_2 \cdot CO$, was prepared by gently warming the parent substance (1 g.) with nitric acid (*d* 1.42; 10 c.c.) until the product which separated from the cooled mixture was crystalline and contained no oil. This material (1.1 g.) was purified from acetone and water; the desired product was then

obtained in fibrous needles, m. p. 151° (Found : C, 39.6; H, 1.7. $C_7H_3O_3NS_2$ requires C, 39.4; H, 1.4%).

2-Phenyl-1 : 3-benzdithiole (IX).—Alcohol (20 c.c.) containing the dithiol (2 g.) and benzaldehyde (1.6 g.) was saturated with hydrogen chloride at about 20° . After 1 hour, a portion of the required material had separated and the remainder was precipitated by water. The substance was obtained from alcohol in colourless needles, m. p. 72° (Found : C, 67.3; H, 4.3; *M*, 228. $C_{13}H_{10}S_2$ requires C, 67.8; H, 4.35%; *M*, 230).

2-Phenyl-2-methyl-1 : 3-benzdithiole (X) was prepared by the same method from the dithiol and acetophenone, anhydrous zinc chloride being added to assist the condensation. The product separated from alcohol in flat, colourless needles, m. p. 83° (Found : C, 68.5; H, 5.1. $C_{14}H_{12}S_2$ requires C, 68.9; H, 4.9%).

2-Phenyl-1 : 3-benzdithiole 2-oxide (XI) was obtained by slowly adding finely powdered *2-phenyl-1 : 3-benzdithiole* (1 g.) to nitric acid (*d* 1.42; 10 c.c.). The mixture was gently warmed—not above 40° —until all had dissolved; the yellow, crystalline *nitrate* which separated (1.4 g.) after the cooled solution had been kept for 2 hours was washed with ether. Analysis of the product (m. p. 96° , decomp.) showed that this was a complex nitrate containing excess of nitric acid. It was hydrolysed with cold water or dilute aqueous alkali, and the flocculent, colourless product purified by addition of ligroin to a solution in benzene, the *oxide* thus being obtained in small, colourless needles, m. p. 134° (Found : C, 65.6; H, 3.9; *M*, 463. $C_{26}H_{18}OS_4$ requires C, 65.8; H, 3.8%; *M*, 474).

This oxide is converted by acids into yellow or orange salts of *2-phenyl-1 : 3-benzdithiole-1-sulphonium*. The *nitrate*, *sulphate*, *perchlorate* and *chloride* were obtained in the crystalline state by adding the acid to a solution of the oxide in ether or acetone. Also the acetate appears to be present in the yellow solution of the oxide in glacial acetic acid. The *chloride* (XII) was more fully investigated. When concentrated hydrochloric acid (2 c.c.) was added to a solution of the oxide (1 g.) in acetone (60 c.c.), greenish-yellow needles of the salt quickly separated; these were washed with acetone and ether. The hydrogen chloride liberated by hydrolysis was determined in different samples [Found : HCl, 19.7, 19.5. $(C_{13}H_9ClS_2)_2 \cdot HCl$ requires HCl, 19.5%]. When this acid salt was kept in a vacuum over soda lime, it lost the excess of hydrogen chloride, the crystals breaking up and yielding the orange chloride. This melted at about 110° after sintering (Found : HCl, 13.6. $C_{13}H_9ClS_2$ requires HCl, 13.8%). The *chloroplatinate* was obtained in yellowish-brown leaflets when a concentrated solution of chloroplatinic acid was added to a solution of the oxide in acetone. The substance blackens

at 240° [Found : C, 35.9; H, 2.2; Pt, 22.5. $(C_{13}H_9ClS_2)_2 PtCl_4$ requires C, 36.0; H, 2.1; Pt, 22.5%].

2-Phenyl-1 : 3-benzdithiole-1-sulphonium perbromide (XIII) was obtained as a yellow, crystalline precipitate (m. p. 212° after sintering) by adding the requisite quantity of bromine to a solution of 2-phenyl-1 : 3-benzdithiole in alcohol or benzene (Found : Br, 51.0. $C_{13}H_9Br_3S_2$ requires Br, 51.1%).

In conclusion, we wish 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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