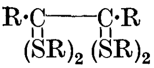
CCXCIX.—2 : 2′-*Bis*-1 : 3-*benzdithiolene.*

By WILLIAM ROBERT HARDY HURTLEY and SAMUEL SMILES.

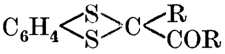
IN a previous communication (Hurtley and Smiles, this vol., p. 1821) dealing with the production of five-membered ring systems from *o*-dithiolbenzene, the formation and properties of derivatives of 1 : 3-benzdithiole were studied. The experiments now described comprise a further study of the formation of cyclic systems from this dithiol, attention being mainly directed to the conditions of formation and stability of the bis-1 : 3-benzdithiole system.

Posner (Ber., 1902, **35**, 506) has shown that 7 : 7′-dithioaryl derivatives of stilbene are formed during the interaction of benzoin and mercaptans. The mechanism of this reaction does not seem at all clear, but since both aromatic and aliphatic mercaptans appear readily to take part in it, it was expected that *o*-dithiolbenzene and benzoin would yield 2 : 3-diphenyl-1 : 4-benzdithien. However, in spite of repeated trial, the formation of this substance containing the six-membered ring has not yet been realised in this manner.

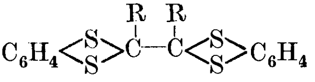
o-Dithiolbenzene and αβ-dithiolethane [dithioethyleneglycol] also differ from the monothiols in their behaviour with diketones. With the monothiols the formation of dimercaptols (I) from α-diketones has been recorded (Posner, *Ber.*, 1900, **33**, 2983; 1902, **35**, 493), but with the dithiols mentioned the reaction of the second carbonyl group under similar conditions has not yet been observed, the product in all the cases examined being of the monomercaptol type (II). Fasbender (*Ber.*, 1888, **21**, 1473) has described the formation of 2 : 2′-bis-1 : 3-dithiolan (IV) from glyoxal and αβ-dithiolethane, but the circumstance now encountered seems to point to the instability or unfavoured configuration of the 2 : 2′-substituted bis-1 : 3-dithiole system (for example, III), and it is worth noting that a similar character has been observed with analogous derivatives of other heterocyclic systems (J., 1924, **125**, 878). It is also remarkable that only the monomercaptol (V) has been isolated from the reaction of *o*-dithiolbenzene with acetylacetone.


$\underset{(SR)_2}{R\cdot C}—\underset{(SR)_2}{C\cdot R}$

(I.)

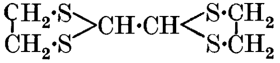

$C_6H_4<\begin{smallmatrix}S\\S\end{smallmatrix}>C<\begin{smallmatrix}R\\COR\end{smallmatrix}$

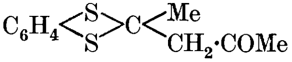
(II.)


$C_6H_4<\begin{smallmatrix}S\\S\end{smallmatrix}>\overset{R}{C}—\overset{R}{C}<\begin{smallmatrix}S\\S\end{smallmatrix}>C_6H_4$

(III.)

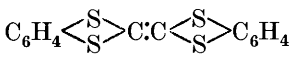
(IV.)

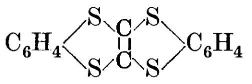

$\begin{smallmatrix}CH_2\cdot S\\CH_2\cdot S\end{smallmatrix}>CH\cdot CH<\begin{smallmatrix}S\cdot CH_2\\S\cdot CH_2\end{smallmatrix}$


$C_6H_4<\begin{smallmatrix}S\\S\end{smallmatrix}>C<\begin{smallmatrix}Me\\CH_2\cdot COMe\end{smallmatrix}$

(V.)

(VI.)

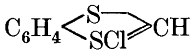

$C_6H_4<\begin{smallmatrix}S\\S\end{smallmatrix}>C{:}C<\begin{smallmatrix}S\\S\end{smallmatrix}>C_6H_4$


(VII.)

Since the unsaturated derivatives of the required type are generally endowed with great stability, the formation of 2 : 2′-bis-1 : 3-benzdithiolene (VI) was sought. From the interaction of tetrachloroethylene and *o*-dithiolbenzene a substance of the anticipated properties, such as high melting point and volatility, was isolated;

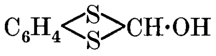
but this method of formation permits no decision between the alternative structures (VI and VII) containing the five- and six-membered systems respectively. Evidence for the constitution of the substance was obtained as follows.

As previously shown (Hurtley and Smiles, *loc. cit.*) in the case of the 2-phenyl derivative, the 2-hydroxy-derivatives of the 1 : 3-benzdithiole system behave as pseudo-bases and are converted by acids into the salts of 1 : 3-benzdithiylium. Accordingly, from *o*-dithiolbenzene and ethyl orthoformate in presence of hydrogen chloride deeply coloured solutions of the 1 : 3-benzdithiylium 1-chloride were obtained (VIII). This salt was not isolated owing to its high solubility, but it was obtained as the crystalline *chloroplatinate* and *zinc chloride* double salt. As in the case of the 2-phenyl derivative, the salts of 1 : 3-benzdithiylium are readily hydrolysed, yielding the pseudo-base, and when the zinc chloride double salt is treated with warm acetic anhydride the pseudo-base (IX) at first liberated suffers dehydration and 2 : 2′-*bis*-1 : 3-*benzdithiolene* (VI) is formed; this product is identical with that obtained from tetrachloroethylene.



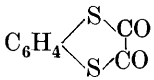
$C_6H_4<^{S}_{SCl}>CH$

(VIII.)



$C_6H_4<^{S}_{S}>CH\cdot OH$

(IX.)

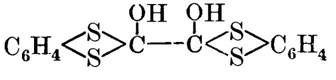


$C_6H_4<\begin{matrix}S\cdot CO\\ S\cdot CO\end{matrix}$

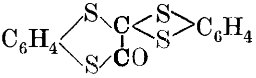
(X.)

Derivatives of this substance are formed in the reaction of oxalyl chloride with *o*-dithiolbenzene. With excess of oxalyl chloride in a suitable solvent the unstable yellow *oxalyl* derivative (X) containing the 1 : 4-benzdithian system is formed, but with excess of the dithiol under carefully regulated conditions a colourless product is formed of entirely different character. The instability of this material prevented isolation in a state suitable for analysis, but the behaviour of the substance clearly shows that it contains the 2 : 2′-bis-1 : 3-benzdithiole system and that it must be regarded as the 2 : 2′-dihydroxy-derivative of this (XI). For example, even when kept in neutral solvents it spontaneously yields among other products 2 : 2′-bis-1 : 3-benzdithiolene (VI). In its capacity of an α-ditertiary alcohol the substance (XI) is sensitive to acid reagents. The stable colourless product then formed does not exhibit the reactions of the thionyl group and for its structure the choice lies between the alternatives (XII) and (XIII).

(XI.)



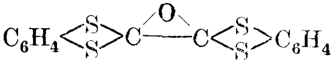
$C_6H_4<^{S}_{S}>\overset{OH}{C}-\overset{OH}{C}<^{S}_{S}>C_6H_4$



$C_6H_4<\begin{matrix}S\cdot C<^{S}_{S}>C_6H_4\\ S\cdot CO\end{matrix}$

(XII.)

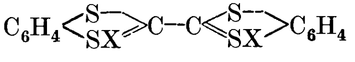
(XIII.)



$C_6H_4<^{S}_{S}>\overset{O}{C-C}<^{S}_{S}>C_6H_4$

The latter (XIII), containing the ethylene oxide ring, must be discarded, since the substance is not attacked by warm hydrogen chloride and does not yield thiylium salts like other 2-oxides of this series. Moreover, the former alternative (XII) is confirmed by the synthesis from the oxalyl derivative (X) and *o*-dithiolbenzene. It is evident that the structure (XI) assigned to the substance yielded by oxalyl chloride and excess of the dithiol accords well with its conversion in acid media into this *spiro*-derivative (XII), which appears to be the result of a pinacolinic change, the case being similar to that of the formation of 10 : 10-diphenylenephenanthrone (Klinger and Lonnes, *Ber.*, 1896, **29**, 2152; Werner and Grot, *Ber.*, 1904, **37**, 2894) during the oxidation of bisdiphenylene-ethylene in presence of acid. Attention may also be directed to the interesting fission which the *spiro*-derivative suffers when heated. At about 200—250°, a smooth decomposition ensues, 1 : 3-benzdithiole-2-one and 2 : 2′-bis-1 : 3-benzdithiolene (VI) being formed. This process, involving a redistribution of the molecule, may be ascribed to the relative instability of the six-membered ring system previously observed in the case of the simple oxalyl derivative.

Finally, it must be remarked that a substance possessing the 2 : 2′-dihydroxy-structure (XI) should under suitable conditions show the character of a pseudo-base in common with other 2-hydroxy derivatives. This condition is fulfilled by the substance in question, since treatment with sulphuric acid in acetic anhydride produces from it a deep purple, crystalline *sulphate*. This salt is rapidly hydrolysed by water, the chief product being the *spiro*-derivative, whilst in presence of ammonia 2 : 2′-bis-1 : 3-benzdithiolene is formed; these substances are the characteristic decomposition products of the pseudo-base (XI) under acid and neutral conditions respectively. Reduction of the sulphate furnished the last-named substance. These reactions indicate that the salt contains the bis-1 : 3-benzdithiole skeleton and that the pseudo-base is regenerated from it by hydrolysis; the dithiylium structure (XIV) is therefore



$$C_6H_4<\begin{smallmatrix}S-\\SX\end{smallmatrix}>C-C<\begin{smallmatrix}S-\\SX\end{smallmatrix}>C_6H_4 \quad \text{(XIV.)}$$

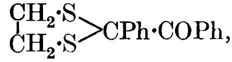
assigned to the substance. In solution this sulphate is stable only in presence of excess of acid; it separates from the medium as a complex sulphate of the type $2BSO_4,H_2SO_4$ and it is worth notice that similar behaviour was observed (Hurtley and Smiles, *loc. cit.*) with the chloride of 2-phenyl-1 : 3-benzdithiylium, which was isolated as the complex 2BCl,HCl. 2 : 2′-Bis-1 : 3-benzdithiolene absorbs four atomic proportions of iodine; the product is remarkably stable and it is doubtful whether it should be assigned to this class of dithiylium salts.

EXPERIMENTAL.

2-*Acetyl*-2-*methyl*-1 : 3-*benzdithiole* (II).—A solution of diacetyl (1 mol.) and *o*-dithiolbenzene (2 mols.) in alcohol was saturated with dry hydrogen chloride at the ordinary temperature. The compound (II) (yield 80—85%), separation of which began in a few minutes, was sparingly soluble in the usual organic media and crystallised from hot alcohol in colourless plates, m. p. 156° (Found : C, 57·3 ; H, 4·7. $C_{10}H_{10}OS_2$ requires C, 57·1 ; H, 4·8%).

With equimolecular proportions of the reagents poor yields of this product were obtained. Similar experiments with αβ-dithiolethane and diacetyl showed that the mercaptan was oxidised by the diketone. Posner (*Ber.*, 1902, **35**, 493) has recorded a similar action of diacetyl with phenyl mercaptan.

2-*Benzoyl*-2-*phenyl*-1 : 3-*benzdithiole* (II).—A solution of benzil (1·5 g.) and *o*-dithiolbenzene (1 g.) in alcohol (25 c.c.) was saturated at 5° with dry hydrogen chloride. The required product was collected (90—95% yield) after 15 minutes; it separated from hot alcohol in pale yellow needles, m. p. 175° (Found : C, 71·7 ; H, 4·5. $C_{20}H_{14}OS_2$ requires C, 71·8 ; H, 4·2%).

2-*Benzoyl*-2-*phenyl*-1 : 3-*dithiolan*,  $\begin{matrix} CH_2\cdot S \\ | \\ CH_2\cdot S \end{matrix}\!\!>CPh\cdot COPh$, was prepared (80% yield) in a similar manner from a solution of benzil (2 g.) and αβ-dithiolethane (0·9 g.) in alcohol (15 c.c.) It separated from hot alcohol in needles, m. p. 94—95° (Found : C, 66·7 ; H, 5·2 ; *M*, 276. $C_{16}H_{14}OS_2$ requires C, 67·1 ; H, 4·9% ; *M*, 286).

2-*Acetonyl*-2-*methyl*-1 : 3-*benzdithiole* (V).—Acetylacetone (1 mol.) was added to a solution of *o*-dithiolbenzene (2 mols.) in alcohol (15 parts). After the mixture had been saturated with hydrogen chloride at 5°, the required mercaptol (60—65% yield) separated in colourless needles which, after purification, had m. p. 119° and gave a purple solution in sulphuric acid (Found : C, 59·1 ; H, 5·2. $C_{11}H_{12}OS_2$ requires C, 58·9 ; H, 5·4%). When equimolecular proportions of the reagents were used, no mercaptol could be isolated ; the resinous product contained the disulphide.

1 : 3-*Benzdithiylium* 1-*Chloride* (VIII).—A mixture of *o*-dithiolbenzene (1·5 g.), ethyl orthoformate (1·6 g.), and alcohol (10 c.c.) was saturated at 5° with hydrogen chloride. After 15 hours, the orange-brown solution was mixed with powdered anhydrous zinc chloride, which rapidly dissolved. The crystals of the *zinc chloride* double salt of the required substance which separated were washed with alcohol and then with ether; the orange needles thus obtained had in most preparations a red tint of varying depth. The material could not be recrystallised (Found : Zn, 13·0. $2C_7H_5ClS_2,ZnCl_2$ requires Zn, 12·7%). The *chloroplatinate* was obtained in glistening

orange prisms by adding aqueous chloroplatinic acid to a solution of this zinc chloride double salt in excess of concentrated hydrochloric acid [Found: C, 23·4; H, 1·6; Pt, 27·2. $(C_7H_5S_2)_2PtCl_6$ requires C, 23·5; H, 1·4; Pt, 27·3%]. The substance darkens at about 220°.

When a solution of αβ-dithiolethane (1 g.) and ethyl orthoformate (2 g.) in alcohol (20 c.c.) was saturated with hydrogen chloride, *ethylene trithioformate* (1·1 g.) rapidly separated; it formed needles, m. p. 104—105°, from hot alcohol (Found: C, 31·9; H, 4·9. $C_8H_{14}S_6$ requires C, 31·8; H, 4·6%). The behaviour of this aliphatic dithiol with the orthoformate is similar to that of ethyl mercaptan, which yields trimethyl orthothioformate (Holmberg, *Ber.*, 1907, **40**, 1740).

The interaction of oxalyl chloride and *o*-dithiolbenzene leads to different products according to the conditions.

(*a*) 1 : 4-Benzdithian-2 : 3-dione. Oxalyl chloride (4 g.; an excess) was carefully added to a solution of *o*-dithiolbenzene (2 g.) in dry acetone (60 c.c.). After 5 minutes, when the vigorous reaction had subsided, the greater part (about 55 c.c.) of the solvent was evaporated.

1 : 4-*Benzdithian*-2 : 3-*dione* (X) separated (0·7 g.) from the cooled residue; it was purified by rapid treatment with warm benzene from which it separated in bright yellow prisms, m. p. 160° (decomp.). It was decomposed by boiling water, alcohol, or acetic acid and quickly dissolved by aqueous alkali hydroxide (2*N*). A resinous material was slowly deposited from the cold solution in benzene (Found: C, 49·0; H, 2·0; *M*, 192. $C_8H_4O_2S_2$ requires C, 48·9; H, 2·1%; *M*, 196).

(*b*) With excess of *o*-dithiolbenzene and without a solvent, derivatives of 2 : 2′-bis-1 : 3-benzdithiole or the spiro-*compound* (XII) are formed. Oxalyl chloride was added to twice its weight of the dithiol and when evolution of hydrogen chloride had almost ceased the mixture was warmed on the water-bath for about ¼ hour. The more soluble part was extracted from the cooled mass with ether, and the solvent rapidly removed at the ordinary temperature. The crystalline residue, which exhibited the properties of 2 : 2′-dihydroxy-bis-1 : 3-benzdithiole (XI), could not be purified by the usual methods; the yield varied considerably according to the conditions of interaction, which were somewhat difficult to control with the small amounts of reagents available. A solution in benzene was allowed to evaporate spontaneously, and 2 : 2′-bis-1 : 3-benzdithiolene (VI) was isolated from the residue. A warm dilute solution of the substance in acetic anhydride was mixed with concentrated sulphuric acid (about 16 drops in 100 c.c. of solution) and kept for 12 hours. 2 : 2′-*Bis*-1 : 3-*benzdithiylium sulphate* was then precipitated in the crystalline state. The yield varied, but was usually about 0·9 g. from 2 g. of the dithiol. The salt was dissolved in hot dilute sulphuric acid (60%), and separated from the cold medium in long, deep purple needles which exhibited a bronze lustre and had m. p. 268—270° (decomp.) (Found : C, 35·8; H, 2·7; SO_4, 31·2, 31·0. $2C_{14}H_8S_4{\cdot}SO_4$, $H_2SO_4,2H_2O$ requires C, 36·0; H, 2·35; SO_4, 30·8%).

Reduction of this sulphate in 60% sulphuric acid with zinc dust yielded 2 : 2′-bis-1 : 3-benzdithiolene, and the same substance was isolated from the product formed on hydrolysis with warm, dilute ammonia. The permanganate-coloured aqueous solution of the salt was rapidly decolorised by boiling; hydrolysis under these weakly acid conditions gave a mixture of 2 : 2′-bis-1 : 3-benzdithiolene and 3-*keto*-1 : 4 - *benzdithian* - 2 : 2′ - spiro - 1′ : 3′ - *benzdithiole* (XII).

The latter substance (XII) was more conveniently prepared directly from the interaction of oxalyl chloride and *o*-dithiolbenzene by prolonging the period of warming and extracting the residue with hot acetic acid. The material (1·3 g. from 2 g. of the dithiol) was isolated by diluting the extract with water and, after purification from acetone with the aid of charcoal, was obtained in short needles, m. p. 168°, which gave an orange solution with concentrated sulphuric acid. It was also obtained by boiling the acetic acid solution of the more soluble product which is formed under milder conditions. This substance seems always to be formed to some extent in the reaction of oxalyl chloride with the dithiol and under the conditions described forms the greater portion of the product. It was synthesised by warming equal weights of the oxalyl derivative (X) and the dithiol on the water-bath. The product was kept for 12 hours and then treated with ether in presence of aqueous sodium hydroxide. Evaporation of the solvent yielded the required material, which was purified and identified in the usual manner (Found : C, 52·8; H, 2·9; S, 39·9; *M*, 312. $C_{14}H_8OS_4$ requires C, 52·5; H, 2·5; S, 40·0%; *M*, 320).

2 : 2′-*Bis*-1 : 3-*benzdithiolene* (VI) was obtained by several methods. (*a*) Decomposition of the substance (XII) described in the preceding paragraph began slightly above the melting point, but was rapid at 200° and above. 1 : 3-Benzdithiole-2-one (this vol., p. 1826) was isolated by distillation in steam and identified in the usual manner, whilst the residue, purified from benzene, yielded the desired substance (0·7 g. from 3 g. of material).

(*b*) A solution of the dithiol (4 g.) and tetrachloroethylene (2·3 g.) in alcohol (15 c.c.), in which the requisite amount of sodium had been dissolved, was kept in a sealed tube at 110—120° for 7 hours. The yellow material obtained after the unchanged dithiol had been removed was purified from benzene (yield 0·5 g.).

(*c*) The zinc chloride double salt of 1 : 3-benzdithiylium (VIII) was added to boiling acetic anhydride. When the action was complete, the solid was separated from the cooled liquid and purified as usual (yield about 30%).

The substance is also formed by alkaline hydrolysis or by reduction of the dithiylium sulphate and in the spontaneous decomposition of the pseudo-base obtained from oxalyl chloride and the dithiol. It is sparingly soluble in the usual organic media and is obtained from benzene in golden needles, m. p. 234°, which volatilise when heated (Found: C, 55·1; H, 2·9; *M*, 291. $C_{14}H_8S_4$ requires C, 55·3; H, 2·6%; *M*, 296). It is oxidised by sulphuric acid, the purple dithiylium sulphate being formed; and when a benzene solution of iodine was added to a similar solution of the substance a *tetraiodo*-additive product was precipitated as a finely-divided black powder (Found: I, 63·0. $C_{14}H_8I_4S_4$ requires I, 62·7%). This substance was remarkably stable and was unattacked by aqueous alkali hydroxide or by aqueous potassium iodide.

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.

King's College, London. [*Received, June* 17*th*, 1926.]