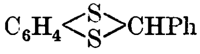
LXXIX.—*Derivatives of 2-Phenyl-1 : 3-benzdithiole.*

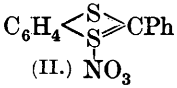
By William Robert Hardy Hurtley and Samuel Smiles.

In a previous communication (J., 1926, 1822), it was shown that 2-phenyl-1 : 3-benzdithiole (I) may be oxidised by nitric acid to the sulphonium nitrate (II), from which the pseudo-base (III) is liberated by alkali. Further experiments on the formation of these sulphonium nitrates have now been made, chiefly with the object of determining whether the process may be generally applied to other members of this group and whether it is subject to the influence of substituents in the 2-phenyl nucleus. The results are summarised as follows.



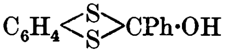
$C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>CHPh$

(I.)



$C_6H_4<\genfrac{}{}{0pt}{}{S}{\underset{NO_3}{S}}\geqslant CPh$

(II.)

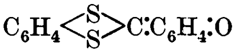


$C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>CPh{\cdot}OH$

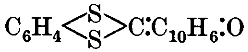
(III.)

The presence of a nitro-group in the 2-phenyl nucleus is unfavourable to the formation of the sulphonium salt by oxidation; *e.g.*, the *o*-nitrophenyl derivative (type I) is not attacked by the usual agents. On the other hand, methoxy- and hydroxy-groups facilitate the process. The *nitrate* of the 2-*p*-methoxyphenyl derivative (type II) is very easily formed from the mercaptol (type I), whilst the corresponding *pseudo-base* (type III), which has been characterised as the *oxide* (compare *loc. cit.*, p. 1827), yields more stable salts than the unsubstituted derivative. Oxidation of the *p*- and *o*-hydroxy-derivatives proceeds so easily that unless precautions are adopted it ensues during the formation of the mercaptol (type I) from the hydroxy-aldehyde and *o*-dithiolbenzene. Attempts to obtain the pseudo-base from the salts of 2-*p*-hydroxyphenylbenzdithiole sulphonium (type II) were unsuccessful, since this substance (type III) at the moment of liberation loses the elements of water and is converted into the scarlet *quinone* (IV). A derivative (V) of this interesting type is formed in a similar manner

(IV.)



$C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>C{:}C_6H_4{:}O$



$C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>C{:}C_{10}H_6{:}O$

(V.)

from 2′-hydroxy-2-naphthyl-1 : 3-benzdithiole. Oxidation of this naphthyl derivative takes place so readily that it has not been possible to isolate the mercaptol (type I), the product from *o*-dithiolbenzene and 2-naphtholaldehyde in presence of hydrogen chloride being the chloride of the pseudo-base, which with alkaline media yields the unimolecular *quinone* (V). These quinonoid derivatives yield hydrochlorides which at present are assumed to be of the sulphonium type (II).

EXPERIMENTAL.

2-*o*-Nitrophenyl-1 : 3-benzdithiole was obtained by saturating a cooled solution of the dithiol (0·5 g.) and *o*-nitrobenzaldehyde (0·6 g.) in alcohol (15 c.c.) with hydrogen chloride in presence of zinc chloride. The substance (m. p. 106°. Compare Guha and Chakladar, *J. Indian Chem. Soc.*, 1925, **2**, 3) was not attacked by cold nitric acid (*d* 1·4) but was destroyed by the boiling reagent. It gave a yellow bromine derivative.

2-p-*Methoxyphenyl*-1 : 3-*benzdithiole* was obtained in almost theoretical yield by treating a solution of the dithiol (1 g.) and anisaldehyde (1 g.) in alcohol (10 c.c.) at 0° with hydrogen chloride for 15 minutes. The liquid product was kept until it had solidified, and after purification from alcohol it melted at 72° (Found : C, 64·6; H, 4·9. $C_{14}H_{12}OS_2$ requires C, 64·6; H, 4·6%). When a warm (not above 40°) solution of this substance in nitric acid (*d* 1·4) was cooled, the *nitrate* of the base (type II) separated in red needles (Found : HNO_3, 32·9. $C_{14}H_{11}OS_2{\cdot}NO_3,2HNO_3$ requires HNO_3, 32·6%). The base (type III) was liberated from this salt by ice-cold 2*N*-aqueous sodium hydroxide and after being dried it was purified from benzene–light petroleum, 2-p-*methoxyphenyl*-1 : 3-*benzdithiole* 2-*oxide* being obtained in colourless prisms, m. p. 158° (Found : C, 62·7; H, 4·5; *M*, 530. $C_{28}H_{22}O_3S_4$ requires C, 62·9; H, 4·1%; *M*, 538). When an acetone solution of this oxide was mixed with concentrated hydrochloric acid, the *chloride* separated in yellow needles [Found : HCl, 18·7. $(C_{14}H_{11}OClS_2)_3,2HCl$ requires HCl, 19·1%].

2-p-*Hydroxyphenyl*-1 : 3-*benzdithiole* (type I) was prepared as in the case of the *p*-methoxy-derivative, but being more soluble, it was isolated by the addition of ice to the reaction mixture. The purification of the product required care owing to the ease with which it is oxidised. The substance was obtained in needles, m. p. 118°, which persistently retained a faint pink tinge (Found : C, 63·3; H, 4·4. $C_{13}H_{10}OS_2$ requires C, 63·4; H, 4·1%). Oxidation of the mercaptol was conducted by trituration with cooled nitric acid; the *nitrate* was then obtained in orange needles [Found : HNO_3, 11·7. $(C_{13}H_9OS_2)_2,HNO_3$ requires HNO_3, 11·4%].

1 : 3-*Benzdithiole*-2-p-*benzoquinone* (IV) was obtained by treating the foregoing nitrate with aqueous potassium carbonate. It was sparingly soluble in warm benzene, from which it separated in scarlet leaflets, m. p. 212—213° (Found : C, 63·9; H, 3·5. $C_{13}H_8OS_2$ requires C, 63·9; H, 3·5%). The substance was easily reduced by a solution of sulphur dioxide in alcohol and yielded a colourless additive product when treated with aqueous sodium bisulphite. The orange *hydrochloride* was obtained from an acetone solution of this substance (Found : HCl, 13·2. $C_{13}H_9OClS_2$ requires HCl, 13·0%).

1 : 3-*Benzdithiole*-2-β-*naphthaquinone* (V).—The normal mercaptol (type I) could not be obtained by interaction of the dithiol and 2-naphthol-1-aldehyde; instead, the oxidation product was isolated as the hydrochloride (II). A cooled solution of the dithiol (2 g.) and the aldehyde (2 g.) in ether (40 c.c.) was treated with hydrogen chloride and kept for 12 hours. On treatment with aqueous

sodium hydroxide the brown impure salt yielded the desired material (2·4 g.). This separated from acetone in small, red needles, m. p. 165° (Found: C, 69·1; H, 3·5; *M*, 293. $C_{17}H_{10}OS_2$ requires C, 69·4; H, 3·4%; *M*, 294). The substance yielded a colourless additive product with sodium bisulphite, but it was not reduced by an alcoholic solution of sulphur dioxide. The *chloride* was obtained in the usual manner and formed red needles (Found: HCl, 11·2. $C_{17}H_{11}OClS_2$ requires HCl, 11·1%).

2-*Styryl*-1 : 3-*benzdithiole*, obtained from cinnamaldehyde and the dithiol in the usual manner, formed needles, m. p. 80° (Found: C, 70·2; H, 5·1. $C_{15}H_{12}S_2$ requires C, 70·3; H, 4·7%). When this mercaptol was treated with concentrated nitric acid at 0° for 15 minutes, the *nitrate* of the base (type II) was obtained in orange needles of complex composition [Found: HNO_3, 25·0. $(C_{15}H_{11}S_2\cdot NO_3)_4,HNO_3$ requires HNO_3, 24·8%]. The base liberated from this nitrate by alkaline media was too unstable for isolation in the pure condition.

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

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