CCCLXXVIII.—*o-Sulphinobenzoic Acid.*

By William Bennett Price and Samuel Smiles.

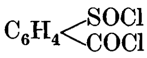
In the course of experiments with hydroxy-derivatives of thioxanthone dioxide, *o*-sulphinobenzoic acid was required. Two methods are recorded for the preparation of this acid, either from *o*-diazobenzoic acid with sulphurous acid (Gattermann, *Ber.*, 1899, **32**, 1144) or from the dichloride of *o*-sulphobenzoic acid by reduction with alkaline sulphite (Davis and Smiles, J., 1910, **97**, 1290), but neither is suitable for the preparation of large quantities of the material, the yield being variable and the quality of the product, particularly when the latter method is used, often poor.

According to patent literature (D.R.-P. 35230), a solution of *o*-chlorothiolbenzoic acid is obtained when *o*-thiolbenzoic acid is treated with chlorine in presence of an inert solvent. No mention is made of the isolation of the chlorothiol, but assuming the formation of the substance, it was expected that on treatment with water the usual decomposition of chlorothiols observed by Zincke (for example, *Annalen*, 1918, **416**, 86) would ensue, yielding the sulphinic acid and the disulphide, the latter of which would be available for renewed treatment with chlorine. Accordingly, the action of chlorine on *o*-thiol- or *o*-dithio-benzoic acid in presence of carbon tetrachloride has now been more fully studied. As a result, although the *o*-chlorothiolbenzoic acid has not been encountered, good yields of an unstable *dichloro*-derivative have been obtained. This material, when carefully treated with water, yields the almost pure sulphinic acid. As described in the experimental part, a trustworthy and simple method for preparing the acid is thus available.

The reactions of this dichloro-derivative have been further studied with the object of determining its structure. The halogen is entirely and quickly removed by ice-cold water; *o*-sulphinobenzoic acid alone is formed, no disulphide being observed. In fact titration with alkali hydroxide accords with the equation

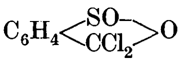
$$C_7H_4O_2Cl_2S + 4NaOH = 2NaCl + 2H_2O + CO_2Na\cdot C_6H_4\cdot SO_2Na.$$

The substance might accordingly be represented in any of the three following ways :



$C_6H_4<\substack{SOCl\\COCl}$

(I.)



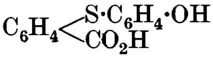
$C_6H_4<\substack{SO-\\CCl_2}>O$

(II.)

$C_6H_4<\substack{SCl_2\\CO}>O$

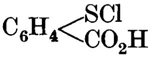
(III.)

but the acyl dichloride (I) and the *C*-dichloro-anhydride (II) structures are discarded for the following reasons. On treatment with *p*-nitrobenzyl alcohol a mononitrobenzyl ester was obtained together with *p*-nitrobenzyl chloride. The first-named product was evidently the *sulphinic ester* $CO_2H\cdot C_6H_4\cdot SO\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2$ (IV), since it yielded the sulphinic acid on hydrolysis and differed from the *sulphone*, $CO_2H\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot C_6H_4\cdot NO_2$ (V), which was obtained from the sodium sulphinate and *p*-nitrobenzyl chloride or by oxidation of the corresponding sulphide. Moreover, the substance did not react with *p*-benzoquinone in the manner characteristic of sulphinic acids (Hinsberg, *Ber.*, 1894, **27**, 3259), and of *o*-sulphinobenzoic acid in particular. On treatment with phenols this chloro-compound yielded hydroxy-derivatives of *o*-carboxydiphenyl sulphide (*e.g.*, VI) together with chlorophenols. Neither with alcohols nor with phenols has any evidence of the formation of carboxylic esters been discovered. The incompatibility of this result with the structures (I) and (II) is evident and it is emphasised by the behaviour of the isomeric chlorides of *o*-sulphobenzoic acid with these reagents (List and Stein, *Ber.*, 1898, **31**, 1648). Moreover, the formation of the acyl dichloride (I) or of the *C*-dichloro-anhydride (II) by the action of chlorine on *o*-thiol- or *o*-dithio-benzoic acid cannot be simply interpreted. On the other hand, the formation of the *S*-dichloro-anhydride (III) by the process is readily explained by assuming the loss of hydrogen chloride from the *o*-chlorothiol (VII) and the subsequent addition of halogen to the sulphenic anhydride (VIII). For these reasons the substance is regarded as the *S*-dichloro-



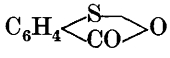
$C_6H_4<\substack{S\cdot C_6H_4\cdot OH\\CO_2H}$

(VI.)



$C_6H_4<\substack{SCl\\CO_2H}$

(VII.)



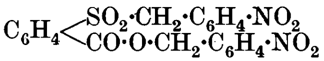
$C_6H_4<\substack{S\\CO}>O$

(VIII.)

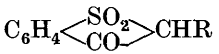
anhydride and it is evident that the reactions with *p*-nitrobenzyl alcohol and with phenols accord with this structure. Bearing in mind the tautomeric behaviour of the two chlorides of *o*-sulphobenzoic acid (List and Stein, *loc. cit.*), it seems not improbable that under suitable conditions conversion into the acyl dichloride might be realised, but as yet this has not been effected and no evidence of tautomeric character has been discovered.

During the investigation of the sulphinic ester (IV) and the isomeric sulphone (V) the p-*nitrobenzylsulphone ester* (IX) was encountered. This substance is attacked by alcoholic sodium hydroxide, yielding the red sodium salt of 3-*keto*-2-p-*nitrophenyl*-2 : 3-*dihydrothionaphthen dioxide* (X; $R = C_6H_4\cdot NO_2$). Further investigation of this method of synthesising 2-derivatives of thionaphthen dioxide is being made; from sodium *o*-sulphinobenzoate and ethyl chloroacetate, 3-keto-2-carbethoxy-2 : 3-dihydrothionaphthen dioxide (X; $R = CO_2Et$) has already been obtained. This product is identical

(IX.)



$$C_6H_4{<}\begin{matrix}SO_2\cdot CH_2\cdot C_6H_4\cdot NO_2\\ CO\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2\end{matrix}$$



$$C_6H_4{<}\begin{matrix}SO_2\\ CO\end{matrix}{>}CHR$$

(X.)

with the " anhydro " derivative obtained by Feist (*Ber.*, 1925, **58**, 2311) from the reaction of fuming sulphuric acid with ethyl benzoylacetate. The structure assigned to the substance by Arndt (*Ber.*, 1926, **59**, 1074), after examining the products of hydrolysis, is thus confirmed.

EXPERIMENTAL.

o-*Sulphinobenzoic Acid.*—Dry chlorine was passed into a mixture of dry carbon tetrachloride (40 c.c.) and *o*-thiolbenzoic acid (10 g.) until the latter had dissolved. Dry air or nitrogen was passed through the clear solution until hydrogen chloride and the excess of chlorine had been removed. The dichloro-anhydride, which separated in the crystalline state as a result of the fall in temperature and loss of solvent, was collected and spread on porous earthenware. Atmospheric moisture liberated hydrogen chloride from the material, and this decomposition was completed by means of ice. The sulphinic acid was then obtained in the crystalline state (yield, *ca.* 70%), the crude product having usually m. p. 123—124°. The purified acid decomposed and solidified a few degrees above its melting point (126°; Gattermann, *loc. cit.*, gives m. p. 125°), forming *o*-dithio- and *o*-sulpho-benzoic acids. With impure samples this decomposition may take place below the m. p., with the result that the material does not fuse until near the m. p. of *o*-dithiobenzoic acid (289°). This behaviour explains the high melting point recorded for the sulphinic acid by Davis and Smiles (*loc. cit.*), their product.

obtained by reduction of *o*-sulphobenzoyl dichloride, being evidently impure.

The *dichloride* (III) of *o*-sulphinobenzoic acid was prepared as described in the foregoing paragraph, purified materials being used. Owing to the instability of the substance and its sensitiveness to moisture, further purification by recrystallisation could not be effected. It formed cream-coloured needles, m. p. 62° (Found: Cl, 29·9; S, 14·3. $C_7H_4O_2Cl_2S$ requires Cl, 31·8; S, 14·3%. $C_7H_5O_2ClS$ requires Cl, 18·8; S, 17·0%). Decomposition with aqueous sodium hydroxide gave equiv., 56·0. $C_7H_4O_2Cl_2S$, according to the equation given on p. 2859, requires equiv., 55·7.

p-*Nitrobenzyl* o-*Carboxybenzenesulphinate* (IV).—A solution of the dichloride (from 4·25 g. of *o*-thiolbenzoic acid) from which excess of chlorine and hydrogen chloride had been removed was mixed with a concentrated solution of *p*-nitrobenzyl alcohol in dry ether. The *ester* separated in the crystalline state and after suitable purification from ether it was obtained in needles, m. p. 121° (Found: C, 52·4; H, 3·2; N, 4·4; S, 10·0. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4; N, 4·3; S, 9·9%). *p*-Nitrobenzyl chloride was isolated from the mother-liquors of the reaction. The ester did not attack a cold aqueous suspension of *p*-benzoquinone. A sample was hydrolysed by boiling water; the products—*p*-nitrobenzyl alcohol and *o*-sulphinobenzoic acid—were isolated and identified in the usual manner.

o-*Carboxyphenyl*-p-*nitrobenzylsulphone* (V) was obtained by boiling the potassium salt of *o*-sulphinobenzoic acid (1 mol.) and *p*-nitrobenzyl bromide (1 mol.) in alcohol which contained a little water. The potassium salt of the required acid separated from the cooled mixture. The *acid* was purified from aqueous acetic acid; it had m. p. 226° and was not attacked by aqueous sodium hydroxide (Found: C, 52·3; H, 3·4; S, 10·0. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4; S, 9·9%).

The p-*nitrobenzyl* ester (IX) of *o*-carboxyphenyl-*p*-nitrobenzylsulphone was obtained when a concentrated alcoholic solution of potassium *o*-sulphinobenzoate (1 mol.) and *p*-nitrobenzyl bromide (2 mols.) was boiled for 2 hours. After purification from acetic acid the product formed plates, m. p. 190° (Found: C, 55·6; H, 3·9; N, 6·4. $C_{21}H_{16}O_8N_2S$ requires C, 55·2; H, 3·5; N, 6·1%). This material was also obtained from the corresponding sulphide (Apitzsch, *Ber.*, 1913, **46**, 3098) by oxidation with hydrogen peroxide in acetic acid solution.

The p-*nitrobenzyl* ester of *m*-carboxyphenyl-*p*-nitrobenzylsulphone (compare IX) was prepared by a similar process and formed plates, m. p. 203° (Found: C, 55·4; H, 4·1; S, 7·0. $C_{21}H_{16}O_8N_2S$ requires C, 55·2; H, 3·5; S, 7·0%).

3-*Keto*-2-p-*nitrophenyl*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (X; R = $C_6H_4{\cdot}NO_2$).—A solution of sodium (0·3 g.) in alcohol (75 c.c.) containing the sulphone ester (IX) (5 g.) was boiled for 2 hours. The red sodium derivative which separated from the cooled liquid was collected and treated with dilute sulphuric acid. The required *dioxide* was then obtained, after purification from acetic acid, in prisms, m. p. 186°. It was sparingly soluble in hot water, the solution being yellow (Found: C, 55·3; H, 3·4. $C_{14}H_9O_5NS$ requires C, 55·4; H, 3·0%).

3-*Keto*-2-*carbethoxy*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (X; R = CO_2Et).—A solution of ethyl chloroacetate (13·5 g.) and potassium *o*-sulphinobenzoate (14 g.) in alcohol (200 c.c.) and a little water was boiled for 2 hours, the precipitated potassium chloride removed, and a solution of sodium ethoxide (2·6 g.) added to the filtrate, which was then gently warmed. The yellow sodium derivative was collected and decomposed with dilute sulphuric acid. From the solution obtained, ether extracted the required substance, which was purified from alcohol and then found to be identical with the "anhydro"-compound of Feist (*loc. cit.*) (Found: C, 51·8; H, 4·0. Calc.: C, 51·9; H, 3·9%).

Hydroxy-derivatives of o-*Carboxydiphenyl Sulphide.*—A solution of the dichloride (III) was prepared by the action of chlorine on *o*-thiolbenzoic acid suspended in carbon tetrachloride (7 c.c. for every gram of the acid). After removal of free chlorine and hydrogen chloride, the usual precautions for the exclusion of moisture being taken, the solution was mixed with a phenol (2 mols.) in a suitable volume of carbon tetrachloride or dry ether. The required material had in most cases separated after 24 hours. The following products are typical of those obtained.

2-*Carboxy*-4′-*hydroxydiphenyl sulphide* (VI) formed small needles from acetic acid, m. p. 193° (Found: C, 63·3; H, 4·1; S, 12·8. $C_{13}H_{10}O_3S$ requires C, 63·4; H, 4·0; S, 13·0%). The structure assigned to the substance was shown by the conversion in warm sulphuric acid into 2-hydroxythioxanthone, the constitution of which has been determined by a method which will be subsequently described.

2-*Carboxy*-2′ : 4′-*dihydroxydiphenyl sulphide*,

$$C_6H_3(OH)_2{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared from resorcinol, separated from hot water in needles, m. p. 190°, which assumed a yellow colour on exposure to light (Found: C, 59·7; H, 4·0; S, 12·1. $C_{13}H_{10}O_4S$ requires C, 59·5; H, 3·8; S, 12·2%).

The interaction of the dichloride and resorcinol in equimolecular proportion under the conditions described gave *bis*-2′-*carboxy*-

phenylthiol-2 : 4-*dihydroxybenzene*, $C_6H_2(OH)_2(S{\cdot}C_6H_4{\cdot}CO_2H)_2$, which was obtained in small needles, m. p. 272°, soluble in hot alcohol and insoluble in water (Found : C, 57·9; H, 3·5. $C_{20}H_{14}O_6S_2$ requires C, 57·9; H, 3·3%).

o-*Carboxyphenyl 2-hydroxy-α-naphthyl sulphide*,

$$C_{10}H_6(OH){\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared from β-naphthol, separated from alcohol in needles, m. p. 237°, which became yellow on exposure to light (Found : C, 68·9; H, 4·1. $C_{17}H_{12}O_3S$ requires C, 68·9; H, 4·0%).

The yields of the *o*-carboxyphenyl sulphides obtained from the process are generally good and the method thus leads to a convenient synthesis of hydroxythioxanthones. Examples of this application will be described in a future communication.

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