

CCXXXVI.—*Aromatic Hydroxy-sulphoxides.*

By MAUD GAZDAR and SAMUEL SMILES.

IN the study of the sulphination of certain phenolic ethers (Smiles and Le Rossignol, *Trans.*, 1908, **93**, 745) several thionyl derivatives of these substances were obtained, and it was found that these methoxy- and ethoxy-sulphoxides when dissolved in concentrated sulphuric acid may be converted by excess of phenolic ether into the triarylsulphonium salts. Later investigation of the corresponding hydroxy-derivatives showed that the reaction is not generally applicable to these substances, for, whilst di-*p*-hydroxyphenyl sulphoxide (Smiles and Bain, *Trans.*, 1907, **91**, 1118) yields the trihydroxyphenyl-sulphonium base, the di-*p*-hydroxy-*m*-tolyl sulphoxide does not (Smiles and Hilditch, *Proc.*, 1907, **23**, 161). The exceptional behaviour of this *p*-cresol sulphoxide is of peculiar interest, for the corresponding dimethyl ether, $(C_6H_3Me \cdot OMe)_2SO$, readily furnishes the triarylsulphonium derivative. Although the so-called "steric" conditions which are set up by substitution in the aromatic nucleus are known to be capable of retarding this reaction (Smiles and Le Rossignol, *loc. cit.*), it cannot be supposed that their influence is the cause of the inactivity of this *p*-cresol sulphoxide. For it is evident from previous experience of "steric hindrance" that, if there be any difference in reactivity between a phenol and its ether, it is the latter that should be less reactive, whereas in the present case the reverse relation holds.

It is a remarkable fact that of the eleven hydroxy- or methoxy-phenyl sulphoxides which have been hitherto examined, all give brilliantly coloured solutions in concentrated sulphuric acid, and it therefore seemed probable that in effecting the condensation of the sulphoxide with the phenolic ether by means of this reagent, some intermediate compound is formed, and that it is the reactivity of this substance that determines the formation of the sulphonium salt.

As a preliminary step in the investigation, we have found it necessary to extend the range of material available, since very little is known of the aromatic hydroxy-sulphoxides, only one, apparently, having been obtained in a pure condition.

The present paper deals with the sulphoxides of *p*-cresol, *p*-chlorophenol, and *o*-chlorophenol. The investigation is not yet complete, but the results are now published, since one of us is unable to carry on the work.

EXPERIMENTAL.

p-Cresol-*m*-sulphoxide, $(OH \cdot C_6H_3Me)_2SO$. ($Me : OH : SO = 1 : 4 : 3$.)

The sulphination of *p*-tolyl methyl ether with sulphurous acid and aluminium chloride yields the sulphoxide and a small quantity of

sulphinic acid, the sulphonium base, which is the final product of normal sulphination, being entirely suppressed (Smiles and Le Rossignol, *loc. cit.*). On applying this method to *p*-cresol, similar products were obtained; but the yields of sulphoxide were poor, hence advantage was taken of the stronger sulphinating power of thionyl chloride. Although this reagent is apt to yield sulphonium salts if allowed to act too energetically, we find that by preserving suitable conditions excellent yields of the sulphoxide are obtained.

Fifteen grams of powdered aluminium chloride were dissolved in an ice-cold solution of 20 grams of *p*-cresol in 50 c.c. of carbon disulphide, and then 20 grams of thionyl chloride were gradually added. The mixture was set aside in a desiccator, and, after the lapse of twenty-four hours, the greater portion of the reaction product—evidently a double salt of the sulphoxide with aluminium chloride—had separated in the form of a yellow, viscous mass. During the next twenty-four hours a further small quantity of this product separated; the supernatant layer of carbon disulphide was then decanted, and the residue decomposed with crushed ice. After being mixed with dilute hydrochloric acid, the mass was treated with a current of steam to remove carbon disulphide and unattacked cresol. After this operation, the contents of the flask were cooled, and the hard, granular mass was collected, dried, powdered, and then extracted with a small quantity of benzene, which removed coloured impurities.

The yield of this product, which consisted of the almost pure sulphoxide, was 20 grams, or about 85 per cent. of the theoretical. It was finally crystallised from hot glacial acetic acid, from which it separated in colourless prisms. The pure substance melts and decomposes at 185°:

0.1706 gave 0.3977 CO₂ and 0.0836 H₂O. C = 63.6; H = 5.4.

C₁₄H₁₄O₃S requires C = 64.12; H = 5.34 per cent.

It furnishes a bright blue solution with concentrated sulphuric acid, but does not then condense with phenolic ethers, as do other sulphoxides of this group.

Some derivatives of this sulphoxide have been previously investigated by Mr. Hilditch and one of the present authors (Proc., 1907, 23, 161), and, together with others since examined, they are now described in detail.

Dibenzoyl-p-cresol sulphoxide was obtained from the parent substance by the action of benzoyl chloride in alkaline solution. It is soluble in hot alcohol, and separates from that medium in colourless plates, melting at 173°:

0.1375 gave 0.3591 CO₂ and 0.0593 H₂O. C = 71.23; H = 4.8.

C₂₈H₂₂O₅S requires C = 71.46; H = 4.68 per cent.

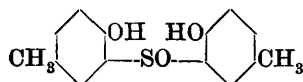
Di-p-cresol Sulphide, (OH·C₆H₃Me)₂S.

The sulphoxide was reduced by the action of zinc dust on the hot solution in glacial acetic acid. On mixing the filtered solution with water, the sulphide separated as a colourless oil, which slowly solidified. After being recrystallised from dilute acetic acid, *di-p-cresol sulphide* was obtained in colourless needles, which melted at 143°:

0.1900 gave 0.4735 CO₂ and 0.0984 H₂O. C = 67.97; H = 5.7.

C₁₄H₁₄O₂S requires C = 68.29; H = 5.68 per cent.

Previous experiments have shown that the sulphoxide which is formed (Smiles and Le Rossignol, *loc. cit.*) by the interaction of thionyl chloride and *p*-tolyl methyl ether contains the quadrivalent sulphur group in the ortho-position with respect to methoxyl, and there can be little doubt that the hydroxy-derivative, which is prepared in a similar manner from *p*-cresol, has the same constitution, namely:



Further and independent evidence in support of this structure will be adduced in a subsequent communication, but at present it may be observed that this is borne out by the behaviour of the substance on nitration. It is extremely easily attacked by nitric acid, two nitro-groups being at first inserted; but attempts to induce further nitration by intensifying the conditions of reaction result in the elimination of the thionyl group with formation of dinitrocresol. The most favourable conditions for nitration are as follows:

Nitric acid (2.7 c.c. of D 1.5) is gradually added to a cooled solution of the sulphoxide (5 grams; about two-thirds of the theoretical amount) in glacial acetic acid (100 c.c.). After three to four minutes a large bulk of water is added. The precipitate is collected and boiled with alcohol to remove soluble impurities, and the insoluble residue finally recrystallised.

Nitro-p-cresol sulphoxide is soluble in hot glacial acetic acid, and very sparingly so in boiling alcohol; it separates from the latter medium in lemon-yellow prisms, which melt at 214°. The scarlet *sodium* salt is readily soluble in water:

0.1718 gave 0.3009 CO₂ and 0.0545 H₂O. C = 47.7; H = 3.8.

C₁₄H₁₂O₇N₂S requires C = 47.73; H = 3.41 per cent.

Action of Hydrochloric Acid.—Five grams of nitro-*p*-cresol sulphoxide were suspended in about 50 c.c. of alcohol, which had previously been saturated with dry hydrogen chloride at the atmospheric temperature. The mixture was heated to 100° in a sealed tube for four to five

hours. Finally, the solid product was collected, washed with alcohol, and then crystallised from hot glacial acetic acid, from which it separated in long, orange needles. The weight of the crude substance was almost equal to that of the sulphoxide employed. When pure it did not contain halogen :

0.1305 gave 0.2382 CO₂ and 0.0410 H₂O. C = 49.78 ; H = 3.5.

0.1392 „ 0.2532 CO₂ „ 0.0490 H₂O. C = 49.6 ; H = 3.9.

C₁₄H₁₂O₆N₂S requires C = 50.00 ; H = 3.5 per cent.

The analytical data and the properties of the substance show that it is *nitro-p-cresol sulphide*. This compound melts at 194°, and is soluble in hot alcohol and insoluble in water ; the *sodium* salt is deep red in colour. Other sulphoxides, which are described in the following pages, have been treated in a similar manner, and similar reactions have been observed ; but with less highly substituted aromatic nuclei chlorination occurs, and even elimination of the sulphur may take place. It may be recalled that other oxygen derivatives of quadrivalent sulphur, namely, the sulphinic acids, are similarly reduced by mineral acids.

p-Chlorophenol Sulphoxide.

The sulphination of *p*-chlorophenol was effected with thionyl chloride under conditions similar to those described in the preparation of the *p*-cresol derivative. The crude product, which was obtained in a yield of about 70 per cent. of the theoretical, was purified by precipitation with dilute hydrochloric acid from an alcoholic solution. The substance was finally crystallised from dilute alcohol, from which it separated in small, colourless prisms. It melts at 202°, and is sparingly soluble in ether or hot water, and readily so in cold alcohol :

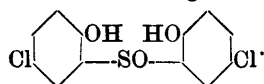
0.1487 gave 0.2580 CO₂ and 0.0366 H₂O. C = 47.33 ; H = 2.73.

0.3538 „ 0.331 AgCl „ 0.2780 BaSO₄. Cl = 23.2 ; S = 10.8.

C₁₂H₈O₃Cl₂S requires C = 47.52 ; H = 2.73 ; Cl = 23.43 ;

S = 10.56 per cent.

p-Chlorophenol sulphoxide is soluble in concentrated sulphuric acid, the solution being at first colourless, but rapidly assuming a bright blue colour, which is slowly discharged by the addition of phenetole, indicating the formation of a sulphonium salt. It will be shown in a subsequent communication that the thionyl group in this sulphoxide occupies the ortho-position with respect to the two hydroxyl groups of the phenolic nuclei, the substance having the structure :



p-Chloronitrophenol Sulphoxide.

When submitted to the action of nitric acid, this chloro-sulphoxide behaves like the similarly constituted *p*-cresol sulphoxide; two nitro-groups are readily absorbed, but further action of the acid results in decomposition. The dinitro-derivative was prepared in the following manner. The sulphoxide was suspended in about thirty times its weight of cold glacial acetic acid, and while the mixture was stirred, exactly the calculated amount of nitric acid (D 1.42) was added. Stirring was continued until almost all the finely-divided solid had dissolved, then the mixture was rapidly filtered, and the dark reddish-brown filtrates were immediately poured into a large bulk of water. The precipitate was collected and extracted with alcohol; finally, the insoluble portion was recrystallised in small quantities from hot glacial acetic acid. In this way, *p-chloronitrophenol sulphoxide* is obtained in fine yellow needles, which melt at 180—181°. It is insoluble in cold water and sparingly soluble in boiling alcohol:

0.1740 gave 0.2342 CO₂ and 0.0341 H₂O. C = 36.7; H = 2.1.

C₁₂H₆O₇N₂Cl₂S requires C = 36.64; H = 1.53 per cent.

p-Chlorophenol Sulphide.

The sulphide may be obtained by the action of hydrochloric acid on the sulphoxide in alcoholic solution under conditions similar to those described in the preparation of the nitrocresol derivative. To isolate the substance, the mixture was poured into water, and, after some hours had elapsed, the solid was collected and recrystallised several times from benzene, when it was obtained in colourless leaflets which melted at 173—174°. It was found difficult completely to purify this substance, since it tenaciously retained sulphides of higher chlorine content. For comparison, the sulphide was prepared by the reduction of the sulphoxide in the usual manner with zinc dust and boiling acetic acid, and the product, after recrystallisation from benzene, melted sharply at 174° and contained the requisite amount of halogen:

0.1280 gave 0.1288 AgCl. Cl = 24.79.

C₁₂H₈O₂Cl₂S requires Cl = 24.71 per cent.

When mixed with this substance, the product obtained by the former method retained the same melting point.

o-Chlorophenol Sulphoxide.

Sulphination of *o*-chlorophenol was conducted as with *p*-cresol and *p*-chlorophenol; the yield of crude sulphoxide was approximately the

same as that recorded in these cases. The coloured impurities were removed by trituration with cold glacial acetic acid, then the insoluble material was collected, and finally purified by recrystallisation from dilute alcohol, to which a little hydrochloric acid had been added. *o*-Chlorophenol sulphoxide forms fine colourless needles, which melt at 195° , and are soluble in most hot organic media :

0.1504 gave 0.2600 CO_2 and $0.0383 \text{ H}_2\text{O}$. $\text{C} = 47.21$; $\text{H} = 2.83$.

0.1535 ,, 0.1415 AgCl . $\text{Cl} = 22.8$.

0.2032 ,, 0.1485 BaSO_4 . $\text{S} = 10.0$.

$\text{C}_{12}\text{H}_8\text{O}_3\text{Cl}_2\text{S}$ requires $\text{C} = 47.52$; $\text{H} = 2.73$; $\text{Cl} = 23.4$; $\text{S} = 10.5$ per cent.

The substance dissolves in concentrated sulphuric acid, forming a blue solution, from which the colour is removed by the addition of a phenolic ether, a sulphonium base being then formed. The action of alcoholic hydrogen chloride on this substance is somewhat different from that observed in the preceding cases. After the usual treatment, the reaction mixture was submitted to distillation in a current of steam. The white, crystalline solid which separated from the distillate was evidently dichlorophenol, for it melted at 43° and contained 43.4 per cent. of chlorine (calc., $\text{Cl} = 43.55$ per cent.). The non-volatile portion consisted of an oil which resisted all attempts at purification ; it apparently consisted of a mixture of polychloro-sulphides.

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ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.