CXVI.—*The Intramolecular Condensation of Aromatic Sulphinic Acids. Part II. The Interaction of Aromatic Disulphoxides and Sulphuric Acid.*

By THOMAS PERCY HILDITCH.

THE action of cold concentrated sulphuric acid on aromatic sulphinic acids or their chlorides has been shown (Trans., 1910, **97**, 2579) to be largely dependent on the nature of the substituents in the benzenoid residues of the latter compounds; when few substituents (none of which occupy a position para- to the thionyl group) are present, considerable quantities of dioxides of diphenylene *p*-disulphide may be formed, whilst with more complex molecules the only products definitely isolated are small amounts of disulphoxides. In the same communication it was pointed out that the various previous syntheses of diphenylene *o*-disulphide were probably (from analogy to the condensation of a sulphinic acid to a dioxide of diphenylene *p*-disulphide) due to the condensation of temporarily produced sulphonylic acid derivatives of the type $R\cdot S\cdot OH$.

Since, as is well known, the simplest products of autoxidation and condensation of the sulphinic acids are the disulphoxides, formulated alternatively as $R\cdot SO\cdot SO\cdot R$ or $R\cdot SO_2\cdot S\cdot R$, the decomposition of these substances has been studied with the aim of throwing further light on the nature of the sulphinic and sulphonylic

1092 HILDITCH: THE INTRAMOLECULAR CONDENSATION OF

condensations. Three types of disulphoxide have been employed, and different results have been obtained in each case, indicating that here again the influence of substitution is very strongly marked:

(a) *Non-substituted*.—Diphenyl disulphoxide.

(b) *Para-substituted*.—Di-*p*-phenetyl disulphoxide.

(c) *Multi-substituted*.—Di-*p*-tolyl methyl ether disulphoxide.

The behaviour of each compound has been studied in cold concentrated sulphuric acid solution (i) alone, and (ii) in presence of a phenolic ether. The latter case will be first considered, for in this instance condensation frequently takes place with formation of sulphonium bases, in much the same way as that found by Smiles and Le Rossignol (*Trans.*, 1906, **89**, 696) in the case of simple aromatic monosulphoxides. There are, however, several possibilities besides that of direct condensation at each thionyl group of the true disulphoxide $R \cdot SO \cdot SO \cdot R$ (which is, as a matter of fact, shown by the analytical data not to occur):

It has been found recently by Prescott and Smiles (this vol., p. 640) that aromatic disulphides, $R \cdot S \cdot S \cdot R$, undergo condensation with phenolic ethers, etc., in concentrated sulphuric acid solution through hydrolytic fission of the disulphide molecule; and although no direct evidence of the existence of the above-mentioned sulphylic compounds, $R \cdot S \cdot OH$, is yet available, these authors have shown that it is certain that in this instance the condensation which occurs takes place between a sulphylic derivative and the phenolic ether:

Evidently a similar hydrolytic decomposition may occur in the case of aromatic disulphoxides, such decomposition leading (according to either of the disputed formulæ) to a mixture of sulphylic and sulphinic acids:

Condensation might then ensue with both parts of the hydrolysed disulphoxide, leading to a mixture of an aromatic sulphonium salt and an aromatic sulphide:

On the other hand, further intermolecular condensation could take place before reaction with the phenolic ether; and here there are three possibilities, as may be readily seen from the example of diphenyl disulphoxide:

Each of these alternative decompositions has been met with in one or other of the disulphoxides studied, indicating that, although the subsequent decomposition is largely conditioned by the nature and position of the other substituents in the benzenoid residue, the first step in the reaction in concentrated sulphuric acid solution is that of the above fission of the disulphoxide molecule.

This will be best realised by consideration of the individual cases investigated.

(a) The non-substituted diphenyl disulphoxide, when dissolved in concentrated sulphuric acid alone for some time, gave a mixture of two products of known constitution, namely, a considerable quantity of the monoxide of diphenylene *p*-disulphide, together with a much smaller amount of the ortho-isomeride. The course of the reaction was accordingly:

When condensed in presence of phenetole, however, a mixture of sulphonium bases was produced, from which two platinichlorides were isolated in a pure condition. The salt obtained in greater quantity melted at 130°, and corresponds with a sulphonium chloride of the formula $(\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4)(\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4)_2\text{S}\text{Cl}$, whilst a small amount of a salt of higher melting point (191°) was also formed, corresponding with a chloride:

It appeared, then, that the rate of condensation of phenetole with the intermediate product $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{OH}$ was appreciably greater than that of the final condensation in the diphenylene disulphide synthesis:

The diphenylene disulphide monoxides formed in the first experiment were also condensed separately with phenetole in sulphuric acid. It was found that neither the *o*- nor the *p*-isomeride yielded any sulphonium base, although both underwent some alteration, possibly owing to sulphonation or similar subsidiary reaction. In either case, however, a considerable proportion of the unchanged monoxide was recovered, as was anticipated from the fact that the colours of the solutions in sulphuric acid were not altered on addition of phenetole.

It therefore seems natural to suppose that the formation of the cyclic sulphonium derivative is due to condensation of the primary product of reaction with phenetole.

(b) The para-substituted di-*p*-phenetyl disulphoxide does not suffer intermolecular condensation when dissolved alone in sulphuric acid, and was recovered therefrom unchanged. When phenetole is also present, however, abundant evolution of sulphur dioxide occurs, and triphenetylsulphonium is, except for a very small quantity of diphenetyl sulphide, the only product. Hence it must be supposed that in this instance the sulphonylic derivative is oxidised to sulphinic or sulphonic acid by the sulphuric acid, and no preliminary condensation takes place:

It was hoped that the remaining phase of the simplest form of the condensation reaction (formation of aromatic sulphides from the sulphonylic portion of the decomposed disulphoxide) might have been accomplished by the condensation of di-*o*-carboxyphenyl disulphoxide to thioxanthone by means of benzene in sulphuric acid, since *o*-carboxybenzenesulphinic acid furnishes that substance under similar conditions (Davis and Smiles, *Trans.*, 1910, **97**, 1292). It was found impossible, however, to prepare this compound by the usual means.

(c) An example of a multi-substituted disulphoxide was found in di-*p*-tolyl methyl ether disulphoxide. This substance, when dissolved alone in concentrated sulphuric acid, was found to condense, not to a derivative of diphenylene disulphide, but to a compound

formed in accordance with method (ii) (p. 1093). The same substance was also formed in sulphuric acid solution in presence of *p*-tolyl methyl ether, whence it appears that the numerous substituents inhibit in this case the formation of a sulphonium base (compare Smiles and Le Rossignol, *Trans.*, 1908, **93**, 751). The reduced reactivity of the disulphoxide system in this compound is further indicated by its failure to undergo reduction by hydriodic acid in acetic acid solution at 100°, a reagent which transforms disulphoxides in general into the corresponding disulphides (Hinsberg, *Ber.*, 1908, **41**, 4294).

This investigation proves, therefore, that the interaction of aromatic disulphoxides with sulphuric acid proceeds on the same general lines as that of aromatic disulphides with the same reagent, and also illustrates once more the great influence of substitution on the capacity for condensation of aromatic sulphides and sulphoxides. Taken in conjunction with the work of Prescott and Smiles (*loc. cit.*), it affords further evidence, moreover, in favour of the view that the formation, not only of the open-chain condensation products of disulphides and disulphoxides, but also of the heterocyclic diphenylene disulphide derivatives, is due to the intermediate production and subsequent condensation of sulphonylic and sulphinic acids.

EXPERIMENTAL.

Condensation of Diphenyl Disulphoxide in Concentrated Sulphuric Acid.

Five grams of diphenyl disulphoxide were dissolved with shaking in cold concentrated sulphuric acid, and set aside for some time. The solution, at first almost colourless, gradually changed through pale green to a deep bluish-green, and finally to an almost black liquid. When no further change could be detected, the whole was mixed with ice-water, and a cream-coloured solid separated. This was collected, dried, and extracted several times with boiling alcohol. The alcoholic extracts deposited white crystals on cooling, and after recrystallisation the latter melted at 146–148°. A mixture of this substance with diphenylene *o*-disulphide monoxide (Part I., *loc. cit.*) melted at 145–148°, and the identity of the substance was further confirmed by analysis. (Found, C=62.09; H=4.22. Calc., C=62.07; H=3.45 per cent.)

A considerable portion of the product was, however, insoluble in hot alcohol. This was boiled with acetic acid, and dried at 130° for analysis; it melted indefinitely at 180–185°, and was found to be the monoxide of diphenylene *p*-disulphide. (Found, C=62.88; H=3.38.)

Condensation of Diphenyl Disulphoxide with Phenetole in Concentrated Sulphuric Acid.

Five grams of the disulphoxide were dissolved in sulphuric acid as before, and a few drops of phenetole added; an intense greenish-blue coloration was produced, which ultimately became faint reddish-brown after excess of the phenolic ether had been added. Very little sulphur dioxide was evolved during the reaction, indicating the absence of any oxidation.

The reaction mixture was poured into ice-water, and extracted with ether to remove phenetole and any non-basic products (in this case a very small amount of a semi-solid substance, which was not further investigated). The aqueous extract, consisting of a turbid solution of sulphonium sulphates, was then heated to boiling, neutralised with barium carbonate, and filtered. The clear filtrates were acidified with hydrochloric acid, and mixed with an aqueous solution of chloroplatinic acid. A copious buff precipitate appeared, and this was collected, dried, and dissolved in as small a quantity as possible of epichlorohydrin. On the addition of alcohol, a brown powder was precipitated. This was collected, and after further purification, melted at 191° ; analysis showed it to be *thio-diphenylenephenetylsulphonium platinichloride*:

0.0782 gave 0.1290 CO_2 and 0.0189 H_2O . $\text{C}=44.99$; $\text{H}=2.69$.

$\text{C}_{40}\text{H}_{34}\text{O}_2\text{S}_4\text{Cl}_6\text{Pt}$ requires $\text{C}=44.36$; $\text{H}=3.15$ per cent.

The alcohol-epichlorohydrin filtrates deposited on spontaneous evaporation a second pale brown, crystalline salt, which, after drying at 100° , melted at 130° . Phenylthiophenyldiphenetylsulphonium platinichloride melts at $135\text{--}137^{\circ}$ (Smiles and Le Rossignol, *loc. cit.*), but equal proportions of this compound and the salt now obtained melted indefinitely at $100\text{--}115^{\circ}$. The distinct nature of the latter salt was also proved by analysis, which showed that it was *phenylthiolphenyldiphenetylsulphonium platinichloride*:

0.1708 gave 0.3160 CO_2 and 0.0544 H_2O . $\text{C}=50.47$; $\text{H}=3.54$.

0.1708 „ 0.0248 Pt. $\text{Pt}=14.52$.

$\text{C}_{56}\text{H}_{54}\text{O}_4\text{S}_4\text{Cl}_6\text{Pt}$ requires $\text{C}=50.68$; $\text{H}=4.07$; $\text{Pt}=14.71$ per cent.

Condensation of Diphenylene o- and p-Disulphide Monoxides respectively with Phenetole.

The monoxide of diphenylene *o*-disulphide dissolves freely in concentrated sulphuric acid, forming a deep purple-red solution. Addition of phenetole produced no alteration in the colour of the solution, even when added in excess, and allowed to remain for half an hour. On pouring the mixture into cold water, a sticky solid separated, which was completely soluble in ether. After removal of the ether and phenetole, an oily residue was left, which on recrystallisation from alcohol gave the original diphenylene *o*-disulphide monoxide, melting at 148° , together with small amounts of a substance of less definite nature. No sulphonium base could, however, be detected.

A similar conclusion was reached with diphenylene *p*-disulphide monoxide; this compound is less readily soluble in sulphuric acid, to which it imparts a dull greenish-brown hue, and the greater portion was recovered unchanged after addition of phenetole, no sulphonium base being formed.

Di-p-phenetyl Disulphoxide.

This compound was prepared by the method which was found most suitable for the preparation of dicamphoryl β -disulphoxide (Trans., 1910, **97**, 1091), and which has since been proved to be of general application. It is based on the superior catalysing action of hydriodic acid, by comparison with other mineral salts, on a sulphinic acid.

Thus, 10 grams of *p*-phenetylsulphinic acid were suspended in very dilute sulphuric acid solution, and warmed on the water-bath. About five drops of hydriodic acid (Zeisel) were then added, together with sufficient sulphurous acid to decolorise the solution. After about two hours, the mixture was rendered alkaline with sodium carbonate, and cooled. The disulphoxide formed solidified at once, and was collected and recrystallised from alcohol. In addition to the superior cleanliness of the crude product, the yield of disulphoxide by this method is greatly improved, being nearly that demanded by the equation:

Di-p-phenetyl disulphoxide forms handsome, colourless or faintly yellow tablets, melting at 89° *:

0.1434 gave 0.2949 CO_2 and 0.0726 H_2O . C=56.08; H=5.62.

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$ requires C=56.80; H=5.33 per cent.

* This melting point was erroneously given (Part I., *loc. cit.*) as 139° .

It was further characterised by reduction with a few drops of hydriodic acid (Zeisel) in glacial acetic acid in presence of sulphurous acid (Hinsberg, *loc. cit.*), when di-*p*-phenetyl disulphide, crystallising in white prisms, and melting at 48°, was produced. (Found, C=62·30; H=5·96. Calc., C=62·75; H=5·88 per cent.)

It may be observed in passing, that the same reagent, hydriodic acid free from iodine, which converts a sulphinic acid into disulphoxide so readily in aqueous solution, reduces the latter compound to disulphide in glacial acetic acid. This somewhat curious fact, together with some experiments on the mechanism of the conversion of sulphuric acids to disulphoxides, will, it is hoped, form the subject of a future communication.

The disulphoxide dissolved in concentrated sulphuric acid to a deep greenish-brown solution, which underwent no further change in colour. On pouring into water and recrystallising from alcohol, the compound was found to have been recovered unchanged (m. p. 85–86°. Found, C=56·39; H=5·36).

Condensation of Di-p-phenetyl Disulphoxide with Phenetole.

On adding phenetole to a solution of the disulphoxide in sulphuric acid, the colour turned to deep brown, and finally, by repeated addition of phenetole, it became faintly red or purple. Much sulphur dioxide was evolved in the course of the reaction. The aqueous acid solution obtained on pouring the mixture into cold water was converted into carbonate as described above, and a portion of it further converted into platinichloride.

The ethereal extract from the crude sulphonium sulphates in water left, on evaporation, a small amount of an oil, with the characteristic odour of an aromatic sulphide. On oxidation with potassium permanganate this yielded a crystalline compound, which melted at 160°; di-*p*-phenetylsulphone melts at 162–163° (Smiles and Le Rossignol, *loc. cit.*).

The crude platinum salt was purified in the usual manner from a mixture of alcohol and epichlorohydrin, when buff-coloured tablets separated, which appeared as a crystalline powder on drying at 100°. The compound melted at 200°, and, when mixed with an equal quantity of triphenetylsulphonium platinichloride, at 203–205°. It was accordingly triphenetylsulphonium platinichloride. (Found, C=47·65; H=4·59; Pt=16·27. Calc., C=48·08; H=4·51; Pt=16·28 per cent.)

The alcohol-epichlorohydrin mother liquor contained a very small quantity of an amorphous platinum salt of low melting point, which was not closely examined.

Another portion of the sulphonium carbonate solution was poured

into aqueous potassium dichromate. A bright orange-coloured dichromate resulted, which melted indefinitely at about 65° , and rapidly decomposed in presence of air:

0.1275 gave 0.0202 Cr_2O_3 . Cr=10.84.

$\text{C}_{48}\text{H}_{54}\text{O}_{13}\text{S}_2\text{Cr}_2$ requires Cr=10.32 per cent.

Triphenetylsulphonium dichromate was also prepared from a sample of the sulphonium chloride, and agreed in its properties with the above compound. (Found, Cr=10.97.)

Attempted Preparation of Di-o-carboxyphenyl Disulphoxide.

Attempts were made to oxidise di-o-carboxyphenyl disulphide by the following reagents: solid potassium permanganate in cold and in boiling acetic acid, hydrogen dioxide in hot acetic acid, and solid potassium permanganate in acetone; but without success. Similarly, o-carboxybenzenesulphinic acid did not give the desired product, either by the hydriodic acid method, or when heated with water at 130° . Finally, the oxidation of di-o-carbethoxyphenyl disulphide by hydrogen dioxide in acetone was tried, but again without success.

The ethyl ester was obtained by boiling the acid chloride with alcohol for an hour; the latter compound was prepared from the free acid and boiling thionyl chloride in slight excess, and crystallised from acetone in small prisms, melting at 152° (List and Stein, *Ber.*, 1898, **31**, 1670, using the phosphorus pentachloride method, obtained a sample melting at 135°). (Found, C=48.60; H=2.63. Calc., S=48.99; H=2.33 per cent.)

The diethyl ester melted at 118° (Found, C=59.34; H=5.56. Calc., C=59.65; H=4.97 per cent.), and after recovering it from treatment with hydrogen dioxide, it again melted at 118° . (Found, C=59.74; H=4.99.)

Di-p-tolyl Methyl Ether Disulphoxide.

Smiles and Le Rossignol (*loc. cit.*) have shown that the sulphination of p-tolyl methyl ether in presence of anhydrous aluminium chloride leads to formation of sulphoxide as the main product, but it has been found possible, by using light petroleum as a diluent, to increase the yield of the sulphinic acid (the first step in the sulphination process) to almost 50 per cent. of the starting material. It is interesting to record that the use of ether in place of light petroleum entirely stopped all sulphination; this was probably owing to the fact that the aluminium chloride combined with the ether instead of with the phenolic ether.

The sulphinic acid obtained by the use of light petroleum melted at 95—97°. (Found, C=51·44; H=4·94. Calc., C=51·62; H=5·38 per cent.) On attempting to convert it into the disulphoxide in the conventional way by heating with water at 130°, an uncrystallisable, brown oil was produced, but by the hydriodic acid method a solid product was formed, which separated from alcohol in pale yellow, soft prisms. *Di-p-tolyl methyl ether disulphoxide* melts at 83—86°:

0·1138 gave 0·2358 CO₂ and 0·0530 H₂O. C=56·53; H=5·18.

C₁₆H₁₈O₄S₂ requires C=56·80; H=5·33 per cent.

The substance was reduced by hydriodic acid in glacial acetic acid, with rather more difficulty than usual, to *di-p-tolyl methyl ether disulphide*, which crystallised from ether in soft tablets, melting at 73—74°:

0·0861 gave 0·1979 CO₂ and 0·0470 H₂O. C=62·69; H=6·07.

C₁₆H₁₈O₂S₂ requires C=62·75; H=5·88 per cent.

The disulphoxide dissolved in cold sulphuric acid with a deep greenish-black colour; the product obtained after pouring into water was a cream-coloured solid, readily soluble in alcohol, and crystallising therefrom in soft laminæ, which contracted together at 160°, and melted at 184°. Analysis showed this compound to be a substance of the formula:

0·1313 gave 0·2808 CO₂ and 0·0660 H₂O. C=58·31; H=5·58.

C₃₂H₃₄O₇S₄ requires C=58·35; H=5·17 per cent.

The addition of *p*-tolyl methyl ether to the solution of the disulphoxide in sulphuric acid produced no change in appearance, and, indeed, the same product as before was subsequently isolated (m. p. 184°. Found, C=57·79; H=5·32).

Moreover, this complex condensation product was submitted to reduction by hydriodic acid (free from iodine) in hot glacial acetic acid, but without result, the compound being recovered intact (m. p. 180—182°. Found, C=57·98; H=5·63).

UNIVERSITY COLLEGE,
UNIVERSITY OF LONDON.