CXLI.—*The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides.*

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IN continuing the study of the derivatives of *S*-phenylphenazothionium, we desired to obtain a sulphoxide of diphenylamine which possesses stronger acidic properties than the dinitro-compounds previously employed, and for this purpose we undertook the preparation of the polynitro-derivatives of this group. The nitration of thiodiphenylamine has been studied by Bernthsen (*Annalen*, 1885, **230**, 116), who, by carefully regulating the action of the nitric acid, isolated the di-para- and *isodinitro*-derivatives. We find that by conducting the nitration under more severe conditions, the tetranitrosulphoxide is formed. In accordance with the facts previously

collected by Bernthsen (*loc. cit.*) from the dinitro-compounds, and by Störmer and Hoffmann (*Ber.*, 1898, **31**, 2535) from the nitration of diphenylamine, and also from the general rules governing the nitration of aromatic amines, the tetranitro-sulphoxide must have the constitution (I).

During the investigation of this substance it was observed that with certain reagents—such as a solution of hydrochloric acid in concentrated sulphuric acid—it is transformed into an isomeric compound, and, extending the inquiry to other sulphoxides of this series, we have found that the transformation is a general one.

It will be shown that the reaction consists essentially in the conversion of the imino-sulphoxide structure (II) into the ortho-quinonoid azothionium arrangement (III).

The reaction cannot be strictly termed an isomeric change, since under ordinary circumstances the azothionium products are found to contain a supplementary molecule of water, which as a rule does not occur in the sulphoxides. This molecule of water may, however, be removed, and the tetranitro-sulphoxide which contains the additional water yields an isomeric azothionium hydroxide.

On general considerations it might be considered possible that in this reaction fission of the thiazine ring (IV) takes place. If this were the case, the red substances obtained would have either the structure of a diphenylaminesulphinic acid (V) or that of an aminophenol sulphoxide (VI).

But apart from the improbability of this occurrence, these structures for the products of the reaction must be rejected, chiefly for the following reasons:

(i) It is difficult to imagine how substances of either of these types could lose water without producing the original sulphoxide.

(ii) The dinitro-products do not show the weakly acidic properties of the corresponding sulphoxides. They do not form sodium salts under the usual conditions with aqueous alkali hydroxide, whereas substances of either of these structures (V or VI) must do so.

(iii) The unsubstituted derivative obtained from diphenylamine ortho-sulphoxide is a base of moderate strength, since the salt is incompletely hydrolysed by boiling aqueous sodium carbonate. According to the latter of the given structures, the substance should be a weak base, and according to the former, an acid.

(iv) We have not been able to obtain benzoyl or alkyl derivatives of these substances.

The reaction was first studied with the previously-mentioned nitro-sulphoxides, and in these cases there are only two alternative structures for the isomeric products :

According to the first scheme they would be represented as para-quinonoid nitronic acids, and according to the second, as ortho-quinonoid sulphonium hydroxides.

That the first alternative cannot be entertained is evident from the following considerations :

(i) The tetranitro-sulphoxide when treated with dilute aqueous sodium hydroxide is converted into a red sodium salt, which, according to the researches of Hantzsch and many others on similarly constituted compounds, must contain the para-quinonoid structure. By carefully treating the sodium salt with mineral acid, the red nitronic acid is liberated, but it is very unstable, and, during the process of isolation, changes into the original bright yellow sulphoxide. The product obtained from the tetranitro-sulphoxide by the action of hydrochloric acid cannot be the nitronic acid, for it is a quite stable substance, and, in fact, is formed when the sulphoxide is heated to about 180° .

(ii) In alcoholic solution with sodium ethoxide the tetranitro-, di-para-nitro-, and isodinitro-sulphoxides form red solutions of the nitronic salts. If the red isomeric forms of these sulphoxides had the nitronic structure, they should yield the same salts under these conditions ; but they do not, their salts being green or blue in alcoholic solution.

(iii) The dinitro-compounds do not form salts with dilute aqueous sodium hydroxide, and are thus of weaker acid character than the sulphoxide forms, which yield salts under these conditions. It has previously been shown (Smiles and Hilditch, *Trans.*, 1908, **93**, 149) that the entrance of nitro-groups into the benzene nucleus of thiodyphenylamine weakens the basic properties of the quadrivalent

sulphur in the derivatives of *S*-phenylphenazothionium. Moreover, Kehrman (*Ber.*, 1906, **39**, 914) has observed a similar relation in the ortho-quinonoid derivatives of phenazothionium. If this intramolecular rearrangement does not involve the nitro-groups, but merely concerns the thionyl and imino-groups of these sulphoxides, it follows that the unsubstituted diphenylamine sulphoxide (IX) should undergo the same change; moreover, the nitro-groups

being removed, the sulphonium base should be of stronger character and should furnish more stable salts (X). This is actually the case. Diphenylamine ortho-sulphoxide is formed by the interaction of hydrogen dioxide and thiodiphenylamine. The constitution of the product of this reaction might be considered doubtful, since Dunstan and Goulding (*Trans.*, 1899, **75**, 792, 1004) have shown that hydrogen dioxide converts the secondary aliphatic amines into di- β -alkylhydroxylamines, but ample proof that the substance is a sulphoxide and does not contain the alternative hydroxylamine structure is afforded by the facts: (i) that under the same conditions diphenylamine is not attacked by hydrogen dioxide; (ii) that the substance does not show the strong reducing properties to be expected of a hydroxylamine derivative; and (iii) that hydrogen dioxide converts the aromatic sulphides into sulphoxides (Gazdar and Smiles, *Trans.*, 1908, **93**, 1833).

When this sulphoxide is submitted to the action of aqueous hydrochloric acid it is at once converted into phenazothionium chloride, thus giving final proof that the products of this reaction possess the azothionium structure. It may be observed that Kehrman (*Ber.*, 1901, **34**, 4170) has already obtained the chloride and other salts of phenazothionium by the acid oxidation of thiodiphenylamine.

From a comparison of the formulæ of the sulphoxides with those of the corresponding sulphonium bases, it would seem that this intramolecular change merely consists of the migration of hydrogen from the imino-group to the oxygen of the thionyl group. We have found reason for believing that this is not the true explanation of the reaction, but that the latter instead takes place by migration of hydroxyl from the quadrivalent sulphur to tervalent nitrogen. Since, however, our experiments are not yet complete, we reserve the discussion of this question for a future occasion. At present it is

sufficient to observe that, to be satisfactory, any theory of the mechanism must account for the following facts:

(i) The reaction proceeds more easily the stronger the basic character of the quadrivalent sulphur.

(ii) At least with the unsubstituted sulphoxide, the change is favoured by increasing the concentration and strength of the acid.

(iii) The anomalous behaviour of the tetranitro-sulphoxide, which, although the most difficult of the series to convert with acid reagents, is the only one transformed by the action of heat.

(iv) The absorption of the elements of water during the reaction.

It is our intention to extend the study of this reaction to aromatic hydroxy- and amino-sulphoxides and sulphonium bases.

EXPERIMENTAL.

Tetranitro-derivatives.

Tetranitrodiphenylamine Sulphoxide,

—Thiodiphenylamine is heated in an open vessel for about two hours with an excess of fuming nitric acid (D 1.5), and the solution is then poured into an excess of water and washed until the acid is completely removed. It is difficult exactly to define the conditions necessary to obtain a pure product. If the action be allowed to proceed too far, the liquid will be found to contain sulphuric acid, and the product must then be treated with acetone to remove the polynitro-derivatives of diphenylamine which are formed. If, however, the reaction be stopped at a suitable point before sulphuric acid appears in the solution, the product is almost pure and the yield quantitative. A sample was prepared for analysis by crystallisation from nitrobenzene, and it was thus obtained in minute, lemon-yellow crystals:

0.0966 gave 0.1285 CO_2 and 0.0219 H_2O . C = 36.27; H = 2.5.

0.1984 „ 0.2671 CO_2 „ 0.0378 H_2O . C = 36.71; H = 2.1.

0.4278 „ 0.2484 BaSO_4 . S = 7.97.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires C = 36.54; H = 1.27; S = 8.10 per cent.

When recrystallised from *p*-tolyl methyl ether the substance separates in long needles which contain the solvent, but the latter may be removed by washing with alcohol or ether, when the crystals break up into a fine powder. Probably these crystals contain two molecular proportions of the phenolic ether, but the correct amount is difficult to determine, since it is very loosely combined. Two samples were analysed.

(1) Dried in a vacuum :

0.0843 gave 0.1500 CO_2 and 0.0306 H_2O . $\text{C} = 48.53$; $\text{H} = 4.03$.

(2) Dried in air at atmospheric temperature and pressure :

0.1391 gave 0.2572 CO_2 and 0.0562 H_2O . $\text{C} = 50.42$; $\text{H} = 4.49$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, \text{C}_8\text{H}_{10}\text{O}$ requires $\text{C} = 46.4$ per cent.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, (\text{C}_8\text{H}_{10}\text{O})_2$ „ $\text{C} = 56.3$ „

The product obtained by the correct nitration of thiodiphenylamine, and without further purification with high boiling solvents, is the pure sulphoxide, but it now contains an additional molecule of water. A sample which had been dried in the steam-oven was analysed :

0.1041 gave 0.1331 CO_2 and 0.0162 H_2O . $\text{C} = 34.87$; $\text{H} = 1.73$.

0.4462 „ 0.2540 BaSO_4 . $\text{S} = 7.88$.

0.1876 „ 27.8 c.c. N_2 at 20° and 744 mm. $\text{N} = 16.90$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}, \text{H}_2\text{O}$ requires $\text{C} = 34.81$; $\text{H} = 1.69$; $\text{S} = 7.75$; $\text{N} = 16.95$ per cent.

When this substance is heated to $180\text{--}200^\circ$, only a slight loss in weight occurs, but the greater portion of the sulphoxide is transformed into the sulphonium hydroxide. That this hydrated sulphoxide is not the sulphone, which differs from it only slightly in elemental composition, is proved by the fact that it may be reduced to diaminothionine, and it appears from the work of Bernthsen (*Ber.*, 1906, **39**, 1807) that the nitrosulphones of this series are not thus converted into thionine derivatives. Moreover, it will be later shown that the substance may be condensed with phenetole, yielding the salt of the *S*-phenetyl derivative, and this reaction shows the presence of the thionyl grouping.

Tetranitrodiphenylamine ortho-sulphoxide does not melt below 250° and it is very sparingly soluble in the usual organic media of low boiling point.

Sodium Salt.—This sulphoxide behaves as a weak acid, and with aqueous sodium hydroxide furnishes a scarlet sodium salt. When boiled with this reagent some decomposition takes place, one or more nitro-groups being displaced, but when triturated with a warm aqueous solution of the alkali hydroxide a red, flocculent precipitate is deposited. Estimation of sodium in two different samples showed that it is probably an acid salt :

0.3533 gave 0.0269 Na_2SO_4 . $\text{Na} = 2.47$.

0.4160 „ 0.0369 Na_2SO_4 . $\text{Na} = 2.87$.

$\text{C}_{12}\text{H}_4\text{O}_9\text{N}_5\text{SNa}, \text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{Na} = 2.85$ per cent.

It seems to be very readily decomposed into its components by treatment with cold acetone, which dissolves the normal sodium salt, leaving the sparingly soluble yellow acid.

A sample of the sodium salt obtained in this manner was analysed:

0.4160 gave 0.0503 Na_2SO_4 . $\text{Na} = 4.36$.

$\text{C}_{12}\text{H}_4\text{O}_9\text{N}_5\text{SNa}$ requires $\text{Na} = 5.52$ per cent.

The addition of dilute mineral acids to the aqueous solution of the sodium salt furnishes a precipitate of a red form of the sulphoxide. A sample of this substance was collected and washed with cold water until free from excess of acid, but on being dried in the steam-oven for analysis it rapidly changed colour, and finally became orange-coloured:

0.1010 gave 0.1287 CO_2 and 0.0187 H_2O . $\text{C} = 34.75$; $\text{H} = 2.10$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{C} = 34.81$; $\text{H} = 1.69$ per cent.

Diaminothionine.—Tetranitrodiphenylamine ortho-sulphoxide was mixed with alcohol and reduced with tin and hydrochloric acid in the usual manner. The colourless solution was mixed with excess of aqueous ferric chloride, and finally the precipitation of the dye was completed by the addition of salt solution. The precipitate was collected and treated with concentrated hydrochloric acid, which dissolved the amino-derivative, leaving the insoluble residue of inorganic matter. The dye-stuff was obtained in deep blue scales by mixing the hydrochloric acid solution with water and keeping the mixture for some days at the atmospheric temperature. Several unsuccessful attempts were made to remove by physical means the excess of hydrochloric acid contained in this substance, but analysis showed that the content of carbon was too low, and that of halogen too high, for the monochloride, and these did not correspond with any definite formula. However, it seems that treatment with dilute aqueous sodium carbonate removes the excess of acid, since it was found that

0.1006 gave 0.1615 CO_2 and 0.0354 H_2O . $\text{C} = 43.7$; $\text{H} = 3.9$.

$\text{C}_{12}\text{H}_{12}\text{N}_5\text{ClS} \cdot 2\text{H}_2\text{O}$ requires $\text{C} = 43.76$; $\text{H} = 4.25$ per cent.

but further analysis of the substance was not made.

Diaminothionine chloride is soluble in hot water or alcohol. In the latter solvent it exhibits a red fluorescence.

The *platinichloride* was obtained as a brown, crystalline powder by adding aqueous chloroplatinic acid to a solution of the chloride:

0.3351 gave 0.0732 Pt . $\text{Pt} = 21.55$.

$\text{C}_{24}\text{H}_{24}\text{N}_{10}\text{Cl}_6\text{S}_2\text{Pt}$ requires $\text{Pt} = 21.10$ per cent.

Tetranitrophenazothionium hydroxide,

—The following methods of preparation were carried out with the

hydrated form of the sulphoxide, the analysis of which is described on a former page.

(a) *With Hydrochloric Acid in Sulphuric Acid Solution.*—Unlike the other sulphoxides of this series, the tetranitro-derivative dissolves in concentrated sulphuric acid without intense colour; the solution is a greenish-yellow colour. The addition of hydrochloric acid to this solution causes the appearance of a bright red colour, and the reaction is a very delicate one. The same effect is produced by phenetole and similar compounds, and it will be shown later that with these reagents the *S*-phenyl derivatives of the series are formed. It may be remarked that with thiophen the reaction is so delicate that it may be used as a test for the presence of this substance in benzene.

A mixture of excess of concentrated sulphuric acid with tetranitro-thiodiphenylamine ortho-sulphoxide was saturated at atmospheric temperature with hydrogen chloride. The passage of the gas was continued for about twenty-four hours, and the mixture was continually stirred. When the yellow particles of the sulphoxide seemed to have completely disappeared, the deep red solution was filtered through glass wool and then slowly poured on to pounded ice. The precipitate was collected and washed until the sulphuric and hydrochloric acids were completely removed. After purification the substance contained no halogen:

0.1926 gave 0.2594 CO_2 and 0.0392 H_2O . $\text{C} = 36.73$; $\text{H} = 2.26$.

0.1974 „ 0.1007 BaSO_4 . $\text{S} = 7.70$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{C} = 36.46$; $\text{H} = 1.27$; $\text{S} = 8.09$ per cent.

It may be observed that the transformation does not take place with sulphuric acid alone, and this distinguishes the tetranitro- from the other derivatives which are readily converted by this reagent.

(b) *With an Alcoholic Solution of Hydrochloric Acid.*—The tetranitro-sulphoxide was mixed with a solution of hydrogen chloride in absolute alcohol which had been saturated with the gas at the atmospheric temperature. A portion of the sulphoxide at once dissolved, giving a deep red solution. The reaction was allowed to continue (1) by keeping the mixture at the laboratory temperature for twenty-six days, or (2) by heating the mixture in a sealed tube to 150° for five hours. In the latter case, when the cold tube had been opened and the excess of ethyl chloride had been allowed to evaporate, the thionium hydroxide was obtained in large, blunt, bright red prisms. After purification, the products from the two sources were dried at 100° and analysed:

(I) 0.1045 gave 0.1337 CO_2 and 0.0194 H_2O . $\text{C} = 34.89$; $\text{H} = 2.07$.

(II) 0.1033 „ 0.1316 CO_2 „ 0.0205 H_2O . $\text{C} = 34.84$; $\text{H} = 1.81$.

$\text{C}_{12}\text{H}_5\text{O}_9\text{N}_5\text{S}$ requires $\text{C} = 34.81$; $\text{H} = 1.69$ per cent.

Tetranitrophenazothionium hydroxide does not melt below 250° . It is insoluble in water and very sparingly soluble in the usual organic

solvents, but it is rather more soluble in acetone, giving a red solution from which it is deposited on spontaneous evaporation in red needles. Tetranitrophenazothionium hydroxide may also be obtained by heating the sulphoxide to 180—200° for a few hours. No appreciable loss of weight takes place, and the product is dark red in colour, and furnishes the green colour with alcoholic alkali hydroxide which is characteristic of the azothionium form.

Sodium Salt.—When triturated at the ordinary temperature with 10 per cent. aqueous alkali hydroxide, tetranitrophenazothionium hydroxide forms a sticky, green mass, which is converted by cold water into a red sodium salt. This could not be obtained sufficiently pure for analysis. The alcoholic solution of this tetranitro-derivative gives a green colour with sodium ethoxide.

Oxidation.—Tetranitrophenazothionium hydroxide is readily attacked by concentrated nitric acid, and is thereby oxidised to the sulphone. After purification, the product of this reaction was analysed :

0.1004 gave 0.1292 CO₂ and 0.0250 H₂O. C = 35.05 ; H = 2.76.

C₁₂H₅O₁₀N₅S requires C = 35.04 ; H = 1.22 per cent.

That the substance is not the hydrated form of the sulphoxide is shown by the action of alkali hydroxide, which furnishes a well-defined crystalline salt, and by the very weak red coloration produced by adding hydrochloric acid to the sulphuric acid solution of the substance. The weak colour produced is no doubt due to the presence of traces of the sulphoxide in the azothionium hydroxide.

Dinitro-derivatives.

The dinitrodiphenylamine sulphoxides employed were those previously obtained by Bernthsen (*loc. cit.*) by the regulated action of nitric acid on thiodiphenylamine. These substances are far more readily converted into the azothionium compounds than the tetranitro-compounds described in the previous pages ; in fact, the rearrangement can be effected by sulphuric acid or alcoholic hydrochloric acid in a few hours at the laboratory temperature.

3 : 9-Dinitrophenazothionium Hydroxide,

Di-*p*-nitrophenylamine sulphoxide was treated in the three following ways :

(a) *Concentrated Sulphuric Acid.*—The rearrangement of the sulphoxide to the azothionium form takes place only slowly with this reagent, and it is difficult to obtain a pure product, since the azothionium hydroxide is decomposed by the acid before the sulphoxide has been completely transformed. In one experiment the brown

solution of the sulphoxide in sulphuric acid was kept for one hour and then poured into water. After being purified and dried, a sample was analysed:

0.1011 gave 0.1745 CO_2 and 0.0269 H_2O . $\text{C} = 47.07$; $\text{H} = 2.9$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}$ requires $\text{C} = 47.2$; $\text{H} = 2.3$ per cent.

The product was evidently a mixture of the sulphoxide and the sulphonium form, since it was pale brown in colour and did not give the pure green with alcoholic alkali hydroxide.

In another experiment the solution of the sulphoxide in concentrated sulphuric acid was kept for a longer time. After sixteen hours the solution had become green, and had a strong odour of oxides of nitrogen. The precipitate now formed by pouring into cold water was collected, and, after thorough washing, was extracted with cold dilute sodium hydroxide solution, in which the greater part dissolved. The alkaline solution was acidified, and the precipitate was collected, dried, and recrystallised from nitrobenzene. The treatment with aqueous sodium hydroxide was repeated. An analysis of a purified sample gave the following result:

0.1856 gave 0.3292 CO_2 and 0.0646 H_2O . $\text{C} = 48.4$; $\text{H} = 3.8$.

$\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2\text{S}$ requires $\text{C} = 48.9$; $\text{H} = 3.4$ per cent.

These data show that the dinitrophenazothionium hydroxide (I) at first produced is acted on by the excess of sulphuric acid, nitrous acid being liberated and hydroxyl being introduced in place of the nitro-group.

3-Nitro-9-hydroxyphenazothionium hydroxide forms minute, reddish-brown crystals, which are insoluble in water and alcohol. The solutions in aqueous sodium hydroxide are reddish-violet.

(b) *With Hydrochloric Acid in Sulphuric Acid Solution.*—The process employed was similar to that described under the tetranitro-derivative; but here the reaction was complete in about four hours. As obtained by this method, the product was isomeric with the original sulphoxide, and it did not contain halogen:

0.1000 gave 0.1725 CO_2 and 0.0264 H_2O . $\text{C} = 47.04$; $\text{H} = 2.9$.

0.2655 „ 0.2084 BaSO_4 . $\text{S} = 10.76$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S}$ requires $\text{C} = 47.2$; $\text{H} = 2.3$; $\text{S} = 10.49$ per cent.

Analysis of the sample of sulphoxide employed in this reaction gave $\text{C} = 47.2$ per cent.

(c) *With Alcoholic Hydrochloric Acid*.—The finely powdered sulphoxide was shaken with this reagent for four or five hours at the laboratory temperature. If the quantity of the reagent taken be sufficient to dissolve the sulphoxide, the transformation can be more rapidly effected, since then the azothionium hydroxide crystallises from the solution in about one hour or even less. In either case the crystalline mass was separated from the mother liquor, and washed with alcohol and, finally, with water. The product did not contain ionisable halogen, but it was observed that if the action of the halogen acid was prolonged, or if the temperature was allowed to rise above the ordinary limits, traces of halogens may be present in other forms of combination. This impurity seems to consist of a colourless substance, which we have isolated but not yet fully examined. The crude product was crystallised from nitrobenzene or from aniline:

0.1502 gave 0.2432 CO_2 and 0.0396 H_2O . $\text{C} = 44.16$; $\text{H} = 2.93$.

0.0967 „ 10.8 c.c. N_2 at 13° and 767 mm. $\text{N} = 13.25$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S} \cdot \text{H}_2\text{O}$ requires $\text{C} = 44.58$; $\text{H} = 2.8$; $\text{N} = 13.0$ per cent.

The supplementary molecule of water present in the substance prepared in this manner cannot be removed at 100° , and attempts to displace it at higher temperatures were unsatisfactory, since some decomposition seemed to take place.

3 : 9-*Dinitrophenazothionium hydroxide* is insoluble in water, alcohol, or ether, slightly soluble in hot glacial acetic acid, and easily so in hot aniline or nitrobenzene. It forms chocolate-brown needles, which melt and decompose at about 240° . Solutions in concentrated sulphuric acid are deep green in colour.

Sodium Salts.—The azothionium hydroxide does not form salts with cold aqueous alkali hydroxide, and it is apparently decomposed by the boiling reagent. With alcoholic alkali hydroxide it yields an intense green coloration. This behaviour sharply distinguishes the substance from the corresponding sulphoxide. The latter is sparingly attacked by cold aqueous alkali, giving bright red solutions of the sodium salt, and it is readily soluble in the alcoholic reagent, producing the same colour. When the sulphoxide is warmed with aqueous sodium hydroxide, the sodium salt is readily obtained in well defined, glistening scales. Two recrystallised specimens of this salt were dried in the steam-oven and analysed:

(a) 0.2198 gave 0.0310 Na_2SO_4 . $\text{Na} = 4.59$.

0.2181 „ 0.1560 BaSO_4 . $\text{S} = 9.81$.

(b) 0.2844 „ 0.0381 Na_2SO_4 . $\text{Na} = 4.34$.

$\text{C}_{12}\text{H}_7\text{O}_5\text{N}_3\text{S} \cdot 2\text{C}_{12}\text{H}_6\text{O}_5\text{N}_3\text{SNa}$ requires $\text{Na} = 4.79$; $\text{S} = 10.0$ per cent.

Reduction of the dinitroazothionium hydroxide with zinc dust and

hydrochloric acid, and subsequent oxidation of the leuco-base with ferric chloride, furnishes thionine.

Oxidation with chromic acid in glacial acetic acid solution yields a bright yellow, crystalline substance, which is soluble in hot nitrobenzene and does not melt below 250°:

0.1047 gave 0.1642 CO₂ and 0.0264 H₂O. C = 42.76; H = 2.8.

C₁₂H₇O₆N₃S.H₂O requires C = 42.48 and H = 2.65 per cent.

This substance is therefore probably the sulphone, but we have been unable to prove that fission of the thiazine ring has not taken place.

isoDinitrophenazothionium Hydroxide, NO₂·C₆H₃⌞ $\begin{array}{c} \text{N} \\ \text{S}(\text{OH}) \end{array}$ ⌟C₆H₃·NO₂.

—This was prepared from *isodinitrodiphenylamine* sulphoxide by the action of alcoholic hydrogen chloride, the procedure being the same as that previously described for the other nitro-derivatives. The transformation is effected in about the same time as that of the di-*p*-nitro-sulphoxide. The product which crystallised from the acid mother liquor was thoroughly washed with alcohol and water, and if care be taken to regulate the action of the halogen acid, the substance thus obtained is quite free from halogen, and consists of the pure hydrated form of the thionine derivative. A sample which had been dried at 100° was analysed:

0.1000 gave 0.1622 CO₂ and 0.0255 H₂O. C = 44.24; H = 2.83.

0.2551 „ 0.1854 BaSO₄. S = 9.96.

C₁₂H₇O₅N₃S.H₂O requires C = 44.58; H = 2.8; S = 9.91 per cent.

When the substance was crystallised from aniline, it was obtained in the anhydrous form:

0.1002 gave 0.1749 CO₂ and 0.0242 H₂O. C = 47.60; H = 2.6.

0.1596 „ 19.2 c.c. N₂ at 12° and 744.6 mm. N = 13.93.

C₁₂H₇O₅N₃S requires C = 47.2; H = 2.3; N = 13.77 per cent.

isoDinitrophenazothionium hydroxide is insoluble in cold alcohol or water, and readily soluble in hot aniline or nitrobenzene. It forms chocolate-coloured needles, which melt and decompose at 199°. In its chemical behaviour the substance closely resembles the di-*p*-nitro-compound. It does not yield an alkali salt with cold aqueous sodium hydroxide, but the alcoholic solution when mixed with sodium hydroxide develops a deep blue colour. It is readily soluble in concentrated sulphuric acid, the solution being reddish-brown in colour.

Reduction and oxidation furnish similar products to those obtained from the di-*p*-nitro-compound.

Unsubstituted Derivatives.

Diphenylamine ortho-Sulphoxide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NH} \\ \text{SO}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$.—A solution of 5 grams of thiodiphenylamine in about 150 c.c. of acetone was rendered alkaline with a few drops of sodium ethoxide solution. Three grams of a 30 per cent. solution of hydrogen dioxide were then added, more acetone being added if necessary to retain the diphenylamine in solution. The mixture was then kept at the atmospheric temperature. The sulphoxide was gradually deposited in large, prismatic needles, which at the end of ten days were collected, 3 grams being obtained. Diphenylamine ortho-sulphoxide obtained in this manner is almost pure, but it may be recrystallised from acetone, in which it is sparingly soluble :

0.1023 gave 0.2501 CO_2 and 0.0411 H_2O . $\text{C} = 66.68$; $\text{H} = 4.4$.

$\text{C}_{12}\text{H}_9\text{ONS}$ requires $\text{C} = 66.98$; $\text{H} = 4.16$ per cent.

The substance melts with profound decomposition at about 250° .

This unsubstituted sulphoxide is converted into the azothionium base more easily than any of the others here described. The change is instantaneously effected by aqueous mineral acids, and slowly by hot glacial acetic acid. With concentrated sulphuric acid it gives a green solution, which turns red on dilution with water.

Phenazothionium Chloride, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}^- \\ \text{SCl}\end{smallmatrix}\rangle\text{C}_6\text{H}_4, \text{H}_2\text{O}$.—Diphenylamine ortho-sulphoxide, in quantities of about 1 gram at a time, was shaken with a freshly prepared solution (15 c.c.) of hydrogen chloride in dry alcohol. Care was taken not to allow the temperature to rise above the ordinary limits. The sulphoxide at once dissolved, the liquid assuming an intense reddish-brown colour, and in about ten minutes phenazothionium chloride crystallised from the mother liquor in dark brown needles. These were collected, and, after being washed with alcohol, were dried for analysis to constant weight in a vacuum over solid alkali hydroxide :

0.1013 gave 0.2130 CO_2 and 0.0331 H_2O . $\text{C} = 57.34$; $\text{H} = 3.63$.

When this sample had remained for two days longer under diminished pressure it was again analysed :

0.1592 gave 0.3338 CO_2 and 0.0572 H_2O . $\text{C} = 57.19$; $\text{H} = 3.99$.

$\text{C}_{12}\text{H}_8\text{NClS}, \text{H}_2\text{O}$ requires $\text{C} = 57.22$; $\text{H} = 3.98$ per cent.

When heated at 100° for a short time, this substance is transformed into a green compound, which is apparently also formed by diluting the aqueous solution. Alkali hydroxide precipitates this green substance from an aqueous solution of the chloride. Phenazo-

thionium chloride contains ionisable chlorine, but the salt is not completely hydrolysed by boiling aqueous sodium carbonate solution. Other salts of this and similar bases have been previously described by Kehrman (*Ber.*, 1901, **34**, 4170), who obtained them by the acid oxidation of thiodiphenylamine derivatives.

The investigation of this rearrangement is being continued with the object of determining the mechanism of the reaction.

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