

XV.—*Derivatives of S-Phenylphenazothionium. Part I.*

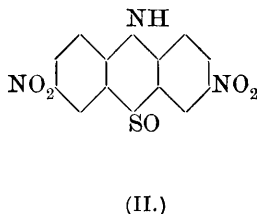
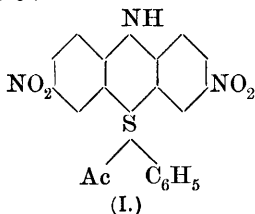
By SAMUEL SMILES and THOMAS PERCY HILDITCH.

BERNTSEN (*Annalen*, 1885, **230**, 116) has shown that thiodiphenylamine when treated with concentrated nitric acid is converted to a mixture of two isomeric nitro-compounds of formula:  $C_{12}H_7O_5N_3S$ . The less soluble of these was called the  $\alpha$ -, and the more soluble the  $\beta$ -, derivative. The  $\alpha$ -dinitro-compound was shown to contain the nitro-groups in the 3 : 3'-positions by its relationship to the diamino-compound, namely, thionine, which was obtained synthetically in another manner. Bernthsén further showed from a quantitative study of the reduction of the substance that it is probably a sulfoxide, and this view was supported by the consideration that the action of nitric acid on aromatic sulphides in nearly every case furnishes compounds of that nature.

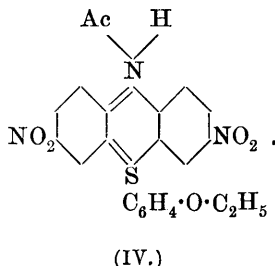
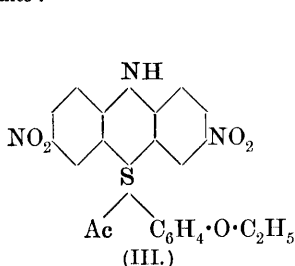
We are now able to advance additional and perhaps more conclusive evidence that these compounds are sulfoxides. It will be shown in the experimental part of the paper, and elsewhere, that either the  $\alpha$ - or  $\beta$ -derivatives may be condensed with the simple phenols, phenolic ethers, and aromatic amines, yielding salts of bases, and it has

been found (Trans., 1906, **89**, 696 ; 1907, **91**, 519, 1118) that this reaction is characteristic of the thionyl group.

The products which these dinitrosulphoxides give by condensation with aromatic compounds are of interest, not only on account of their tinctorial properties, but also because they form the first representatives of the *S*-phenylphenazothionium group (I). We have therefore examined these substances more closely ; the present paper deals with the product of condensation of the  $\alpha$ -dinitrosulphoxide (II) with phenetole :



If phenetole is added to the solution of this sulphoxide in concentrated sulphuric acid, a green sulphate of a base is formed, and the structure of this product might be represented by either of the following formulæ :



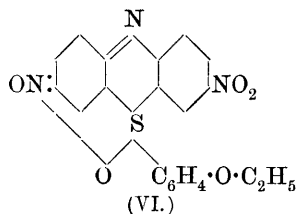
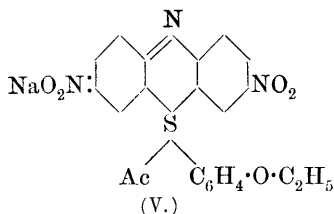
The first of these (III) represents the simple sulphonium salt, which would be directly formed by the change of the thionyl to the sulphonium group ; the second (IV) contains the quinonoid sulphonium structure, and this might be formed from the first by rearrangement of the acid group whereby the basic function of the molecule would be transferred to nitrogen. The substance is coloured, and the second alternative contains the quinonoid structure, but, in spite of this, we prefer the first, since all the evidence which can be collected shows that nitrogen in this dinitro-derivative would not be of a basic character. Thus di-*p*-nitrodiphenylamine and di-*p*-nitrodiphenylamine sulphoxide do not exhibit basic properties, but are of acidic nature, forming red salts with alkali hydroxide. Even thiodiphenylamine itself is an extremely weak base, and the hydrochloride, which can only be obtained by the action of dry hydrogen chloride on the ethereal solution, decomposes rapidly on exposure to the air (Unger

and Hoffmann, *Ber.*, 1895, **29**, 1365). Further, it may be remarked that the phenethylsulphoxide of di-*p*-nitrodiphenylamine, which is described below, is devoid of basic properties.

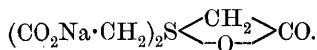
When the above-mentioned green salt is treated with aqueous alkali hydroxide, a dark reddish-brown substance of basic character is formed by removal of the elements of the mineral acid from the salt. Now, when di-*p*-nitrodiphenylamine or its sulphoxide is treated with alkali hydroxide, red salts are formed (Störmer and Hoffmann, *Ber.*, 1898, **31**, 2035; Bernthsen, *Annalen*, 1885, **230**, 116, 133), and these undoubtedly have the quinonoid structure,



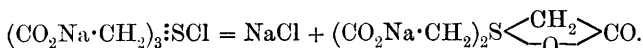
analogous to that of the salts of the nitrophenols. It may therefore be supposed that the green salts in question react with alkali, forming first the quinonoid salt (V):



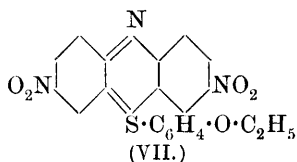
which then, losing the elements of the alkali salt, changes into the nitrothetine (VI). The latter stage in this reaction is analogous to that already observed in the preparation of a carboxythetine. Delisle (*Ber.*, 1892, **25**, 2451) found that the sodium salts of chloroacetic and thiodiglycollic acids interact in warm aqueous solution, giving the sodium salt of dicarboxymethylthetine,



Here it is evident that the sodium salts first unite to form the tri-sodium salt of the chloride, which then, losing sodium chloride, passes into the thetine.

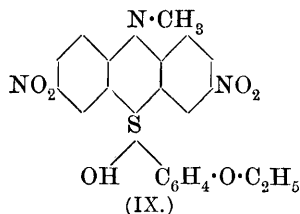
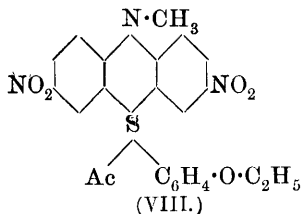


Between the above nitrothetine formula for the base and the alternative sulphonium quinone (VII) there appears to us to be little choice; indeed, it is possible that in solution the

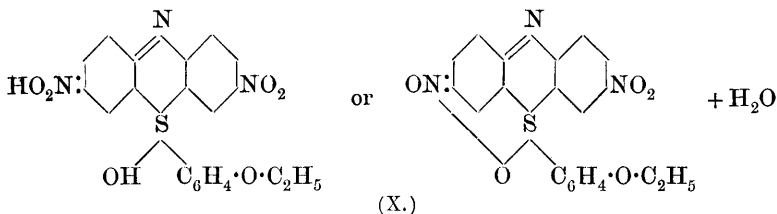


substance is an *isodynamic* mixture of the two forms. The green salts

are also attacked by a large excess of boiling water, undergoing hydrolysis to a bright, crimson base. The product, which is formed from the salt by exchange of the acid group for hydroxyl, contains one molecule of water more than the above anhydride (VI or VII). Solutions of this base are deep red or orange, and exhibit a strong fluorescence. The base obtained by hydrolysis from the sulphate of the *N*-methyl derivative (VIII) must have the constitution (IX):



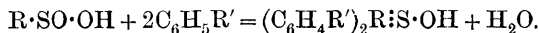
It has physical properties entirely different from those of the crimson substance mentioned above, being of a dull olive-brown colour and not fluorescent. The base obtained from the unsubstituted salt therefore is almost certainly of different structure, and this may be represented as:



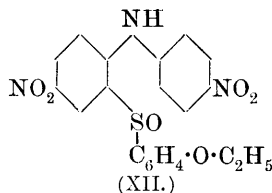
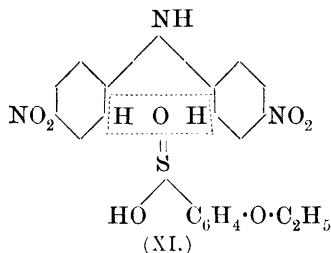
As with other thietines and betaines, it is difficult to determine the nature of this supplementary molecule of water, but it may be remarked that in this case a temperature of 150—180° is required to remove it, and then further decomposition occurs on prolonged heating.

On resuming, it is seen that the green salts (III) are converted by hydrolysis to the red base (X), and by the action of alkali hydroxide to the anhydride (VI), the colour change in either case being accompanied by the formation of the quinonoid structure.

A synthesis of these substances has been attempted in the following manner. It has been previously shown (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 697) that sulphinic acids may be transformed by condensation with certain aromatic substances to aromatic sulphonium bases:



We therefore hoped that di-*p*-nitrodiphenylamine and phenetole-*p*-sulphinic acid would yield (XI) the salts mentioned above:



Employing the usual condensing reagent, namely, sulphuric acid, it was found that these substances do not interact, but when heated with phosphoryl chloride they yield an olive-green sulphoxide (XII), which forms the intermediate stage in the expected reaction. Efforts to complete the reaction have been unsuccessful, but this is not surprising, for, as will be shown later in other experiments, the formation of sulphonium bases is hindered by ortho-substitution, and, further, there is no doubt that the nitro-groups exert a disturbing influence on the course of the reaction.

The position of the ethoxyl in the *S*-phenyl group of the salts and bases dealt with cannot at present be determined, but, judging from former experience, it almost certainly occupies either the ortho- or para-position with respect to the quadrivalent sulphur atom.

The ease with which the salts of *S*-phenetylphenazothionium are hydrolysed shows the base to be of weak character, and this is in striking contrast to the aromatic sulphonium bases which were formerly examined (Smiles and Le Rossignol, *loc. cit.*). From Kehrmann's experiments on the basicity of derivatives of phenazothionium (*Ber.*, 1906, **39**, 914), it seems certain that the nitro-groups in the above substances would weaken the basicity of the sulphonium group; we hope from the study of other derivatives to ascertain the nature of the parent substance, namely, *S*-phenylphenazothionium.

Since it seems to be a general rule that the introduction of nitro-groups into a fluorescent molecule leads to weakly or non-fluorescent derivatives (Kauffmann, "Die Beziehungen zwischen Fluoreszenz und Chemischer Konstitution," 1906, p. 80), it is worth noticing that the nitro-compounds at present dealt with exhibit this property in a marked degree. In this respect, they are exceptional.

#### EXPERIMENTAL.

*Derivatives of S-Phenetyl-3 : 3'-dinitrophenazothionium.*—The requisite  $\alpha$ -dinitrodiphenylamine sulphoxide was obtained by the process recommended by Bernthsen (*loc. cit.*), in which thioldiphenylamine is treated with excess of nitric acid (sp. gr. 1.4). The  $\alpha$ -dinitro-sulphoxide is precipitated during the reaction, whilst the  $\beta$ -derivative

remains for the greater part dissolved in the mother liquor, from which it may be obtained by precipitation with water. The  $\alpha$ -derivative was employed in the following experiments.

*S-Phenetyl-3 : 3'-dinitrophenazothionium Sulphate*.—Five grams of *p*-nitrodiphenylamine sulfoxide were dissolved in excess of concentrated sulphuric acid; phenetole was then gradually added to the deep yellowish-brown solution, which was kept thoroughly cooled during the reaction. It was found necessary to add a large excess of phenetole, since the greater portion was sulphonated before condensation could take place. The course of the reaction was followed by withdrawing a drop from the mixture after each addition of phenetole and adding it to a few c.c. of cold water; when the condensation was complete, the precipitate was bright bluish-green, and, on the other hand, if much sulfoxide remained condensed the colour was dull brown.

When the reaction was over, the strongly acid solution, now olive-green in colour, was poured into a large bulk of cold water, and the mixture set aside at the atmospheric temperature for a few hours. The bluish-green precipitate of the sulphate was then collected by the aid of the pump, and thoroughly washed with cold water; the yield was almost theoretical. After being dried on a porous tile in a vacuum, the *sulphate* appeared as a bright green powder, which, on further drying at  $100^{\circ}$ , apparently lost water and was converted into a dark blue substance with metallic lustre. It was slightly soluble in cold water, fairly readily so in alcohol, and, as previously mentioned, was hydrolysed by a large excess of hot water.

*Anhydro-S-phenetyl-3 : 3'-dinitrophenazothionium*.—This anhydrous base was obtained from the above sulphate by the action of aqueous alkali hydroxide. The salt was thoroughly triturated with a 5 per cent. aqueous solution of sodium hydroxide at about  $25^{\circ}$ ; the solid base was then filtered from the deep red solution, and washed with cold water until the filtrates were almost colourless and quite neutral towards litmus. After being dried in the steam-oven, the brown solid was purified by precipitation with dry ether from chloroform solution. In this way, the *anhydro-base* was obtained as a brown, crystalline powder with a green metallic lustre; it melted at  $221\text{--}222^{\circ}$ , and was readily soluble in chloroform or alcohol, but very sparingly so in ether or hot water. The fluorescent light emitted by the brown chloroform solution is dull crimson in colour, whilst that of the ethereal solution is bright greenish-yellow; the aqueous solution is purplish-red, but not fluorescent. For analysis, the substance was dried at  $100^{\circ}$ :

0.1385 gave 0.2976  $\text{CO}_2$  and 0.0515  $\text{H}_2\text{O}$ . C = 58.60; H = 3.83.

0.1697 „ 0.3631  $\text{CO}_2$  „ 0.0616  $\text{H}_2\text{O}$ . C = 58.37; H = 4.03.

0.1496 gave 12.7 c.c. of nitrogen at 20° and 761 mm. N = 9.94.

0.2093 „ 0.1212 BaSO<sub>4</sub>. S = 7.82.

C<sub>20</sub>H<sub>15</sub>O<sub>5</sub>N<sub>3</sub>S requires C = 58.68 ; H = 3.67 ; N = 10.27 ; S = 7.96 per cent.

*S-Phenetyl-3 : 3'-dinitrophenazothionium chloride* was prepared by dissolving the anhydro-base in concentrated hydrochloric acid and precipitating the solution with water. On allowing the salt to separate slowly, it was obtained as a yellowish-green, crystalline powder, which, after repeated precipitation, melted at 202—204°. A dried sample was analysed :

0.1101 gave 0.2168 CO<sub>2</sub> and 0.0372 H<sub>2</sub>O. C = 53.64 ; H = 3.76.

0.2065 „ 0.1028 BaSO<sub>4</sub>. S = 6.84.

0.1977 „ 0.0619 AgCl. Cl = 7.74.

C<sub>20</sub>H<sub>16</sub>O<sub>5</sub>N<sub>3</sub>ClS requires C = 53.89 ; H = 3.59 ; S = 7.18 ; Cl = 7.97 per cent.

This *chloride* is soluble in alcohol, giving a blue solution with a crimson fluorescence, which is doubtless due to a small quantity of the anhydro-base, since it vanishes on the addition of hydrochloric acid, the solution then becomes a clear greenish-blue. The action of water on the salt is described later. The compound possesses tinctorial properties ; silk is dyed a pale green tint, which in presence of alkalis becomes reddish-brown.

The *platinichloride* was precipitated as a dark green powder by mixing an alcoholic solution of the chloride with platinic chloride ; it is insoluble in water, but slightly soluble in concentrated hydrochloric acid. After being dried in the steam-oven :

0.1860 gave 0.0290 Pt. Pt = 15.59.

(C<sub>20</sub>H<sub>16</sub>O<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>PtCl<sub>6</sub> requires Pt = 15.88 per cent.

The *picrate* was obtained by adding an aqueous solution of picric acid to an alcoholic solution of the base. It formed a green powder, which melted at 216—218°, and was insoluble in cold water :

0.1089 gave 0.1982 CO<sub>2</sub> and 0.0299 H<sub>2</sub>O. C = 49.63 ; H = 3.05.

C<sub>20</sub>H<sub>15</sub>O<sub>5</sub>N<sub>3</sub>S.C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires C = 48.90 ; H = 2.82 per cent.

The *dichromate* was prepared by mixing solutions of the chloride or sulphate with aqueous potassium dichromate. It is an olive-green powder of high melting point :

0.1123 gave 0.0167 Cr<sub>2</sub>O<sub>3</sub>. Cr = 10.00.

C<sub>40</sub>H<sub>32</sub>O<sub>17</sub>N<sub>6</sub>S<sub>2</sub>Cr<sub>2</sub> requires Cr = 10.04 per cent.

*S-Phenetyl-3 : 3'-dinitrophenazothionium Hydroxide*.—When aqueous solutions of the sulphate are boiled, the blue colour changes to red and a crimson precipitate separates. The latter is the thionium hydroxide, which is formed together with mineral acid by hydrolysis of the salt ;

but the reaction, being reversible in presence of acid, is not complete, and a state of equilibrium is attained which can only be disturbed by the addition of alkali or by diluting the solution. To prepare this hydroxide in larger quantity, a concentrated solution of the salt in hot alcohol was poured into a large bulk of water. After the mixture had remained some hours at the ordinary temperature, the crimson precipitate was collected by the aid of the pump, then dried in the steam-oven, and analysed:

A sample prepared from the sulphate gave the following results on analysis:

0.1472 gave 0.3041  $\text{CO}_2$  and 0.0487  $\text{H}_2\text{O}$ .  $\text{C} = 56.41$ ;  $\text{H} = 3.71$ .

A specimen made from the chloride was also analysed:

0.1245 gave 0.2549  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ .  $\text{C} = 55.84$ ;  $\text{H} = 3.82$ .

$\text{C}_{20}\text{H}_{17}\text{O}_6\text{N}_8\text{S}$  requires  $\text{C} = 56.21$ ;  $\text{H} = 3.98$  per cent.

The substance is soluble in chloroform or ether with the same fluorescence as that observed in corresponding solutions of the anhydro-base. By spontaneous evaporation, it is deposited from the former solvent in red, feathery needles, which, on heating, darken and contract at  $150-180^\circ$ , and finally melt rather indistinctly at about  $220^\circ$ . When the crystals are powdered, they assume a metallic lustre. The substance does not lose water at  $100^\circ$ , but on heating a sample to  $150^\circ$  for some hours it was found that:

0.3188 lost 0.015  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 4.70$ .

$\text{C}_{20}\text{H}_{15}\text{O}_5\text{N}_8\text{S}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.22$  per cent.

Analysis of the residue showed that some decomposition had taken place at the same time.

*S-Phenetyl-N-methyl-3 : 3'-dinitrophenazothionium*.—*N*-methylthiodiphenylamine, prepared by methylation of thiodiphenylamine with methyl iodide under pressure (Bernthsen, *Annalen*, 1885, 230, 88), was converted into the dinitrosulphoxide by the process described by Bernthsen. The latter substance was then treated with phenetole and concentrated sulphuric acid in the manner which has been previously described in the case of the homologous sulphoxide. On pouring the green solution into water, the crude sulphate was precipitated as a sticky, green mass, which rapidly set to a brittle solid. This was separated from the mother liquor, and then triturated with excess of a 5 per cent. aqueous solution of sodium hydroxide. The resulting base was collected by the aid of the pump, washed, dried in the steam-oven, and finally purified by dissolving in chloroform and precipitating the solution with dry ether. *S-Phenetyl-N-methyl-3 : 3'-dinitrophenazothionium hydroxide* was thus obtained as an olive-brown powder, which melted at about  $200^\circ$ , and was insoluble in ether, but soluble in chloro-



form or alcohol without fluorescence. The hot dilute aqueous solution is brown :

0.1386 gave 0.2919  $\text{CO}_2$  and 0.0531  $\text{H}_2\text{O}$ .  $\text{C} = 57.44$  ;  $\text{H} = 4.26$ .

$\text{C}_{21}\text{H}_{20}\text{O}_6\text{N}_3\text{S}$  requires  $\text{C} = 57.14$  ;  $\text{H} = 4.31$  per cent.

The *chloride* was obtained by mixing the base with excess of hydrochloric acid ; it was purified from aqueous alcohol containing a little free hydrochloric acid to prevent dissociation. The substance formed a dark green powder, which was soluble in alcohol, and sparingly so in hot water :

0.1269 gave 0.2530  $\text{CO}_2$  and 0.0492  $\text{H}_2\text{O}$ .  $\text{C} = 54.80$  ;  $\text{H} = 4.31$ .

$\text{C}_{21}\text{H}_{19}\text{O}_5\text{N}_3\text{ClS}$  requires  $\text{C} = 54.84$  ;  $\text{H} = 3.92$  per cent.

The *platinichloride* forms a green powder, which is insoluble in water or alcohol :

0.1427 gave 0.0224 Pt.  $\text{Pt} = 15.69$ .

0.1647 „ 0.2393  $\text{CO}_2$  and 0.0467  $\text{H}_2\text{O}$ .  $\text{C} = 59.63$  ;  $\text{H} = 3.16$ .

$(\text{C}_{21}\text{H}_{19}\text{O}_5\text{N}_3\text{S})_2\text{PtCl}_6$  requires  $\text{Pt} = 15.53$  ;  $\text{C} = 40.13$  ;  $\text{H} = 2.87$  per cent.

#### *Condensation of Di-p-nitrodiphenylamine and Phenetyl-p-sulphinic Acid.*

The amine was prepared by the process recommended by Goldberg (*Ber.*, 1907, **40**, 4525) for obtaining derivatives of diphenylamine. A mixture of 14 grams of *p*-bromonitrobenzene, 10 grams of *p*-nitroaniline, 5 grams of potassium carbonate, 0.2 gram of copper iodide, and 75 grams of nitrobenzene was heated for twenty hours in a flask provided with a reflux condenser. The dark brown product was distilled in a current of steam to remove nitrobenzene and unchanged bromonitrobenzene ; the residue, which solidified on cooling, was collected and repeatedly extracted with concentrated hydrochloric acid. The insoluble, crystalline mass of crude di-*p*-nitrodiphenylamine weighed 10 grams.

Equal weights of phenetole-*p*-sulphinic acid and di-*p*-nitrodiphenylamine were dissolved in excess of phosphoryl chloride, and the brown solution was gradually heated on a sand-bath in a flask provided with a reflux apparatus. The reaction commenced suddenly, the liquid frothing up and becoming bright green ; the mixture was boiled for ten minutes longer, and then poured on to pounded ice to decompose the excess of oxychloride. An olive-green solid separated, which was collected, triturated with aqueous alkali hydroxide, thoroughly washed with water, and dried. The substance was purified by precipitation with dry ether from chloroform solution. In this way, di-*p*-nitrodiphenylamine 2-*p*-phenetylsulphoxide was obtained as a deep olive-green, crystalline powder, which melted at  $170^\circ$ . It was sparingly soluble in ether and readily so in chloroform or alcohol, giving brown or

brownish-green solutions. The colour of the alcoholic solution changed to crimson when aqueous sodium hydroxide was added :

0·1002 gave 0·2067  $\text{CO}_2$  and 0·0384  $\text{H}_2\text{O}$ .  $\text{C} = 56\cdot27$  ;  $\text{H} = 4\cdot25$ .

0·1013 „ 0·2092  $\text{CO}_2$  „ 0·0352  $\text{H}_2\text{O}$ .  $\text{C} = 56\cdot32$  ;  $\text{H} = 3\cdot98$ .

0·1458 „ 0·0844  $\text{BaSO}_4$ .  $\text{S} = 7\cdot95$ .

$\text{C}_{20}\text{H}_{17}\text{O}_6\text{N}_3\text{S}$  requires  $\text{C} = 56\cdot21$  ;  $\text{H} = 3\cdot98$  ;  $\text{S} = 7\cdot49$  per cent.

Derivatives of these substances and other condensation products of the  $\alpha$ - and  $\beta$ -sulphoxides are being at present studied, and we hope to publish the results at an early date.

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