

XXXIII.—*The Action of Nitrogen Sulphide on Organic Substances. Part I.*

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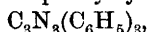
AN investigation of the action of nitrogen sulphide on organic substances has been undertaken in the hope that it may throw some light on the constitution of this substance.

Nitrogen sulphide is formed together with other products when ammonia acts on a solution of sulphur dichloride in carbon disulphide or benzene. According to the investigations of Fordos and Gélis (*Compt. rend.*, 1850, 31, 702), this substance has the empirical formula NS. The molecular weight, which was first given by Schenck as N_4S_4 , was determined by the cryoscopic method in naphthalene, and this was confirmed by Muthmann (*Ber.*, 1896, 29, 340), who obtained the same result with the ebullioscopic method in carbon disulphide. By employing the latter method, with benzene as solvent, we have also found the same molecular complexity.

The sulphide is best prepared by passing ammonia into a 10–15 per cent. solution of sulphur dichloride in benzene. When the ordinary chloride is employed, the yield is much smaller. A rapid

current of the dry gas is passed into the solution until red fumes appear, the flask in which the operation is being conducted is then cooled, and on maintaining the current for a short time the reaction is completed. After filtering off the ammonium chloride formed, the solution, on evaporation, deposits long, orange-red prisms of nitrogen sulphide. This is a beautifully crystalline substance, and may be readily purified by recrystallisation from either boiling benzene, toluene, or carbon disulphide; our specimens always showed a perfectly constant decomposition point at 185° , although Muthmann gives 178° , and earlier determinations were even lower, these results being probably owing to contamination with free sulphur. The properties of nitrogen sulphide have been fully described, but it may be of interest to state that Prof. Muthmann informed us that it was unwise to keep more than a few grams of the substance in one vessel, since it is apt to explode spontaneously with considerable violence. Although dealing with moderately large quantities, we have never observed this change, and are inclined to believe that the sulphide is rather more stable than is usually supposed.

The first group of organic substances investigated were the aromatic aldehydes. With benzaldehyde, a violent reaction takes place near the boiling point of this liquid; sulphur dioxide and water are evolved, and considerable amounts of triphenylcyanidine (cyaphenin),



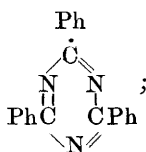
are formed. The reaction proceeds more slowly at lower temperatures, and at 100° was complete in about 30 hours. In each case, the main product is cyaphenin, and a much smaller quantity of a less fusible, crystalline substance, which was only isolated with difficulty. This product appears to be $\alpha\beta\mu$ -triphenylglyoxaline or lophin, $\text{C}_3\text{N}_2\text{H}(\text{C}_6\text{H}_5)_3$; it is probably formed by the reduction of cyaphenin by sulphur dioxide; this view of its formation is strengthened by the fact that small quantities of ammonium sulphate were detected among the products of the reaction. This interesting reaction does not seem to be dependent on the intermediate formation of benzonitrile, since nitrogen sulphide does not yield cyaphenin when treated with this substance. Benzylideneaniline, in a similar way, yields cyaphenin, and we are at present investigating the other products of this reaction. With *p*-tolu-aldehyde and nitrogen sulphide, the action is very similar, and the corresponding tritolycyanidine is easily obtained.

G. Glock (*Ber.*, 1888, 21, 2652) described the preparation of a polymerised toluonitrile, which he considered was probably "kyan-tolin," and there is no doubt that the substance he obtained is identical with our preparation, which, judging from the method of its formation, is very probably tritolycyanidine, $\text{C}_3\text{N}_3(\text{C}_6\text{H}_4\cdot\text{CH}_3)_3$.

With anisaldehyde and nitrogen sulphide, the action proceeds rather

more rapidly at 100° than in previous cases, and the main product is a white, crystalline powder which is still under investigation. We only found it possible to isolate very small quantities of what appeared to be tri-*p*-methoxyphenylecyanidine, $C_3N_3(C_6H_4 \cdot O \cdot CH_3)_3$. Like cyanophenin, this substance, although only slightly soluble in boiling alcohol, is readily recrystallised from hot benzene; it dissolves in concentrated sulphuric acid to a deep yellow solution, and is precipitated unchanged on the addition of water. Similarly, it has been found by one of us that salicylonitrile, on heating, readily polymerises into a yellow, crystalline compound with a high melting point, this product being also soluble without decomposition in concentrated sulphuric acid giving a yellow solution. From its great stability, it is not decomposed at 350° , and from the fact that its molecular weight was found to be approximately three times that of salicylonitrile, it appears probable that this substance is tri-*o*-hydroxyphenylecyanidine, $C_3N_3(C_6H_4 \cdot OH)_3$. Want of material prevented us from obtaining the corresponding tri-*p*-hydroxyphenylecyanidine from the foregoing trimethyl ether and comparing its reactions with those of the *o*-derivative.

The constitution of these cyanidines or 1:3:5-triazine compounds may in all probability be represented by the formula



they are very stable substances having high melting points, and they are not decomposed by aqueous or alcoholic potassium hydroxide. The cyanidine ring is broken by reducing agents, as when the triphenyl

derivative yields lophin, $\begin{array}{c} C_6H_5 \cdot C \cdot NH \\ | \\ C_6H_5 \cdot C - N \end{array} \Rightarrow C \cdot C_6H_5$. The complete decomposition into ammonia and benzoic acid can, however, only be effected by more powerful reducing agents, such as hydriodic acid at 220° .

We are at present pursuing the investigation of the interaction of nitrogen sulphide and aldehydes, and propose trying similar reactions with other groups of organic substances.

EXPERIMENTAL.

1. Action of Nitrogen Sulphide on Benzaldehyde.

Two grams of nitrogen sulphide were dissolved in a small quantity of benzene and treated with 10 grams of benzaldehyde; no reaction took place on boiling for 8 hours. On distilling off the benzene and

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heating with a free flame, the reaction became violent near the boiling point of the aldehyde, sulphur dioxide, water, and the excess of aldehyde distilled off, and the solid residue, after repeated crystallisation from benzene, gave about 1.3 grams of triphenylcyanidine.

The following results were obtained on analysis :

C = 81.52 ; H = 5.18 ; N = 13.61.

$C_3N_3(C_6H_5)_3$ requires C = 81.55 ; H = 4.85 ; N = 13.59 per cent.

The melting point was 230°, the numbers given for triphenylcyanidine by different authors being between 231° and 233°.

An attempt was made to follow quantitatively the course of the reaction, but without any very definite result. One gram of nitrogen sulphide was treated with a large excess of benzaldehyde, the operation being carried out in absence of air, and the sulphur dioxide liberated passed into a standard iodine solution. It was found that, approximately, 0.2 gram of sulphur was liberated as sulphur dioxide, and, after distilling off the unchanged aldehyde, nearly 0.12 gram was obtained from various crystallisations, the amount unaccounted for being 0.37 gram. The experiment could only, of course, be regarded as an approximation, but in attempting to account for the loss in sulphur, we were led to detect, among the residues, ammonium sulphate (in another experiment, carried out under similar conditions, this amounted to nearly 1 gram, which was equivalent to 0.24 gram of sulphur) and a substance much more soluble in absolute alcohol, and less so in benzene than triphenylcyanidine. The isolation of the latter substance in the pure state was extremely difficult, and, judging from the analysis given later, the compound we eventually obtained was not quite pure. The reaction between the aldehyde and nitrogen sulphide was then carried out on a larger scale, and the excess of aldehyde removed by distillation in steam ; the aqueous solution in the distilling flask contained ammonium sulphate and a very small quantity of a substance containing nitrogen, but not sulphur ; this was extracted by means of ether, recrystallised from benzene, and found to melt at 128°. The amount obtained was insufficient for an analysis. The residual solid, insoluble in water, was dried and treated several times with boiling alcohol ; from the filtrate, small quantities of triphenylcyanidine crystallised on cooling, and on adding water it was found that the substance which separated had a much higher melting point. On repeating this process many times, a white, feathery, crystalline mass was eventually obtained, only slightly soluble in benzene, but much more so in alcohol, from which it crystallises in characteristic tufts. From its appearance, we thought it might be lophin, although its melting point was 265—267°, whereas that substance is stated to melt at 275°. The following data were obtained on analysis :

C = 85.63 ; H = 5.66 ; N = 9.87.

(C₆H₅)₂C₃N₂H requires C = 85.13 ; H = 5.40 ; N = 9.46 per cent.

Laurent and Brunner (*Annalen*, 1869, 151, 135) state that lophin gives a hydrochloride melting at 155°, which is soluble in alcohol but insoluble in water. In order to confirm our view that we were actually dealing with this substance, the small amount at our disposal was converted into the hydrochloride, which decomposed at 157–159°, and was soluble in alcohol but insoluble in water. In all probability then, the substance was impure lophin, formed, possibly, by the reduction of triphenylcyanidine by sulphur dioxide, this view of its formation being strengthened by the presence of ammonium sulphate in the products of the reaction. We were unable to obtain a better yield of this substance, and as many experiments gave only 0.7 gram of this product, its further investigation was consequently abandoned. The reaction between the aldehyde and nitrogen sulphide was then carried out in an inert atmosphere at 100°, and although the velocity of the reaction was thereby greatly reduced—the time required for 5 grams of nitrogen sulphide to react being about 30 hours—yet the products were very similar. The yield of triphenylcyanidine was slightly increased, the amount of free sulphur was not quite so large, and the lophin was formed in about the same proportion as in previous cases. When benzylideneaniline was employed in place of benzaldehyde, the reaction takes place much less energetically, and the products contained triphenylcyanidine and a large amount of an oil which we are at present investigating.

2. Action of Nitrogen Sulphide on *p*-Tolualdehyde.

On warming together *p*-tolualdehyde and nitrogen sulphide, a reaction takes place very similar to that described with benzaldehyde; the solution darkens on heating, sulphur dioxide is slowly evolved, and a crystalline substance separates, which, after washing with ether and recrystallising from boiling benzene, melts sharply at 278°; it is slightly soluble in boiling alcohol and crystallises from hot benzene in long needles. The following results were obtained on analysis:

C = 82.32 ; H = 6.20.

C₃N₃(C₆H₄·CH₃)₃ requires C = 82.05 ; H = 5.98 per cent.

This substance appears to be identical with a polymeride of toluonitrile, termed by Gustav Glock "kyantolin" and described as crystallising in long needles melting above 260°.

3. Action of Nitrogen Sulphide on Anisaldehyde.

Five grams of nitrogen sulphide were heated for 20 hours with 12 grams of anisaldehyde in an inert atmosphere. The solid mass obtained at the end of that time was extracted with boiling alcohol to remove any unchanged aldehyde, and then extracted with boiling benzene. The insoluble matter constituted by far the larger bulk (about 5.6 grams); it was a white, crystalline powder, partially soluble in water, and at present it is still under investigation. The soluble matter consisted chiefly of sulphur, together with a very small quantity of a substance crystallising from benzene in white leaflets, and best separated from the sulphur by solution in acetone or concentrated sulphuric acid. This compound melts sharply at 217° , and is but slightly soluble in alcohol. On analysis, it gave the following result: $N = 10.70$. $C_3N_3(C_6H_4 \cdot O \cdot CH_3)_3$ requires $N = 10.52$ per cent.

It appears to be tri-*p*-methoxycyanidine, which is soluble in concentrated sulphuric acid forming a deep yellow solution and is precipitated unchanged on the addition of water. As previously mentioned, tri-*o*-hydroxycyanidine is a yellow, crystalline substance also soluble in sulphuric acid to a yellow solution.

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