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CLXXVI.—*The Action of Nitrogen Sulphide on Organic Substances. Part III.*

By Oliver Charles Minty Davis.

The investigation of the action of nitrogen sulphide on aldehydes has been continued, and it has been observed that, unlike the reactive benzaldehyde, tolualdehyde, and anisaldehyde previously examined (Trans., 1904, **85**, 259, 1535), several of the aldehydes reacted so slightly that it was not found possible to isolate any organic substance resulting from the decomposition.

In the case of cinnamaldehyde, salicylaldehyde, and cuminaldehyde, for example, although small amounts of sulphur dioxide were evolved, and traces of ammonium sulphate could be detected in the reaction products, yet no organic product could be isolated.

m- and *p*-Nitrobenzaldehydes react in a very similar manner to benzaldehyde, yielding their corresponding cyanidine derivatives; in

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addition, the meta-compound gave rise to a small quantity of a substance containing sulphur.

In the case of the chlorobenzaldehydes, an interesting case of steric hindrance was noticed; whereas the para-compound gives the corresponding cyanidine derivative, the ortho-compound does not react, and although the experimental conditions were varied the nitrogen sulphide was recovered unchanged. The influence of the ortho-substituent was so well marked in this instance that it was of interest to see whether it could be noticed in other cases.

p-Methoxybenzaldehyde, which had been previously examined, gave the corresponding cyanidine derivative, anisamidine sulphate, and a sulphur compound; on trying the same experiment with *o*-methoxybenzaldehyde, it was found that only a small amount of decomposition took place, and mere traces of a substance which behaved like a cyanidine derivative were isolated. On the other hand, piperonaldehyde, a substance in which both the ortho-positions with respect to the aldehyde group are unsubstituted, behaved exactly like anisaldehyde, giving tripiperonylcyanidine, piperonylamidine sulphate, and a derivative containing sulphur, which appeared to be quite analogous to that obtained in the case of anisaldehyde.

Various aliphatic aldehydes were also employed, but in every case negative results only were obtained.

It had been noticed that in the majority of the experiments carried out with these aldehydes the nitrogen present in the reaction products was much less than that contained in the nitrogen sulphide employed.

It accordingly appeared more than likely that this was caused by decomposition of the sulphide into free nitrogen and sulphur.

To test this supposition, an experiment was carried out with 5 grams of nitrogen sulphide and excess of benzaldehyde. The two substances were heated together in an apparatus from which the air had been expelled by means of carbon dioxide, and 55 c.c. of nitrogen were collected. A similar result was also obtained in the case of *p*-chlorobenzaldehyde.

The further investigation of the interaction of aldehydes and nitrogen sulphide has been abandoned, since the substances obtained have given no clue to the nature of the nitrogen sulphide molecule.

The type of substances which result in these reactions is such that it is extremely difficult to form any picture of the mechanism of the decomposition which takes place, and, beyond the fact that nitrogen sulphide appears to have no analogy at all to any of the known sulphides of phosphorus, no further statement as to its constitution seems possible.

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EXPERIMENTAL.

Interaction of Nitrogen Sulphide and Aldehydes.

(1) m-*Nitrobenzaldehyde.*—Sixty grams of the aldehyde and 17 grams of nitrogen sulphide were heated together at 110—115° for thirty-eight hours; at the end of this period, some toluene was added, and the reaction continued for a further forty-eight hours. Sulphur dioxide was continuously evolved during this period. The solid product which had separated was filtered off from the hot toluene, and when dried weighed 22 grams.

The filtrate on cooling deposited an oily substance, which, after treatment with ether and boiling alcohol, gave small amounts of a crystalline substance melting at 180°. This was purified by recrystallising from benzene, but the amount obtained was insufficient for a complete investigation. It gave the following data on analysis, which agree fairly well with the empirical formula $C_{14}H_{10}O_4N_4S$.

Found, $C = 51{\cdot}1$; $H = 3{\cdot}5$; $N = 17{\cdot}7$; $S = 9{\cdot}2$.
Calculated, $C = 50{\cdot}9$; $H = 3{\cdot}3$; $N = 16{\cdot}9$; $S = 9{\cdot}7$ per cent.

The main product of the reaction was treated with boiling benzene, which dissolved about 4 grams of sulphur.

The residue was then dried, and on treatment with hot water a small amount of ammonium sulphate was dissolved out, leaving a substance which was found to be insoluble in the usual solvents, but which could be crystallised with difficulty from boiling nitrobenzene, giving crystals which melted sharply at 342°.

The compound possesses the characteristic properties of the cyanidine derivatives: it melts at a high temperature without decomposition, and dissolves in strong sulphuric acid, giving a brown solution from which water precipitates the unchanged cyanidine. On analysis, the following results were obtained: $C = 57{\cdot}10$, $57{\cdot}19$; $H = 3{\cdot}51$, $3{\cdot}13$; $N = 19{\cdot}23$, the calculated values for *m*-trinitrotriphenylcyanidine, $(C_6H_4{\cdot}NO_2)_3C_3N_3$ being $C = 56{\cdot}75$; $H = 2{\cdot}7$; $N = 18{\cdot}91$ per cent.

(2) p-*Nitrobenzaldehyde.*—The reaction between nitrogen sulphide and *p*-nitrobenzaldehyde is very violent; it commences a little above the melting point of the aldehyde, and proceeds with great velocity at about 120°. If large quantities of the reagents are used, so much heat is evolved that an almost explosive decomposition occurs. Sulphur dioxide and ammonium sulphate are formed, and a small amount of a crystalline product melting above 360° was isolated. This substance possesses the characteristic stability of the cyanidine derivatives, and may be recrystallised from boiling nitrobenzene. A nitrogen deter-

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mination gave N = 18·63, the calculated value for *p*-trinitrotriphenylcyanidine being 18·91 per cent.

(3) p-*Chlorobenzaldehyde.*—Five grams of nitrogen sulphide and 10 grams of *p*-chlorobenzaldehyde, when heated together in an inert atmosphere for forty-four hours at 100°, continuously evolved sulphur dioxide, and towards the end of the reaction a little toluene was added. Whilst still hot, the solid which separated was filtered off, and after washing with ether and drying weighed 5 grams.

The filtrate, which was heated for a further twenty-four hours, when cooled and treated with light petroleum yielded a very small amount of a crystalline product, which, when recrystallised from alcohol, melts sharply at 145°.

A further quantity of this was obtained by treating the insoluble product of reaction with boiling alcohol, but the total amount was insufficient for complete analysis.

A qualitative examination showed that it contains nitrogen and sulphur.

The insoluble residue, after treatment with boiling alcohol, was freed from ammonium sulphate by water. When dry it was slightly soluble in boiling benzene, but much more so in boiling nitrobenzene. From either solvent, pale yellow silky needles separate on cooling, melting without decomposition at 334°. The substance has the characteristic properties of the cyanidine derivatives, and is soluble in concentrated sulphuric acid, giving a deep yellow solution, which deposits the unchanged compound on dilution with water.

The following analytical data showed that the substance was *p*-trichlorotriphenylcyanidine.

Found Cl = 25·67 ; N = 10·36.

$(C_6H_4Cl)_3C_3N_3$ requires Cl = 25·78 ; N = 10·21 per cent.

(4) o-*Methoxybenzaldehyde.*—From 8 grams of nitrogen sulphide and 22 grams of the aldehyde, less than 0·5 gram of a crystalline substance was obtained, which, when recrystallised from boiling alcohol, melted sharply at 158° and dissolved in concentrated sulphuric acid to form a yellow solution, which deposits colourless crystals on treatment with water. When fused with caustic potash, the compound evolved ammonia.

A nitrogen estimation indicated that the substance was *o*-trimethoxytriphenylcyanidine, but the amount obtained was insufficient for further analysis.

Found N = 10·39. $(C_6H_4OCH_3)_3C_3N_3$ requires N = 10·5 per cent.

(5) *Piperonaldehyde.*—Twenty grams of piperonaldehyde and 5 grams of nitrogen sulphide were heated together at 100°, as in previous cases,

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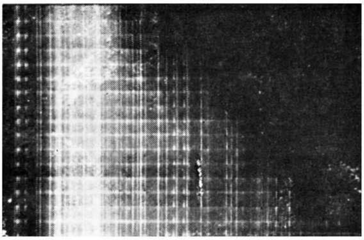
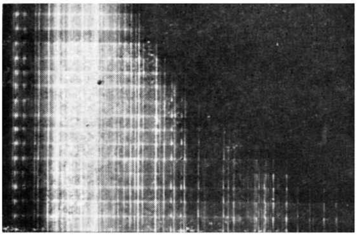
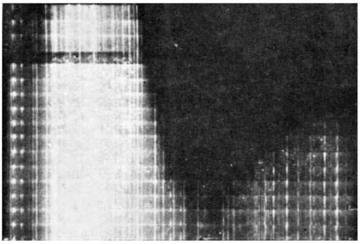


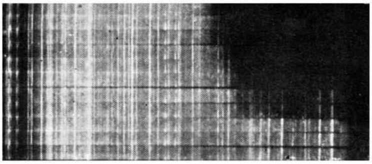
1. Violuric Acid. Alcoholic Solution.



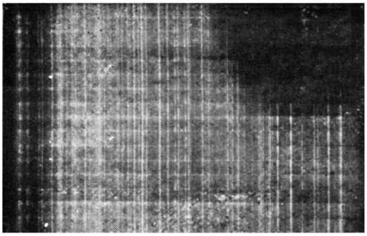
2. Violuric Acid. Aqueous Solution.



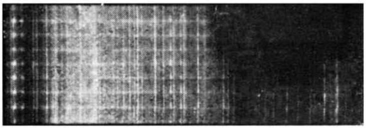
3. Sodium Violurate.



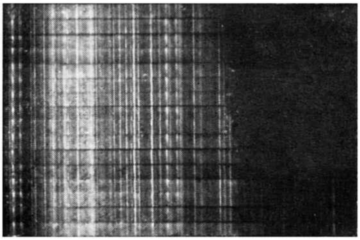
4. Alloxantin.



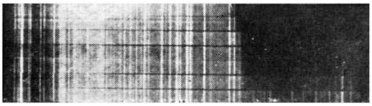
5. Dialuric Acid.



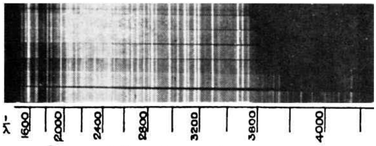
6. Uric Acid.



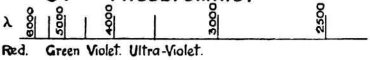
7. Caffeine.



8. Ethoxycaffeine



9. Theobromine.



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the reaction being complete in forty-six hours. Sulphur dioxide was evolved during the whole of that period.

The excess of aldehyde was removed by boiling alcohol and the dried product, which weighed 9·5 grams, was treated with benzene to remove the sulphur formed during the reaction, and after drying was warmed with water, which dissolved out about one gram of piperonylamidine sulphate. The residue was partially soluble in dilute aqueous caustic potash, leaving undissolved a brown powder, which, after crystallisation from boiling nitrobenzene, melted at 266°.

(i) The aqueous solution deposited crystals of piperonylamidine sulphate on cooling, and after several crystallisations from hot water these were obtained pure and free from ammonium sulphate. The substance melts with decomposition at 253°, when boiled with alkaline solutions ammonia is evolved, and on acidifying a crystalline substance separates, melting at 222°; this, in all probability, is piperonylic acid, which is stated to fuse at 228°. The piperonylamidine sulphate gave the following analytical results:

Found $H_2SO_4 = 23{\cdot}8$; $N = 12{\cdot}57$.

$[C_6H_3{:}O_2{:}CH_2C{:}NH{\cdot}NH_2]_2,H_2SO_4$ requires $H_2SO_4 = 23{\cdot}0$; $N = 13{\cdot}15$ per cent.

On recrystallising a specimen from glacial acetic acid, the melting point was raised to 268°, an acetyl derivative being presumably formed. On analysis, this gave $N = 11{\cdot}3$, the calculated value for the acetyl derivative being $N = 10{\cdot}98$ per cent.

(ii) That part removed by warming the product of reaction with dilute aqueous caustic potash is reprecipitated on the addition of dilute acids; it contains sulphur, and behaves in a somewhat similar way to the sulphur derivative obtained from anisaldehyde. It may be recrystallised from nitrobenzene, and the melting point of the crystallised product is 207°. Treated with warm sulphuric or hydrochloric acid, the compound evolves sulphur dioxide. The amounts obtained were insufficient for any detailed examination, but a nitrogen determination, combined with the foregoing properties, makes it appear quite probable that the product is the piperonyl analogue of the substance obtained by the interaction of nitrogen sulphide and anisaldehyde.

Found $N = 11{\cdot}8$. $C_{16}H_{11}O_5N_3S$ requires $N = 11{\cdot}76$ per cent.

(iii) The brown powder left after the removal of the sulphur compound is insoluble in most solvents, but may be crystallised from boiling nitrobenzene, when it melts without decomposition at 266°; it dissolves in concentrated sulphuric acid to a deep red solution, and is reprecipitated unchanged by water in the form of yellow crystals.

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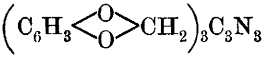
On analysis, the following results were obtained, showing that the substance was tripiperonylcyanidine.

Found C = 65·8 ; H = 3·6 ; N = 9·2.



$\left(C_6H_3<\!\substack{O\\O}\!>CH_2\right)_3C_3N_3$ requires C = 65·3 ; H = 3·4 ; N = 9·5 per cent.

The substances used in the course of this investigation, which were placed at my disposal by Dr. Francis, were purchased with a grant from the Chemical Society.

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