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Chemistry. — "*On some nitro-derivatives of dimethylaniline*".

By M. J. SMIT. (Communicated by Prof. VAN ROMBURGH).

(Communicated at the meeting of June 28 1919).

In 1914 a paper was published by VAN ROMBURGH and Miss WENSINK ¹⁾ in which the action of ammonia and methylamine on 1, 2, 3, 4. trinitrodimethylaniline was described. The remarkable phenomenon was here described that, besides the nitro-group in the 3-position, also the dimethylamino-group was replaced by the amino- or the methylamino-group as the case might be. At the instigation of Prof. VAN ROMBURGH I have undertaken a more extensive investigation into the behaviour of amines and, in general, of compounds containing an amino-group, with respect to the trinitro-derivatives of dimethylaniline, in particular the 1.3.4.6. isomeride. These investigations are, however, still in the initial stage, and will be described in due course in a thesis.

Before undertaking the research above indicated, it appeared to me desirable to study somewhat more accurately the reaction in which the two isomeric trinitro derivatives of dimethylaniline are produced. In the nitration of 1.3.4 dinitromethylaniline ²⁾ the principal product is always the 1.3.4.6. derivative; the isomeric 1.2.3.4. compound is only formed in small quantities. Since, however, it is precisely the latter, in consideration of the position of the nitro-groups, which reacts the most easily, it seemed to me to be worth while to try to establish the conditions in which a better yield of this substance could be obtained.

In spite of numerous attempts in which the experimental conditions were varied between the widest limits, I was not successful in so modifying the conditions that the yield of 1.2.3.4 trinitro-dimethylamine was increased to any appreciable extent. In these experiments the great influence which the presence of nitrous acid exerts on the reaction velocity, was again most distinctly apparent; a phenomenon which has already been repeatedly observed in nitration experiments,

¹⁾ These Proceedings, XVII, 1034 (1915).

²⁾ VAN ROMBURGH, Verslagen Kon. Akad. v. Wet. 23 Febr. 1895, III, 257.

and which was also noticed in the nitration of 1.3.6 dinitro dimethylaniline. (See below). Moreover it appeared to be important not to allow the action of the nitric acid to be unduly prolonged.

If for the nitration nitric acid is used which is completely free from nitrous acid, it is necessary to use a fairly concentrated acid (Sp. Gr. 1.37—1.40) in order to avoid prolonging the reaction unduly. To prevent excessive rise of temperature a moderate excess of nitric acid should be used.

As a rule 10—12 c.c. of nitric acid was added to 1 gram of the amine. If necessary the reaction may be accelerated by the addition of a small portion of sodium nitrite. In these conditions the two isomeric trinitro-derivatives are probably the only products.

If, however, nitric acid is used containing much nitrous acid, or if the reaction is allowed to proceed for a long time, or, again, if the temperature rises appreciably above 20° C., then the action of the nitrous acid becomes manifest, and nitroso-compounds are easily formed. The isolation of the required isomerides is thus rendered extremely difficult, and, of course, the yield is reduced. In these conditions two light yellow substances of melting points 108°—109° C. and 201° C. respectively, were isolated. Both could be crystallised from alcohol and are obtained in the form of fine light yellow needles with a greenish reflection. The first can be obtained, as appeared later, by the action of nitrous acid on 1.3.4 dinitrodime-
thylaniline and is transformed on treatment with nitric acid (Sp. Gr. 1.41) into the other. The latter is obtained by the action of nitrous acid on 1.3.4.6 trinitrodime-
thylaniline.

In all probability these substances are therefore 1.3.4 dinitro-phenylmethylnitrosamine (M.p. 108°—109° C.) and 1.3.4.6 trinitro-phenylmethylnitrosamine (M.p. 201° C.).

The presence of the product of the reaction of nitrous acid on the 1.2.3.4 trinitro-compound, also a yellow substance with greenish reflection, which melts at 96°—97° C. after recrystallisation from alcohol, could not be detected. This is not surprising seeing that only a minute quantity of the 1.2.3.4 isomeride is produced in the reaction.

Direct nitration of *m*-nitrodime-
thylaniline (M.p. 60° C.) with nitric acid (Sp. Gr. 1.4) did not lead to a better result. Here also the chief product was the 1.3.4.6 compound.

The nitration of the 1.3.6 dinitrodime-
thylaniline which, like the corresponding 1.3.4 isomeride, is formed from dimethylaniline in presence of excess of sulphuric acid¹⁾, was also investigated.

¹⁾ Rec. VI, 253 [1887].

VAN ROMBURGH had already found¹⁾ that the principal product of the reaction is 1.3.4.6 trinitrodimethylaniline.

Besides this compound there is also formed in small quantity a substance which crystallises from ethyl acetate in beautiful yellow crystals. The substance melted with slight decomposition at 132° forming a pale yellow liquid.

At first I was of opinion that I had obtained a new trinitro-isomeride, probably the 1.2.3.6 compound. On varying the conditions however, with the object of increasing the yield, when a smaller quantity of nitric acid was used for the nitration, a rise in temperature to 40° C. was observed, and a copious evolution of brown fumes took place. I was surprised to find that more of the substance had been formed. It occurred to me that the compound might be a product of the action of nitrous acid. This assumption appeared to be correct. If the 1.3.6 compound is dissolved in dilute sulphuric acid (1:1) and sodium nitrite is added, an almost quantitative yield of the above substance is obtained. On treatment with nitric acid (Sp. Gr. 1.4) the substance is transformed into the nitrosamine (M.p. 201°) already described. It must therefore be considered as the nitrosamine of the 1.3.6 compound.

In the nitration of the 1.3.6 dinitro-derivative the effect of nitrous acid on the reaction velocity is extraordinarily great. By the addition of urea it is possible to stop the reaction altogether. If the temperature of the reaction is perceptibly higher than room temperature the only final product obtained is the substance melting at 201°. Both the substance melting at 132° and the 1.3.4.6 trinitro-derivative are transformed into the above nitrosamine.

Repeated attempts to obtain an isomeric trinitro-derivative were all unsuccessful, the only product obtained being the nitrosamine.

This research is being continued, and the results will be described in greater detail later.

Bergen op Zoom, June 1919.

¹⁾ These Proceedings, III, 258.