

Citation:

Romburgh, P. van, On the action of nitrous acid on dinitrodialkylanilines, in:
KNAW, Proceedings, 13 II, 1910-1911, Amsterdam, 1911, pp. 820-822

Chemistry. — “*On the action of nitrous acid on dinitroalkyl-anilines*”. By Prof. P. VAN ROMBURGH.

According to HANTZSCH (B. 43, 1674 [1910]) there is formed by the action of nitric acid (D. 1.3) on dimethylaniline, 3.4 dinitrodimethylaniline which is regarded by him as a new compound. Apart from the fact that I obtained this substance many years ago (Rec. VI, 253 [1887]) and explained its structure in 1895¹⁾, the communication of HANTZSCH attracted my attention because in my investigations as to the action of nitric acid of widely different concentrations on dimethylaniline, I always obtained — dependent on circumstances — besides tetranitrotetramethylbenzidine²⁾, derivatives of mono- and dimethylaniline in which the nitro groups occupied in regard to the amino group, the *ortho* or *para*-position, but never the *meta*-position. Derivatives with a nitro group in the *meta*-position could only be obtained by nitrating dimethylaniline in the presence of a large excess of strong sulphuric acid.

I therefore, have had the action of nitric acid (D 1.3) on dimethylaniline repeated by one of my students, Mr. JANSEN. As one of the reaction products there is formed indeed a yellow substance (m. p. 175°—176°) which, however, is nothing else but the well known 2.4 dinitromonomethylaniline, as was shown from the analytical results, and also by a comparison with a preparation obtained by oxidation of 2.4 dinitrodimethylaniline, and with one obtained from methylamine and bromodinitrobenzene with which it did not cause a depression of the melting point.

On the other hand when it is mixed with the 3.4 dinitrodimethylaniline (m. p. 176°) previously obtained by me, it causes a strong decrease of the melting point.

As in the reaction described nitrous acid is generated, it is obvious to assume that by its action on the dimethylamino-group one methyl-group is split off, a reaction of which, moreover, many instances are known.

If to the nitric acid (D. 1.3) a little urea is first added to remove any nitrous acid generated, the monomethyl derivative is not formed, but as main product 2.4 dinitrodimethylaniline (m. p. 87°) is obtained.

In an experiment where a solution of dimethylaniline in ten times its volume of nitric acid (D. 1.3) had stood over night, there was

¹⁾ Meeting Febr. 23, 1895.

²⁾ Rec. 5, 244 [1886].

obtained, besides the monomethyl derivative, a quantity of 2.4 dinitrophenylmethylnitrosamine.

That, in conjunction with the results of the nitration experiment in the presence of urea, we may explain the reaction in this way, viz. that first of all the nitrated dimethyl compound is generated, and that this is then converted by the nitrous acid (which is formed by the oxidising action of the nitric acid) into the monomethyl compound (or the nitroso derivative, respectively) is very probable, but by no means certain. Experiments are still in progress to establish this. In the meantime, I have studied the action of nitrous acid on some of the dialkyl derivatives of dinitroanilines.

If we dissolve 2.4 dinitrodimethylaniline in 5 times its weight of nitric acid (D. 1.3) and then add to that solution sodium nitrite until it acquires a strong odour of nitrous acid, a pale yellow compound crystallises, which melts at 86° ¹⁾ and is identical with the 2.4 dinitrophenylmethylnitrosamine prepared according to STÖRMER²⁾. On boiling with acetic acid, the nitrogroup is replaced by hydrogen and we obtain the 2.4 dinitromonomethylaniline (m.p. 176°). With 2.4 dinitrodiethylaniline the reaction proceeds in quite an analogous manner. 2.4 dinitrophenylethylnitrosamine³⁾ (m.p. 52°) is formed which also readily loses NO by boiling with acetic acid, and yields 2.4 dinitroethylaniline (m.p. 114°).

2.4 dinitrodipropylaniline⁴⁾ is also converted by nitrous acid into a nitroso compound from which, by means of boiling acetic acid, the dinitromonopropylaniline (m.p. 97°) may be again obtained.

In the dialkyl derivatives of 3.4-dinitroaniline an alkyl group is also eliminated by nitrous acid. If, however, we carry out the reaction in a nitric acid solution (D. 1.3) it is accompanied by a further nitration because, as it seems, the nitrous acid accelerates the nitrating action of the dilute nitric acid.

If, however, we work in a sulphuric acid solution (1 vol. of acid, 1 vol. of water) a nitroso monoalkyl compound is formed even with these derivatives.

With 3.4-dinitrodiethylaniline, for instance, a beautiful pale yellow nitroso derivative (m. p. 79° — 80°) is formed from which the nitroso

¹⁾ It is sometimes contaminated with the non-nitrosated monomethyl compound. It will be ascertained whether this is formed primarily, or by the action of the nitric acid on the nitroso compound. (Compare STÖRMER loc. cit.)

²⁾ B. 31, 2530 [1893].

³⁾ STÖRMER loc. cit. pag. 2531.

⁴⁾ This compound which I described fully 20 years ago (Rec. 8, 252 [1889]), is described in HANTZSCH's paper loc. cit. p. 1675 as a new one.

group is split off by boiling with phenol or acetic acid. The 3,4-dimethyl derivative also reacts readily with nitrous acid in sulphuric acid solution; the compound formed is still under investigation.

Finally, I have allowed nitrous acid to act on the dark red 3,6-dinitrodiethylaniline (m. p. 76°) when a beautiful pale yellow nitroso compound (m. p. 69°) is formed, which on being boiled for a moment with acetic acid, yields on dilution with water beautiful red needles of the 3,6-dinitromonoethylaniline (m. p. 120°) previously described by me, so that in this case also one of the ethyl groups has been eliminated. The 3,6-dinitrodimethyl compound behaves in quite an analogous manner, just like p. nitrodiethylaniline.

These experiments are being continued with other tertiary nitrated amines.

Utrecht. *University Org. Chem. Lab.*

Chemistry. — “*Confirmations of the new theory of the phenomenon of allotropy.*” I. By Prof. A. SMITS and Dr. H. L. DE LEROUW. (Communicated by Prof. VAN DER WAALS).

(Communicated in the meeting of December 24, 1910).

As was set forth before¹⁾ the above-mentioned theory leads us to expect that for every substance which presents the phenomenon of *heterogeneous* allotropy, so *monotropy* or *enantiotropy*, the phenomenon of *homogeneous* allotropy will also occur, because the two phenomena are in the closest connection.

So in virtue of this theory we can expect for the monotropic and enantiotropic substances that every vapour, liquid, or solid phase in stable condition consists of an internal equilibrium between different kinds of molecules. A consequence of this is then that when we make the temperature vary so rapidly that the internal equilibrium cannot keep pace with the temperature, the more complex nature of the substance will appear, which will, among others, manifest itself in a boiling or melting range of temperature, in which the final boiling point, resp. final melting point will lie higher or lower than the unary stable boiling point, resp. melting point, dependent on the type of the pseudo-system and of the direction of the line which indicates the internal equilibrium in the vapour, resp. liquid phase.

¹⁾ These Proc. March 1910 p. 763.