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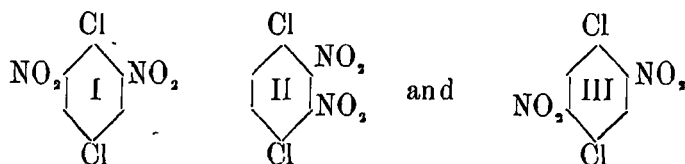
Haeften, F.E. & Hollander, A.J. den, On the Nitration-Products of p-Dichlor-Benzene, in:
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Chemistry. — “*On the Nitration-Products of p-Dichlor-Benzene*”.

By DR. A. J. DEN HOLLANDER and Dr. F. E. VAN HAEFTEN.
(Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of November 29, 1919).

In 1868 JUNGFLAISCH¹⁾ nitrated p-dichlor-benzene by boiling it with a mixture of fuming nitric acid and sulphuric acid for some hours. In this way he obtained a mixture of dinitro-p-dichlor-benzenes, about whose constitution opinions are still divided. Theoretically three isomers are possible, viz.:



JUNGFLAISCH himself isolated two compounds out of it, which he denoted by α and β , but of which he did not determine the structure. For the α -compound he gave 87° as melting-point, for the β -compound 107° . There is formed much more of the former compound according to him than of the latter. KÖRNER²⁾, and much later ULLMANN and SAKE³⁾, proved that structure I applies to this chief product; the melting-point was, however, found at 105° by them. ENGELHARDT and LATSCHINOFF⁴⁾ had also observed this higher melting-point, and could isolate the β -compound also from the reaction-product; hence they confirmed JUNGFLAISCH's results in the main.

On the other hand MORGAN and NORMAN⁵⁾ assert that compound III is formed as chief product; HARTLEY and COHEN⁶⁾, who repeated the former's experiments, confirm this, and give as melting-point $105-106^\circ$. Two year ago, Miss EDITH NASON⁷⁾ nitrated p-dichlor-benzene anew, and succeeded in also isolating III from the reaction mixture in a yield of 45,6%, for which she, however, found the melting-point 81° .

¹⁾ A. ch. (4), 15 259.

²⁾ J. 1875, 324.

³⁾ B. 44, 3730 (1912).

⁴⁾ Z. 1870, 234.

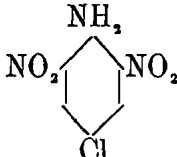
⁵⁾ Soc. 81, 1378, 1382 (1902).

⁶⁾ Soc. 85, 868 (1904).

⁷⁾ Am. Soc. 40, 1602 (1918).

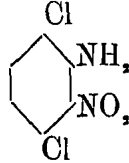
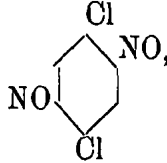
The structure proofs which these investigators bring forward for their supposed isomer III, are, however, quite insufficient. It, therefore, remained: 1st to decide what isomer or what isomers arise by the side of I (about which there is no difference of opinion); 2nd to furnish a conclusive structure proof for this isomer or these isomers.

In the first place we have now found that all three isomers are formed, I as chief product, II and III as bye-products. In this we have proceeded as follows: The crude reaction product is perfused with an excess of 4 N-alcoholic ammonia, 4 mol. NH₃ to 1 mol. dichlor-dinitro-benzene. After some stirring most of it goes into solution. It is then left standing for two days at the temperature

of the room. Then I is converted into  2-6-dinitro-4-

chloraniline, melting-point 145°, which is for the greater part deposited in fine needles and almost pure ¹⁾. After filtration the alcoholic filtrate is distilled; then a residue is left, which consists of the isomers II and III, but also contains a certain quantity of the above mentioned chlor-dinitraniline. This residue is washed with water to remove Am-nitrite, then dried, and dissolved in about ½ liter of benzene (when 1 mol. of reaction product was started from). This solution is shaken out a few times with 20 cc. concentrated sulphuric acid, by which means the chlordinitraniline is removed. This is the case when the sulphuric acid gives no further colour.

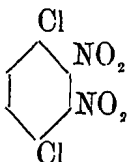
Then the benzene is distilled off, after which a residue remains, consisting chiefly of the compounds II and III, as can be shown by treating it again with alcoholic ammonia, 100 cc. 4 N. NH₃ to 50 gr. mixture. Then the liquid is digested (temp. in the flask 80—85°) for 24 hours on a waterbath at a reflux condenser, and ammonia gas is led in a few times to compensate the loss. Then the liquid is neutralized, the greater part of the alcohol is distilled off, and the rest is poured into water. Through treatment of the reaction product with sulphuric acid, as given above, 2 nitro-3-6-dichloraniline

 goes into solution and  benzene remains behind.

¹⁾ It contains still a certain quantity of the isomer III, from which it can be separated by sulphuric acid, see below.

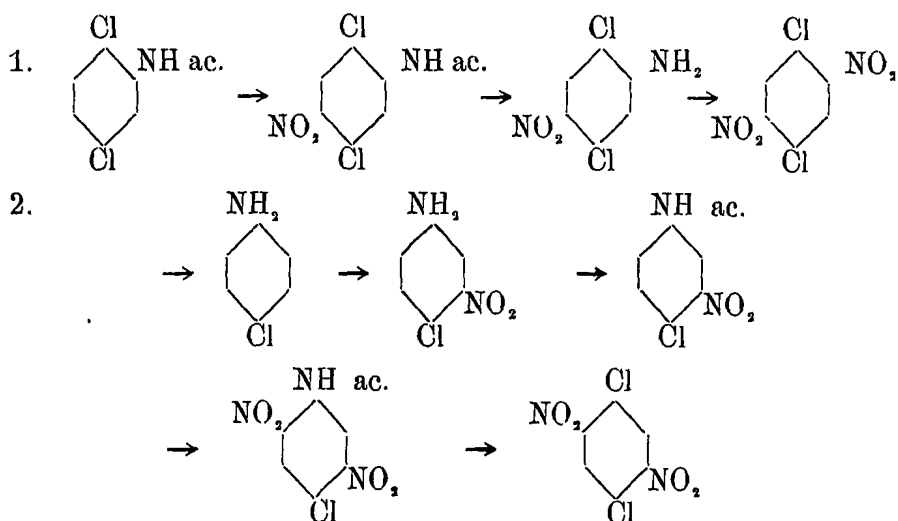
After recrystallisation from alcohol the latter is pure and presents the melting-point of 119°.

The formation of 2-nitro-3,6-dichlor-aniline, melting-point 68°, the structure of which has been ascertained through a research of BRILSTEIN and KURBATOW¹⁾, proves that in the crude reaction product

the 1,4-dichlor-2,3-dinitrobenzene  must be present.

Through prolonged fractionated crystallisation from alcohol this could actually be separated out of it. It is probably JUNGFLMISCH's isomer β , and melts at 103°. The structure was proved by replacing the NH_2 group in 2-nitro-3,6-dichloraniline by NO_2 according to the method of KÖRNER and CONTARDI²⁾.

Hence only the structure formula III remains for the third isomer of the melting-point 119°. This was, however, proved more closely in the two following ways:



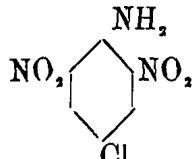
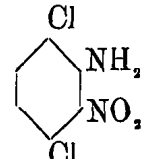
in which the structure of the intermediate products was every time determined.

When we try to separate the three components out of the crude nitration-product of JUNGFLMISCH, we succeed by means of very prolonged continued fractionated crystallisation from alcohol in obtaining the compounds I and II in pure state, but not III. We get at last a pretty considerable quantity of a cauliflowery mass, which is no longer liable to further separation by crystalli-

¹⁾ A. 196, 221 (1879).

²⁾ Atti (5) 22 II, 632 (1913).

sation, and which — as appears from the treatment with alcoholic ammonia applied to it as given above — consists chiefly of I, further of a little II, and pretty much III.

From the obtained compounds  and  the

corresponding dichlorodinitro benzenes can be easily regained through diazotation.

A full description of this investigation will shortly appear in the *Recueil*.

November 1919. *Org. chem. lab. of the Univ. of Amsterdam.*