

Citation:

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invariant point exists, always arrange that these arcs do not cohere, and within O (see fig. 10) an arc of simple curve β can be constructed, running from infinite to infinite, lying entirely outside its image β' , and enclosing with β' a new transformation domain ω . According to the SCHÖNFLIES process of representation ¹⁾ the domains $\omega', \omega'', \omega''', \dots$, determined by a series of successive repetitions of the transformation, can then be represented on regions enclosed by straight lines $x = na$ and $x = (n+1)a$ in such a way that a series of corresponding points in $\omega, \omega', \omega'', \omega''', \dots$ answers to a series of points $(p, q), (p+a, q), (p+2a, q), (p+3a, q), \dots$; furthermore, if no invariant point exists, we can arrange, that the just-mentioned series of images of ω , continued indefinitely on both sides, covers the whole Cartesian plane, i. o. w. we have proved:

THEOREM 3. *An arbitrary continuous one-one transformation of the Cartesian plane in itself with invariant indicatrix either leaves at least one point invariant, or is a continuous one-one image of a translation.*

ERRATUM.

In my paper: "*The force field of the non-Euclidean spaces with positive curvature*", these *Proceedings* IX 1, p. 261, l. 6 from top:

for: The unilateral elliptic Sp_n is enclosed by a plane Sp_{n-1} ,

read: The elliptic Sp_n is enclosed by a unilateral plane Sp_{n-1} .

Chemistry. — "*On the nitration of diethylaniline*". By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of September 25, 1909).

A considerable time ago I communicated to the Academy the results of the action of nitric acid on dimethylaniline dissolved in a large excess of sulphuric acid²⁾. The difference in behaviour which dimethyl- and diethylaniline exhibit when nitrated under other conditions induced me to study also the action of nitric acid on diethylaniline in presence of an excess of sulphuric acid, and indeed this amine and some of its nitro-derivatives appeared to behave in many respects differently from dimethylaniline.

If we dissolve diethylaniline in double its volume of concentrated sulphuric acid and pour this solution into an excess of nitric acid

¹⁾ Mathem. Ann. 62, p. 319—324

²⁾ Verslagen Akad. v. W. Febr. 23, 1895 and These Proc. Dec. 30, 1900.

(D. 1.48) we obtain 1.2.4 dinitrodiethylalaniline (m.p. 80°) as I have demonstrated previously¹⁾.

If, however, diethylalaniline (1 mol.) is dissolved in twenty times its weight of sulphuric acid (D. 1.84) and if to this solution are cautiously added 2 mols. of nitric acid dissolved in about five times the weight of sulphuric acid, care being taken that the temperature of the nitrating mixture does not rise above 5°, and if, after a few hours it is poured into iced water, a more or less deep yellow, crystalline product is obtained.

If this is collected and the filtrate neutralised to a large extent with sodium carbonate, a fine dark red compound is separated.

It may be stated here that this experiment has been carried out many times; strange to say the results were often quite different although the conditions of working were practically the same; as will now appear, it depends on the quantity of iced water into which the mixture is poured.

Recrystallisation of the yellow crystalline mass from alcohol gave as main product a compound melting at 59°, a small quantity of a fine orange red product m.p. 95°, being also occasionally deposited. If the latter was recrystallised I often obtained yellow as well as orange red crystals which, however, melted at the same temperature (95°). Sometimes, on recrystallising the compound melting at 59°, the orange crystals melting at 95° were obtained, so that it looked as if the compound with the lower melting point passed into that with the higher one.

The dark red substance separated by means of the alkali, when recrystallised from alcohol, melted at 76°.

The elementary analysis gave the same result for all these substances; the figures obtained showed that they all had the composition of dinitrodiethylalaniline.

The peculiar behaviour of the above products melting at 59° and 95° rendered a closer investigation desirable and finally I succeeded in finding the key to the problem; the substance melting at 59° is a compound of two different dinitroderivatives of diethylalaniline, and the one melting at 95° occurs in two, and probably more, modifications.

If we dissolve one part of the substance melting at 59° in 11.4 parts of hydrochloric acid (D. 1.14) and then cautiously add water whilst shaking, a yellow product separates, which, however, soon turns orange, as a rule. After 6 parts of water have been added the crystals are collected and washed with a little hydrochloric acid

¹⁾ Rec. T. II p. 36 [1883].

D. 1.08. If now to the filtrate is added much water a yellow product is precipitated. The melting point of the orange-red product is 95° , that of the yellow one 80° . This last one proved identical with the 1.2.4 dinitrodiethylaniline described previously.

In a quantitative experiment there was obtained from 0.750 gram of the substance melting at 59° , 0.370 gram of the orange and 0.358 gram of the yellow product, and from the neutralised mother liquors another 0.021 gram of solid matter was obtained.

If we dissolve a mixture of equal weights of the two nitro-compounds in boiling alcohol, the compound melting at 59° crystallises on cooling. The curve of the melting points of mixtures of both nitro-compounds in different proportions showed undoubtedly the existence of a compound formed from equal molecules of the said substances.

The compound melting at 95° is, as will be shown presently, 1.3.4- dinitrodiethylaniline. It is soluble in most of the organic solvents at the boiling heat. If the hot concentrated solution is cooled rapidly yellow crystals only are often obtained, whereas on cooling slowly orange crystals are generally formed. The yellow ones represent the labile (β), the orange ones the stable α -modification¹⁾. Occasionally and under definite conditions, a third modification is formed which is also yellow, but very unstable, much more so than the β -modification, and which in the dry state passes very slowly into the orange one.

The products formed in the nitration in presence of strong sulphuric acid being now known, the progressive change of the reaction was investigated more closely.

In the first place it appeared that in the case of diethylaniline, the nitration under the conditions described, that is when 2 mols. of nitric acid are used, does also not proceed further than the formation of mononitroderivatives. In fact, if to the mixture of diethylaniline with sulphuric and nitric acid, is added another mol. of diethylaniline, also dissolved in 20 parts of sulphuric acid, and the mass poured into iced water, no *di*-nitro-compounds appear to have formed, and we obtain only m. and p. nitrodiethylaniline.

If, however, we dissolve m. nitrodiethylaniline in 75 times its weight of dilute sulphuric acid (1:2) and then add 1 mol. of colourless nitric acid, the solution obtained remains clear for days. If, however, we add a trace of sodium nitrite, a separation of the

¹⁾ Prof. JAEGER has examined this compound crystallographically, also the compounds melting at 59° and 76° , for which I again wish to express my thanks. The results are described in *Zeitschr. f. Kristallographie* (1905) XL 129.

dinitroderivative m. p. 95° starts immediately, evidently owing to the catalytic action of the nitrous acid, and on addition of sodium carbonate to the filtrate the red product m. p. 76° is obtained¹⁾. Nitro-diethylaniline is also readily converted into the 1.2.4-dinitroderivative. We may, therefore, conclude that even when we use pure sulphuric acid and colourless nitric acid, traces of nitrous acid are formed in the nitration of diethylaniline, which accelerate the further nitration in the aqueous solution, (after pouring into iced water) particularly if the liquid has not become too diluted.

A judicious choice of the acid-concentration in the liquid obtained, after pouring the nitration mixture into water, might render it possible not to obtain the compound of 1.2.4- and 1.3.4-dinitro-diethylaniline (m. p. 59°), but these components separately, because, as we have noticed, the 1.2.4-compound, m. p. 80°, has somewhat stronger basic properties than the 1.3.4-compound.

A series of experiments now demonstrated that both conditions may be fulfilled, while it was shown also that within definite limits, a quantity of nitric acid larger than that calculated for 2 mols. has a favourable influence.

The following *modus operandi* can now be recommended when large quantities of those new dinitroderivatives have to be procured in a short time.

100 grams of diethylaniline are dissolved in sulphuric acid (D. 1.84) up to 1200 c.c. Of this solution are taken portions of 120 c.c., and after cooling to 0° a solution of 14 grams of nitric acid, (D. 1.49), in 42 grams of sulphuric acid is added, care being taken that the rise of temperature during the nitration does not exceed 5°. After the mixture has been standing for a few hours it is poured with thorough stirring into a mixture of 250 grams of water and 250 grams of ice. The final temperature is then about 30°.

The solution often clear at first soon becomes turbid and deposits the product m. p. 95°. After about an hour the liquid is filtered, and if the filtrate no longer gets turbid to any extent an equal volume of water is added whilst stirring. A yellow product is precipitated which is also collected; this is the 1.2.4-dinitro-diethylaniline melting at 80°, which is sometimes contaminated with a little red 1.3.6-dinitro-diethylaniline, particularly if more water has been used.

¹⁾ If we dissolve m. nitro-diethylaniline in dilute nitric acid (D 1.22) we obtain, after a long time, besides the products melting at 95° and 76°, also a dinitromono-diethylaniline 1.3.6, which is also formed in the oxidation of the product m. p. 76 with chromic acid in acetic acid solution,

On neutralisation of the filtrate with sodium carbonate the 1.3.6-derivative m. p. 76° is obtained.

We now have a complete control over the reaction. If we use more than the amount of acid indicated, we run the risk of obtaining also trinitroderivatives, which impede the purification of the 1-3-4-dinitrodiethylaniline.

When treated with nitric acid D. 1.37, the compound melting at 95° passes readily into trinitroderivatives. For this purpose 2.5 grams are dissolved in about 21 c.c. of that acid at the ordinary temperature. After standing for about half an hour yellow crystals are deposited, with evolution of heat, which are collected immediately. Generally a little nitrous acid is formed.

When carrying out this experiment for the first time, I obtained as main product a substance melting at 158°¹⁾. On repeating the same in order to prepare a larger quantity and using more nitric acid I obtained, however, as main product a compound melting at 175°.

Judging from the analytical results, the first one is a trinitrodiethylaniline and the other a trinitromono-compound.

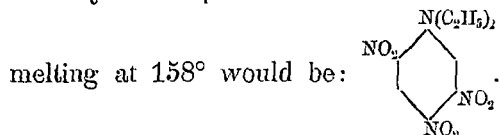
The cause of the different course of the reaction was soon found out: in the second nitration nitric acid had been used prepared by diluting yellow 90%, acid, whereas, in the first one the acid D 1.37 was obtained by diluting colourless acid D 1.40 with water. Owing to the nitrous acid present in the yellow acid, one ethyl-group would have been replaced by hydrogen.

That this explanation is the correct one could be demonstrated by dissolving trinitrodiethylaniline m. p. 158° in moderately strong sulphuric acid, and adding to the solution obtained sodium nitrite. On pouring the mass into water the derivative melting at 175° separated.

This was obtained also by oxidation of the diethyl compound with chromic anhydride in acetic acid solution.

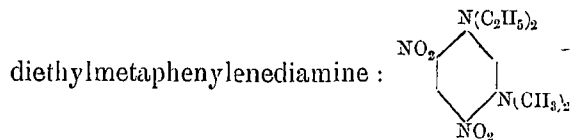
We have succeeded also in determining or deducing the structure of the compounds described.

From analogy with the results of the nitration of dimethylaniline it may be expected that the structure of the trinitro-compound

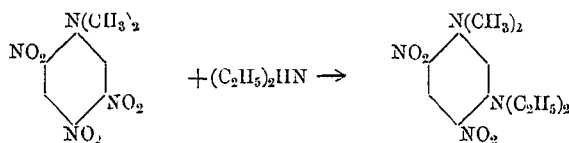


¹⁾ There is also formed a small quantity of an isomeride melting at 117°. By repeated crystallisations from carbontetrachloride the melting point rose to 132°.

If this hypothesis is correct a metaphenylene derivative should be formed by the action of *dimethylamine*, namely 4.6. dinitrodimethyl-



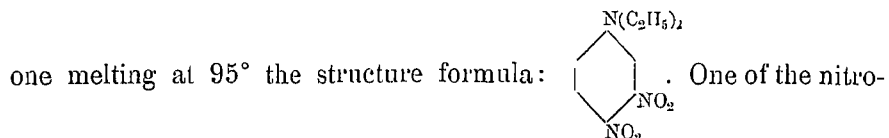
This substance must then, however, be identical with the reaction product of *diethylamine* on the 1.3.4.6. trinitrodimethylaniline m. p. 195° which I prepared previously :



Dr. ULTÉE was kind enough to scrutinise these reactions, and obtained indeed with both an identical product melting at 83°, and which, on analysis, gave the results required for a dinitrodimethyl-diethylphenylenediamine.

A melting point determination of a mixture of the products obtained in both reactions did not show a depression of the melting point.

As regards the two new dinitro-products we must assign to the



groups may be readily substituted by the action of ammonia or amines ¹⁾, which points to the fact that the two nitro-groups are in the *ortho*position in regard to each other. Derivatives of *m*-phenylenediamine are then formed.

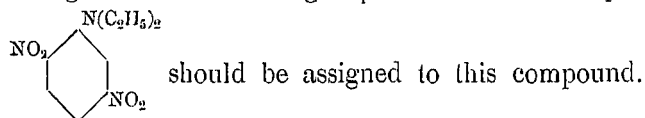
This dinitroderivative is also formed from *m*-nitrodiethylaniline whereas the formation of the 1-3-4-6-trinitroderivative m.p. 158° on subsequent nitration, agrees entirely with that view.

On the other hand, the dinitrodiethylaniline m.p. 76° does not contain any moveable nitro-group so that, taking into consideration that in the nitration with *dilute* nitric acid one nitro-group occupies

¹⁾ With ammonia a compound melting at 135° is formed, which in sulphuric acid solution gives a fine red coloration with traces of nitrous acid.

The description of this compound and of many others obtained in this research will appear in the "Rec."

in regard to the amino-group the *ortho*- or *meta*-position, the structure:



The structure of both these compounds is therefore quite in agreement with those of the nitro-products which I obtained previously from dimethylaniline.

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Chemistry. — “*On sodium alkyl carbonates.*” By Prof. A. P. N. FRANCHIMONT.

(Communicated in the meeting of September 25, 1909).

- Of alkyl carbonates but very little is known. After DUMAS and PÉLIGOT had prepared in 1840 barium-methyl carbonate and potassium-ethyl carbonate, and noticed their property of being decomposed by water into alcohol and a hydrocarbonate, BELSTEIN gave in 1859 a good method for the preparation of sodium-ethyl carbonate. He passed dry carbon dioxide through a solution of sodium ethoxide in absolute alcohol. The sodium salt was obtained in 1868 by GEUTHER from diethyl carbonate and sodium ethoxide, the potassium salt by HABERMANN in 1886 in the electrolysis of anhydrous potassium acetate in absolute alcohol, the barium salt by DESTREM in 1882 by passing dry carbon dioxide into a solution of barium ethoxide in absolute alcohol. Attention was always called to the decomposition of these salts by water. This property is generally believed to be common to all the alkyl carbonates.

Sodium-phenyl carbonate is also decomposed by water into phenol and sodium hydrogen carbonate. Of this, however, it is also known, that it evolves carbon dioxide on warming, and this is not mentioned of the alkyl carbonates. Although, as a rule phenol and primary aliphatic alcohols have but little in common, I thought it would be advisable to make a comparative study of the alkyl carbonates and sodium-phenyl carbonate, particularly since Dr. MOILL VAN CHARANTE had found that the latter salt is decomposed at the ordinary temperature by dry acetone, with evolution of carbon dioxide and formation of phenol.

I, therefore, prepared sodium ethyl carbonate by BELSTEIN'S method, and observed that it is decomposed by water into sodium hydrogen carbonate and alcohol. It is, however, not decomposed by acetone nor when heated to about 180°.