

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents a communication from Prof. A. F. HOLLEMAN: "*The formation of trisubstituted derivatives from di-substituted derivatives of Benzene.*"

(Read February 24, 1900.)

As stated last year (in the Recueil)¹⁾ benzoic acid when nitrated at 0° yields the three possible isomers in the proportion of:

18.5 ortho : 80.2 meta : 1.3 para.

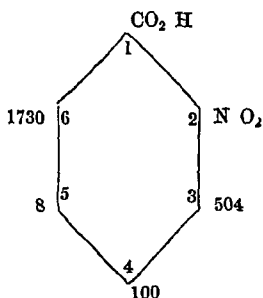
Jointly with Mr. B. R. DE BRUYN, I have now found that on nitrating nitro-benzene at 0°, the three isomers are formed in the proportion of:

6.4 ortho : 93.5 meta : 0.1 para

at all events the amount of the para-compound was less than 0.2.

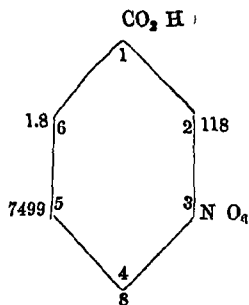
If one now examines, as far as is possible at the present time what relative proportions of the isomeric dinitroacids have been obtained by nitrating the mono-nitrobenzoic acids it appears that the compounds obtained in largest quantity are those for which the products of the above relative numbers are greatest.

In the nitration of *o*-nitrobenzoic acid the products for the still unoccupied places in the benzene nucleus are given in the formula below:



The highest figure is, therefore, in 6; acid in fact, the acid 1 : 2 : 6 is the chief product.

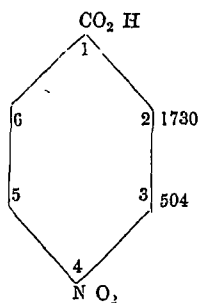
In the nitration of *m*-nitrobenzoic acid the products for the still unoccupied places are:



¹⁾ Proceedings 1899.

Looking at the great value of the product in 5, it is to be expected that the acid 1 : 3 : 5 will be the chief product, while the others will only be obtained in minute quantity. In fact the 1. 3. 5. acid is the only dinitro-acid as yet obtained.

In the nitration of p-nitrobenzoic acid the said products are :



HÜBNER and STROMEYER first obtained the 1. 2. 4 acid by this process and later on CLAUSS and HALBERSTADT working on a larger quantity of material isolated the 1, 3, 4 acid which is no doubt formed to a smaller extent.

In the nitration of chloro-benzene at 0° a semi-solid crystalline mass is obtained; if care is taken to collect together all the products formed in the reaction this mass after being fused solidifies at $58^{\circ}.9$. It is known that ortho- and para-chloro-nitrobenzene are formed in this nitration; whether the meta compound is also formed in small quantities, remains to be seen; at all events its presence in the nitrated mass is not stated in the literature. Since p-chloronitrobenzene melts at 82° and the ortho compound at 32° , it is evident from the solidifying point that the para compound strongly predominates, so that the relation will be: ortho little, meta traces, para very much. This, and the relation in which the three nitrobenzoic acids are formed, proves that in the nitration of ortho-chloro-benzoic acid, the acid 1 : 2 : 5 ($\text{CO}_2 \text{H} = 1$) ought to be formed in large predominating quantity together with small quantities of the acid 1 : 2 : 3; in the nitration of m-chlorobenzoic acid the acid 1 : 3 : 6 should be chiefly formed, the acid 1 : 3 : 2 occurring only in small and the other isomers in very trifling quantities; in the nitration of p-chlorobenzoic acid the acid 1 : 4 : 3 should be almost exclusively formed. This quite confirms the recent research of MONTAGNE ¹⁾.

In the literature, nothing much is said about the relative quantities of the isomers formed in the nitration of benzene derivatives; as a rule the writers confine themselves to such statements as "chief product", or "much" of this "little" of the other isomer. With the aid of such statements it is possible to ascertain whether the above rule is of general application. This seems indeed to be the case.

¹⁾ Dissertation, Leiden 1899.

This does not only apply to nitrations, but also in cases of the introduction of bromine and chlorine. I have met with many instances in which it was possible to predict which of the possible isomers would be the chief product.

The question now arises whether the relative quantities in which the isomeric trisubstituted derivatives are generated corresponds to the relation shown by the above mentioned products, or in other words whether the phenomena observed in the formation of trisubstituted derivatives may be explained quantitatively in this manner. Researches in this direction are in progress in my laboratory.

Chemistry. — Prof. H. W. BAKHUIS ROOZEBOOM presents in the name of Dr. C. VAN EYK, of Breda, the following paper: "*Formation and transformation of the double salt of Silvernitrate and Thalliumnitrate.*"

(Read February 24, 1900.)

1. Silvernitrate and thalliumnitrate are rhombic at the ordinary temperature; at 159° and 142° respectively, they undergo a structural change and become rhombohedral. No records exist as to the formation of mixed crystals. RETGERS (Zeit. phys. Chem. 5, 451) mentions the existence of a double salt without mentioning however whether he has obtained this from the aqueous solution or from the fused mixture. The object of this investigation was to see what kind of crystals are deposited from fused mixtures of various concentrations (varying from 100 per cent of silvernitrate to 100 per cent of thalliumnitrate) and to study the possible changes which these crystals undergo at lower temperatures.

2. Determination of the meltingpoint line.

The solidifying points of mixtures of $TlNO_3$ and $AgNO_3$ (varying from 0 to 100 percent) were observed and the course of the solidification was watched.

It was found that the meltingpoint line, starting from either $TlNO_3$ or $AgNO_3$, took a descending course with a short double salt line situated between the two branches.

Mol. pCt. $AgNO_3$	Commencement of Solidification.
100	208°.5
94	196°
90	188°.5
87	183°