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CONTENTS: "On pentanitrophenylmethylnitramine and tetra- and pentanitrophenol". By Dr. J. J. BLANKSMA. (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 437. — "On the development of the entoderm, of KUPFFER's vesicle of the mesoderm of the head and of the infundibulum in Muraenoids". By Dr. J. BOEKE (Communicated by Prof. T. PLACE), p. 442. — "Ternary systems" (I). By Prof. J. D. VAN DER WAALS, p. 448. — "Examination of specimens of sand from borings done at the works of the outer harbour at Scheveningen". By J. A. GRUTTERINK. (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK), p. 464, (with one plate). — "The relation between the brightness of a luminous point and the moments at which we observe its sudden appearance or disappearance". By Prof. H. G. VAN DE SANDE BAKHUYZEN, p. 465. — "A new law concerning the relation of stimulus and effect" (III). By Prof. J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. C. WINKLER), p. 469. — "The physiological Bacteriology of the intestinal canal (2nd abridged paper. The bacteriological relations in the intestinal canal of the rabbit)". By Dr. ALEX KLEIN. (Communicated by Prof. T. PLACE), p. 477. — "On the motion of variable systems". By Prof. J. CARDINAAL, p. 489. — "On the measurement of very low temperatures. IV. Comparison of the platinum thermometer with the hydrogen thermometer". By B. MELLINK, (Communicated by Prof. H. KAMERLINGH ONNES), p. 495, (with one plate). — "Factorisation of large numbers" (III). By F. J. VAES. (Communicated by Prof. P. H. SCHOUTE), p. 501.

The following papers were read:

Chemistry. — "On pentanitrophenylmethylnitramine and tetra- and pentanitrophenol." By Dr. J. J. BLANKSMA. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of December 28, 1901).

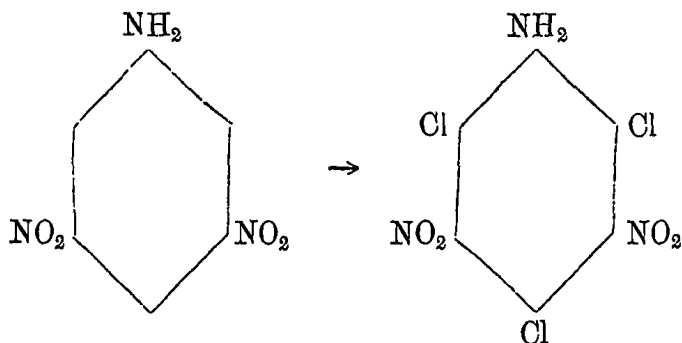
It has been known for a long time that aniline and phenol are very readily converted into trihalogen substitutionproducts by treatment with chlorine- and bromine-water and also that trinitrophenol (picric acid) may be readily obtained from phenol by the action of

nitric acid. The three halogen atoms and the three nitro-groups then always jointly occupy the three free meta-places and, therefore, take up in regard to NH_2 and OH the ortho- and para-positions, but never the two remaining meta-places. It is a remarkable fact that these substitutions take place so much more readily than they do in the case of other benzene derivatives.

Some time ago LANGER¹⁾ has considerably supplemented some existing observations by a systematic investigation of aniline-derivatives and demonstrated that even if one or both meta-places are occupied in regard to NH_2 , the substitution of the three remaining places by halogen proceeds quite as readily as in the case of free aniline.

No similar systematic investigation has been made in the case of phenol; on consulting the literature we find that a number of observations made at the halogenation and nitration of some substituted phenols point to the existence of a similar regularity.

In order to obtain additional confirmatory evidence in the case of the derivatives of aniline and phenol Dr. BLANKSMA has in the first place investigated the behaviour of symmetric dinitro-aniline towards halogens. Trichloro- and tribromodinitro-aniline were very readily formed :

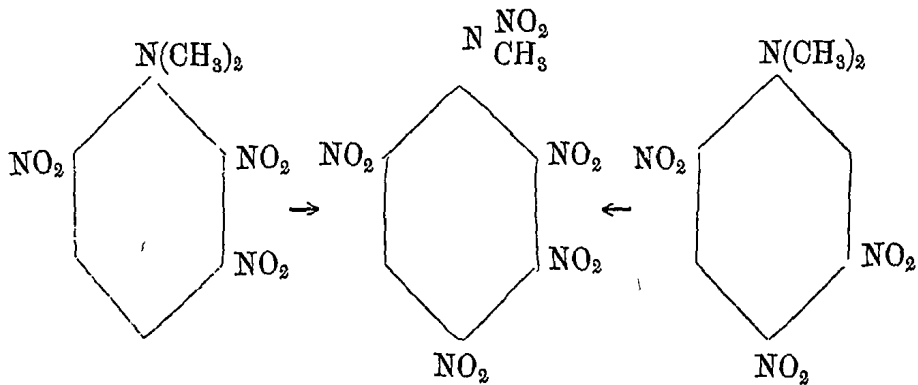


It further appeared that symmetric dinitrophenol was readily converted by bromine water into the already known but differently obtained tribromodinitrophenol; in the case of *m*-nitrophenol the conversion into a tribromoderivative had already been proved.

Dr. BLANKSMA secondly put the question how nitric acid will behave towards nitrated meta-derivatives of aniline and phenol. It is known that by direct nitration no more than three nitro-groups can be introduced into benzene and its derivatives; even picric acid

¹⁾ B. 15. 1061. 1328.

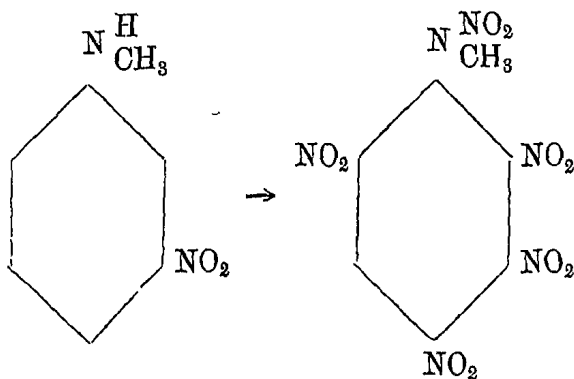
is not capable of taking up a fourth nitro-group. The only exception as yet known is tetranitrophenylmethylnitramine discovered by VAN ROMBURGH in 1889 and obtained by the action of fuming nitric acid on two different trinitrophenyldimethylanilines. ¹⁾



VAN ROMBURGH has proved that the nitro-group placed between two other nitro-groups is very mobile and readily liable to substitution (by OH, OCH₃, etc.)

Of late years, NIETZKI has prepared a tetranitrophenol and a tetranitrobenzene, partly in an indirect way, by oxidation of oximes; the first one by oxidation of a trioxime (in this case a NO₂-group also enters), the second one by oxidation of a dinitro-dinitrosobenzene. ²⁾

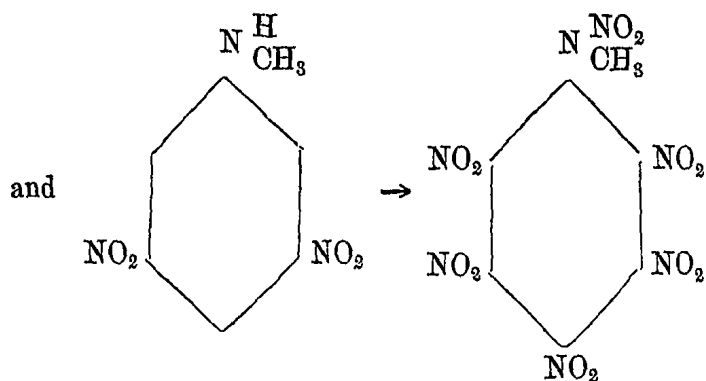
Dr. BLANKSMA now subjected *m.* nitro- and *m.m.* dinitromethylaniline to the action of concentrated nitric acid and proved that the first one yielded VAN ROMBURGH's tetranitrophenylmethylnitramine but that the second one gave the corresponding pentanitroderivative:



¹⁾ Recueil 8. 973. It will be seen that the formation of the tetranitroproduct is accompanied by a substitution of one of the CH₃-groups by NO₂.

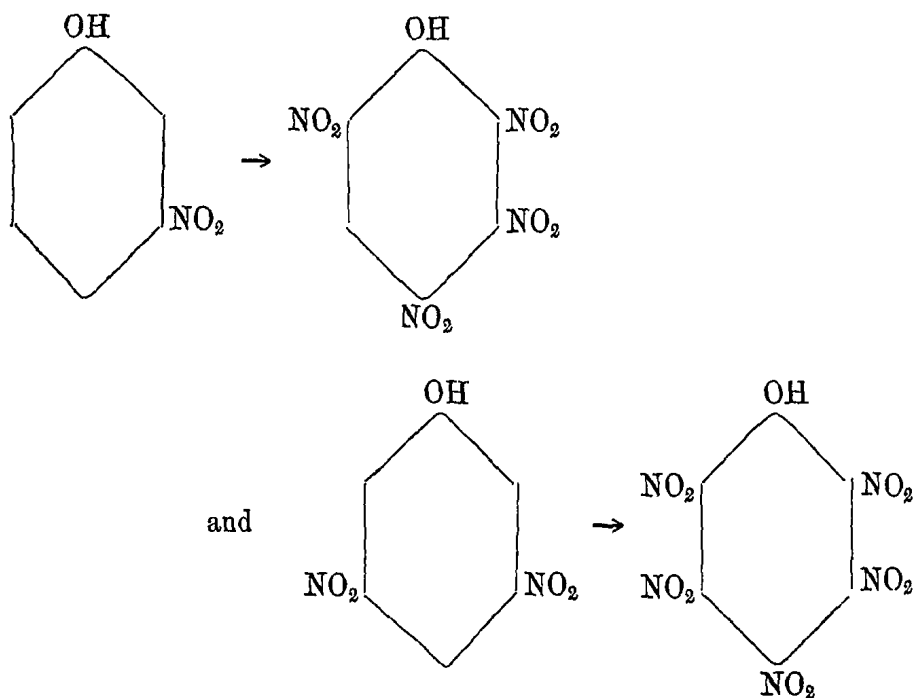
²⁾ B. 30. 181, 34. 55.

(-440)



The last substance is a yellow, properly crystallised substance (m. p. 132°) which explodes when heated on platinum foil. Its properties will be further investigated.

Dr. BLANKSMA next investigated the behaviour of *m.* nitro- and *m.m.* dinitrophenol towards concentrated nitric acid. The result obtained thoroughly agreed with the facts just mentioned as there had been an abundant formation of tetra- and pentanitrophenol, melting respectively at 140° and 190° .



When preparing these two substances Dr. BLANKSMA confirmed his previous idea that a precaution should be taken, which other chemists (BANTLIN, HENRIQUES), having occupied themselves with

the study of the behaviour of nitrated phenols towards nitric acid, have disregarded. The nitration must be done with nitric and sulphuric acids and not by boiling with nitric acid alone; the crystalline mass must then be drained and recrystallised from chloroform. If it is boiled with water, one, respectively two, of the nitrogroups are replaced by hydroxyl and instead of tetra-, respectively pentanitrophenol, trinitroresorcinol and trinitrochloroglucinol are obtained. The appearance of trinitroresorcinol so often noticed during the nitration of phenolic bodies has now been explained by BLANKSMA and the previous opinion expressed by BANTLIN and by VAN ROMBURGH that the formation of trinitroresorcinol from ordinary phenol derivatives is due to the intermediate formation of tetranitrophenol has now been confirmed by experiment.

NIETZKI's tetranitrophenol is evidently not identical with the one described above.

Dr. BLANKSMA has also proved that one nitro-group in tetranitrophenol and two nitro-groups in pentanitrophenol may be readily replaced by OH, OCH₃, OC₂H₅, NH₂ and NHC₆H₅.

In getting the above mentioned results (the particulars of which will be published in the „Recueil”) Dr. BLANKSMA has followed up the same idea which in the case of aniline derivatives had already been successfully tried with an extensive material and which after his experiments may now be considered to apply also to phenol. Briefly summarising, the matter amounts to this (when other unmentioned facts are also taken into consideration): that phenol and aniline (methyl aniline etc.) are very readily halogenated, nitrated and sulphonated, much more readily than benzene and the homologues of other benzene derivatives and further that the presence of one atom or group occupying the meta-position in regard to OH or NH₂ (NH CH₃) does not offer a sterical obstacle, whilst the entering atoms or groups exclusively select the para-place and the two ortho-places.

If we want to explain these phenomena we must begin by assuming (which has already been proved in several other cases) that in the first stage of the action intermediate products are formed which contain the group to be introduced attached to the nitrogen or the oxygen and that these products by intramolecular change are more or less readily converted into the direct benzene derivatives.

If the various observations which have already been made in this matter are collected and arranged, 15 to 20 different cases may be

distinguished, many of which may be illustrated by a great number of special examples and which all amount to this: that an atom or a group linked to N or O shows an inclination to pass from this atom to the nucleus and then always (or nearly so) changes place with the H atoms occupying para- and ortho-places. Whether the meta-places are occupied or not does not affect this isomerisation process.

If we now limit ourselves to nitric acid it may be observed that the idea that in the nitration of aniline derivatives (best in the case of those containing NHX instead of NH₂) the nitro-group should always combine first with the nitrogen forming nitramines, before passing on to the nucleus, has already been suggested by BAMBERGER and confirmed by experiment. After Dr. BLANKSMA's experiments we arrive at a similar conclusion as regards the formation of nitrated phenols. This is confirmed by another observation of Dr. BLANKSMA that if the phenol-hydrogen of symmetric dinitrophenol is replaced by methyl, the ready bromination or nitration is no longer possible. Efforts will be made to prepare the as yet unknown nitrates of the phenols and, if successful, their behaviour will be closely studied.

Physiology. — "*On the development of the entoderm, of KUPFFER's vesicle, of the mesoderm of the head and of the infundibulum in Muraenoids*" (preliminary paper), by Dr. J. BOEKE. (Communicated by Prof. T. PLACE).

(Communicated in the meeting of January 25, 1902).

In his well-known paper on pelagic eggs of the Gulf of Naples, RAFFAELE described five species of big pelagic eggs, which were found in the plankton of the Gulf during the months of August and September, which he suggested that might belong to different members of the Muraenoid group.

In 1893 and 1896 GRASSI and CALANDRUCCIO confirmed this theory, but they did not study the eggs closer.

During the summer of 1900 and 1901 I had the good fortune to secure several hundreds of these eggs during a stay at the Stazione Zoologica at Naples, and was enabled to study all the stages of development of the embryos until the critical period. The description and suggestion of RAFFAELE I found to be perfectly true, and moreover I collected three other species of eggs, which although undoubtedly belonging to Muraenoid species, could be distinguished sharply from the other five spp., described by RAFFAELE. From these they differed in the dimensions of the yolk-sphere and the perivitelline space, in