Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"2.3.4.6-Tetranitro-phenylmethyl- and ethylnitramine."*
By Prof. van Romburgh and Dr. J. H. Schepers.

(Communicated in the meeting of September 27, 1913).

Many years ago appeared a communication[1]) from one of us
(v. R.) on tetranitrophenylmethylnitramine. This substance was the
first aromatic nitramine with four nitro-groups in the nucleus, three
of which were placed vicinally, causing a peculiar mobility of one
of those groups. Thus it was shown that water, alcohol and amines
readily react with it at the ordinary or at a slightly elevated tempera-
ture. As, since the publication of the above paper on this nitramine,
nothing more has been published about it, save an occasional
reference, it did not seem out of place to continue the research in
different directions.

In the first place attempts have been made to improve the method
of preparing the nitramine and we have been entirely successful by
taking advantage of the fact that the *tetra*nitrophenylmethylnitramine
is *insoluble* in concentrated sulphuric acid, whereas the *tri*nitro-compound
is *soluble* therein. After a number of experiments, undertaken with
the object of finding the most favourable conditions for obtaining the
largest possible yield, we can recommend the following method.

10 grams of dimethylaniline are dissolved in 200 grams of strong
sulphuric acid. When cold, a cooled mixture of 60 grams of sulphuric
and 12 grams of nitric acid (D 1.51) is added drop by drop with
vigorous stirring, the whole being cooled in ice and salt so as to
keep the temperature at —2°. Particularly at first the temperature
rises strongly after each drop added. The liquid soon turns an orange-
like colour. After the first half of the acid has been added, the
remainder may be added more freely as there will be no further rise
in temperature. After standing for half an hour in the ice and salt
mixture, 100 c.c. of nitric acid (D. 1.51) are added. The liquid is
then cooled for one day in ice or water and then left at rest for
some days at the ordinary temperature.

After one or two days the liquid is congealed to a thick mass of
crystals. A continuous evolution of carbon dioxide[2]) takes place, not
accompanied, however, by brown vapours, because the nitrous acid
formed combines with the sulphuric acid. After the lapse of a week
the crystals are collected, by filtering, on glass wool and washed

1) Rec. **8**, 282 (1889).
2) It contains traces of carbon monoxide

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with strong sulphuric acid in order to remove the trinitrophenyl-methylnitramine formed as a bye-product. The mother liquor was poured into ice-water and yielded 2.4.6-trinitrophenylmethylnitramine.

The drained crystals of tetranitrophenylmethylnitramine are washed with gradually more diluted sulphuric acid and then with water until the filtrate gives no reaction with barium chloride. This product, having a melting point of 140°—145°, is pure enough for most purposes, but it may be further purified by dissolving in nitric acid (D 1.5) adding a little strong sulphuric acid, so as to protect the nitro-group in position 3, heating on a water-bath to 70° and, when cold, precipitating with strong sulphuric acid. After a day or two the mass is collected on glass wool, washed with sulphuric acid and treated further as described. The compound is now perfectly pure and melts at 146—147°. The yield mounted to 18 grams.

From the mother liquor were obtained 6 grams of the *trinitro*-compound. After being dissolved in nitric acid and heated to 70°, the solution was allowed to cool and then poured into ice water. The product then melted at 127°.

An experiment made with absolute nitric acid gave no higher yield of the *tetra*-nitro-compound. Considering the conditions under which we operated, sulphuric acid, which according to REVERDIN [1] can convert nitramines into nitrosamines will not be able to exert an unfavourable influence.

Interaction of alcohols on tetranitrophenylmethylnitramine.

The fact mentioned previously that tetranitrophenylmethylnitramine is attacked by boiling methyl and ethyl alcohol and gives an odour of nitrous ethers, invited a further research. In the first place it might be possible that in addition to nitrous esters nitrohydrocarbons were formed and further it was thought desirable to extend the reaction, besides to a few more primary, also to secondary and tertiary alcohols. As will appear soon, propyl alcohol, *iso*butyl alcohol and fermentation amyl alcohol form esters, whereas allyl alcohol benzyl alcohol, *iso*propyl alcohol and secondary butyl alcohol, also tertiary amyl alcohol, even when dried with the utmost precautions, do not give the esters, but only the trinitromethylnitraminophenol itself, besides the nitrite corresponding with the alcohol, except in the case of benzyl alcohol.

Methyl alcohol acts already at the ordinary temperature on the nitramine. A gas is evolved that can be collected over a strong

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[1] Journ. f. pract. Ch. 81, 177 (1910); 83, 161 (1911); Diss. LIEBL, Genève 1913.

solution of potassium hydroxide and may be readily identified as methyl nitrite. The presence of nitromethane *cannot* be demonstrated amongst the reaction products.

In an experiment made with 1 gram of nitramine and 5 c.c. of methyl alcohol 60.6 c.c. of methyl nitrite (reduced to 0° and 760 mm.) were collected in 4 hours (Theory 67.5 cc).

The methyl ester of trinitromethylnitraminophenol formed in the reaction has been described previously (l.c.).

Interaction of ethyl alcohol likewise gives ethyl nitrite without formation of nitroethane. The ethyl ester of phenol has already been described.

With dry propyl alcohol is formed the propyl ester, melting at 118°, also propyl nitrite boiling at 57°. Nitropropane is not formed.

*Iso*butyl alcohol on heating with the nitramine (in the water-bath) gives the *iso*butyl ester melting at 95° and *iso*butyl nitrite boiling at 65°.

Fermentation amyl alcohol likewise yielded amyl nitrite and an amyl ester melting at 83°. With this alcohol the mass was coloured darker than with the other alcohols. It also appeared that more free trinitromethylnitraminophenol had formed than is found in the case of the other alcohols where it always occurs in small quantities.

Allyl alcohol, although dried with the greatest care, gave allyl nitrite, but no weighable quantities of ester. Only free phenol was formed:

Benzyl alcohol, which acted violently, gave products containing benzaldehyde but no benzyl ester of the phenol, only the latter itself.

Secondary propyl alcohol and sec. butyl alcohol do not yield esters, but the free trinitromethylnitraminophenol is formed, also the nitrites of those alcohols

Tertiary amyl alcohol (amylene hydrate) reacts in an analogous manner. There is formed in addition to some nitrite also amylene. The main product of the reaction consists of phenol.

In all the above reactions the NO_2-group of the nitramine is substituted in the position 3, either by the group OAlk, or by the group OH.

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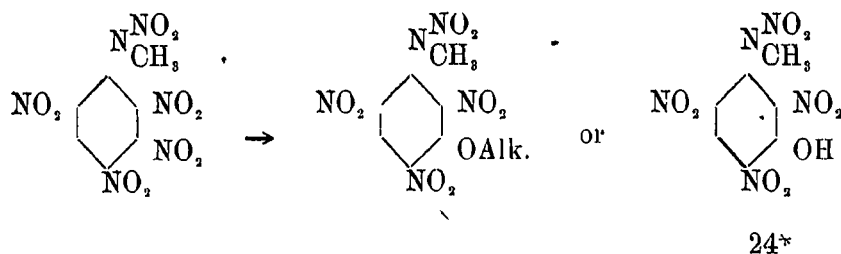
Interaction of ammonia and amines.

As appears from the often-quoted paper, the interaction of methylamine, which is dependent on the conditions prevailing during the experiment gives rise to different results. Not merely one nitro-group of the nucleus may be substituted, but in addition also the methylnitraminogroup. It now seemed not without interest to repeat these reactions not only with ammonia, but also with some other amines, aliphatic as well as aromatic ones. Before stating the results obtained it may be mentioned briefly what is already known as to the interaction of ammonia and amines on the alkylnitramino-group of aromatic nitramines.

Picrylmethylnitramine, according to v. ROMBURGH and MAURENBRECHER[1]) reacts with ammonia, with aliphatic as well as with aromatic amines — such as aniline, paratoluidine etc. — in such a manner that in addition to picramide (substituted picramide respectively) methyl nitramine is formed.

In an analogous manner, using paratoluidine, both methylnitramino-groups in 2.4.6-trinitrometaphenylenedimethylnitramine become substituted.

SOMMER[2]) allowed ammonia and different amines — aliphatic as well as aromatic — to act on 2.3.6-trinitro 4 tolylmethylnitramine which caused the nitro-group in the position 3 to be substituted. Methylamine also reacted on the nitramino-group. With ammonia, methyl- and dimethylamine it was necessary to work at 100° under pressure as no reaction took place at the ordinary temperature. When we allowed ammonia and different amines to react on the tetranitrophenylmethylnitramine we obtained reactions analogous to the action of methylamine. Ammonia, however, reacted slower than the amines.

An exception was noticed in the case of di*iso*propylamine, under the influence of which the nitro-group in the position 3 is replaced by OH. It then yields with the phenol the di*iso*propylamine salt.

The aromatic amines, aniline and paratoluidine act on the movable nitro-group only, even in heating.

Piperidine also acted abnormally, the piperidine salt of tetranitromethylnitraminophenol was formed.

Highly peculiar was the interaction of pyridine and chinoline which, although quite dry, gave salts of the trinitromethylnitraminophenol while simultaneously an evolution of gas took place.

[1]) Proc Roy Akad. Amst. IX, 704 (1907)
[2]) J f Pr. Ch. 67, 513 (1903)

Interaction of ammonia. If gaseous ammonia is passed over the nitramine phenomena of incandescence are noticed.

Aqueous ammonia (0.890—0.903) when acting for a short time at a slightly elevated temperature gives 2.4,6-trinitroaminophenyl-methylnitramine melting at 181°.5. Hence, only one nitro-group in the nucleus has been substituted.

On prolonged interaction (a few days) of a nearly saturated ammonia solution the well-known 2.4.6 trinitro-m-phenylenediamine is obtained.

Interaction of ethylamine. This amine behaves quite analogously to methylamine, with which the reaction has been carried out previously (loc. cit.). A $16°/_0$ solution of methylamine in water (10 c.c.) gives with the nitramine (2 grams) after half an hour a good yield of 2.4.6-trinitroethylaminophenylmethylnitramine m.p. 131°.5.

Heated for a short time with a $33°/_0$ amine solution (12 c.c) and then left at rest for two days, the nitramine (2 grams) gives the 2.4.6-trinitrodiethylaminobenzene previously described by BLANKSMA [1]).

Interaction of dimethylamine. If 3 grams of nitramine are dissolved in 20 c.c. of a $25°/_0$ dimethylamine solution the 2.4.6-trinitrodimethyl-aminophenylmethylnitramine m.p. 177° is formed.

If the reaction mixture is heated for 3 hours at 60°—70° and then left at rest for another 18 hours, the nitro-group in the nucleus as well as the methylnitramino-group are replaced by the dimethyl-amino-group. The resulting 2.4.6-trinitrotetramethyl-m.phenylenedia-mine melts at 141°.

Interaction of diisopropylamine. We did not succeed in replacing the movable nitrogroup by the diisopropylamino-group. A diisopro-pylamine salt of 2.4.6-trinitro-methylnitraminophenol m.p. 147°.5 was formed.

Interaction of aniline. A solution of the nitramine in benzene gives with aniline a dark red substance melting at 114°, which proved to be a compound of aniline with the yellow 2.4.6-trinitro-3-phenylamino-phenylmethylnitramine which melts at 183°. We did not succeed in substituting the methylnitramino-group also.

Interaction of p-toluidine causes the formation of the analogous tolyl compound ,which is coloured red, melts at 141° and formed no compound with p-toluidine.

Interaction of piperidine. This secondary amine behaves analogous to diisopropylamine. The movable nitro-group is substituted by OH and we obtain the pyridine salt of the phenol formed as a pale

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[1]) Rec. **21**, 325 (1902).

yellow substance melting at 172°. It is, however, remarkable that this salt should form even when the piperidine used has been dried for a long time over potassium hydroxyde and when the nitramine is dissolved in toluene, which has been rendered quite anhydrous by means of phosphorus pentoxyde. An evolution of gas could not be observed in the reaction, but an odour resembling that of nitroso-piperidine was noticed.

Interaction of pyridine. In this reaction one of us (v. R.) had obtained many years ago a compound melting at 145°, the analysis of which gave results pointing to the formation of a pyridine salt of trinitromethylnitraminophenol. On repeating the reaction under very varying conditions and carefully excluding even traces of moisture the same compound was always obtained (not always especially pure, however). In this case, however, an evolution of gas takes place. If, for instance, to 2 grams of nitramine dissolved in 60 grams of absolutely dry toluene were added drop by drop 5 grams of dry pyridine and the whole heated at 100° 24.1 c.c. of nitrogen and 43.3 c.c. of nitric oxyde (reduced to 0° and 760 mm.) were collected. The course of the reaction has not as yet been elucidated.

Interaction of chinoline. This takes place analogous to that of pyridine. The chinoline salt of the phenol formed, exhibited no sharp melting point (173° — 190°). Here also an evolution of gas takes place. The gas evolved is a mixture of nitrogen and nitric oxide.

2.4.6. *Trinitro-methylnitraminophenol.*

As is well known, the nitramine passes on boiling with water into this phenol with formation of nitrous acid. This conversion proceeds very perceptibly even at the ordinary temperature. After 0.286 gram of nitramine had been shaken with 1080 grams of water at 11° for 24 hours, 0.197 gram appeared to have been converted.

This phenol is a powerful acid as has been shown by the measurements carried out by Mr. J. SMIT in the VAN 'T HOFF-Laboratory where the velocity of decomposition of diazoacetic ester [1]) by means of $N/_{1300}$ nitric acid was compared with that of a $N/_{1500}$ solution of trinitromethylnitraminophenol.

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[1]) BREDIG, Curtius-Festschrift 1907, 1.
   B. **40**, 4015 (1907).
   W. FRAENKEL, Z. f. Ph. Ch. **60**, 202 (1907).
   MUMM, Z. f. Ph. Ch. **62**, 589 (1908).
   LACHS, Z. f Ph. Ch. **73**, 291 (1910).

Phenol $^1/_{1500}$ N.		Nitric acid $^1/_{1300}$ N.
I K	II K	K
0.0261	0.0243	0.0334
0.0257	0.0236	0.0334
0.0266	0.0236	0.0325
0.0264	0.0233	0.0327
0.0265	0.0237	0.0328
0.0257	0.0236	0.0323

The . arrangement of the experiment was similar to the method used by WALTON[2]) for measuring the reaction between hydrogen peroxyde and iodine-ions.

From the phenol were also prepared, besides the salts mentioned above: the compound with ammonia m.p. 108°; with ethylamine m.p. 179°; with dimethylamine m.p. 183°.·

2.3.4.6-Tetranitrophenylethylnitramine.

For the preparation of this compound could not be applied the direct nitration of diethylaniline because the method of separation with sulphuric acid proved a failure here.

Therefore, 3.4-dinitrodiethylaniline (m.p. 95°) was dissolved, with cooling, in 20 parts of nitric acid (D 1.49). Three parts of sulphuric acid (D 1.84) are then added and after waiting for an hour the whole is heated for a moment to 70°, cooled rapidly and then 12 parts of sulphuric acid are poured in. The mass is poured out into ice-water, the separated yellow, viscid mass is dissolved in nitric acid (D 1.49) with addition of sulphuric acid. After some time almost colourless crystals of the tetranitrophenylethylnitramine m.p. 96° are deposited. The yield is not very favourable. (From 2.8 grams was obtained 1.9 grams and on another occasion 2 grams yielded 1.5 grams).

A better result was attained by treating the 3.4-dinitrodiethylaniline (2 grams) first with 30 c.c. of nitric acid (D. 1.33) and 1 gram of sodium nitrite : the product formed was then dissolved in nitric acid (D 1.49) with addition of sulphuric acid.

The 2.3.4.6-tetranitrophenylethylnitramine dissolves readily in benzene and in toluene ; on heating with bases ethylamine is evolved. Alcohols readily react with it, particularly on heating, with formation of nitrous esters. Amines also react with it. For instance, ethyl-

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[2]) Z. f. Ph. Ch. **47**, 186 (1904).

amine, on heating at 50°—60° in a sealed tube, yielded 2.4.6-trinitro-1.3-di-ethylaminobenzol, m p. 142°.

On boiling with water is formed the 2 4.6-trinitro-ethylnitramino-phenol m.p. 105° described previously by BLANKSMA [1]. We tried to substitute the alkylnitramino-group in this compound, and in the corresponding methyl derivative, by the ethyl-amino-group with the aid of ethylamine. In this, however, we were till now not successful: the OH-group appears to impede the substitution of the nitramino-group in this case.

All the new compounds obtained and mentioned here have been analysed and will be described more in detail in the Rec. des Trav. Chim. des Pays-Bas.

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Chemistry. — *"Contribution to the knowledge of the amides."* By Prof. FRANCHIMONT.

(Communicated in the meeting of September 27, 1913).

Some years ago Dr MOLL VAN CHARANTE had already prepared a substance which, on account of its mode of formation and the results of the analysis, he pronounced to be the diamide of sulphon*iso*butyric acid and which he has lately described under that name [2]. This substance which endures heating to a temperature over 300° without melting and which decomposes at ± 340°, does not react with carbonyl-chloride, not even at 300° and, as appeared afterwards, not even with oxalylchloride. This strange behaviour, looking at the results obtained by BORNWATER in the action of oxalylchloride on amides, and also the fact that benzenesulphonamide *does* react with oxalyl-chloride, although with formation of an oxalylderivative, induced me to investigate the behaviour, in this respect, of the amides of *iso*butyric acid and ethanesulphonic acid which are more closely connected with sulphon*iso*butyric acid than the benzenesulpho-namide.

On adding *iso*butyramide to oxalylchloride in benzene a strong evolution of heat took place immediately and a stream of hydrogen chloride was evolved while a solid substance was being deposited. After warming for a few hours, the evolution of gas ceased and everything had again dissolved. The following day, after cooling, a

[1] Rec. 21, 260 (1902).
[2] Rec. d. tr. ch. d. P. B. T XXXII. p. 90.