

*Citation:*

A.P.N. Franchimont, A new class of nitramines, in:  
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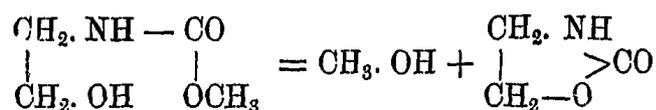
everything had been very carefully organised, through the management of the East-Indian committee and by the observers themselves who, notwithstanding the short time at their disposal, had succeeded in properly mounting and adjusting all the instruments, while, thanks to the collaboration of some officers of the army and the assistance of the officers and the men of H. M. S. Sumatra sent for the purpose to the road of Painan, there was a sufficient number of observers and assistants for each instrument.

**Chemistry.** — Professor A. P. N. FRANCHIMONT presents a communication on “*A new class of nitramines*”.

On January 26 1895 I had the honour of communicating to the Academy that, acting under my directions, Mr. VAN BREUKELEVEEN had prepared a representative of a then unknown class of urea derivatives, *ureo alcohols* or *ureols*. The object was to subject the compound (*ureo-ethanol*) to nitration and in this way to prepare a nitramino-alcohol; this, however, did not succeed as ureo-ethanol in contact with  $\text{NO}_3\text{H}$  at the ordinary temperature at once evolves  $\text{N}_2\text{O}$  and  $\text{CO}_2$ .

At that time only nitraminohydrocarbons, nitramides and derivatives of nitramino acids were known. A free nitramino acid, nitramino-acetic acid has been since prepared by HANTZSCH and METCALF. As the study of nitramino-alcohols and nitramino-aldehydes still interests me very much I have now tried, jointly with Dr. LUBLIN, to prepare a *nitramino-alcohol* in a different way and this has given us the desired result.

As on the previous occasion, we again started from amino-ethanol which was first converted by means of methyl chloro-formate into methyl oxethylamino-formate. This substance is, at the ordinary temperature, a colourless liquid which cannot be submitted to distillation but is decomposed by the action of heat even in vacuo into methyl alcohol and the internal ester of oxethylaminoformic acid, which crystallises beautifully from benzene, although but little soluble therein.



It is a remarkable fact that the ethyl ester of oxethylamino-

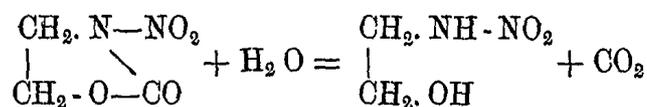
formic acid, which we have also prepared and obtained as a liquid, does not when heated, yield ethyl alcohol or ethylene and water but distils unaltered, at least in vacuo.

The above mentioned internal ester of oxethylaminoformic acid had been previously obtained by GABRIEL in a different and less expensive manner which we have afterwards imitated.

Viewed in connection with oxazol, we may call this heterocyclic compound:  $\mu$  ketotetrahydro-oxazol,  $\mu$  keto-oxazolidin or tetrahydro-oxazolon.

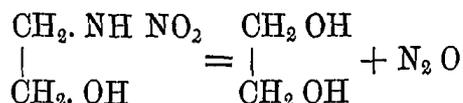
It proved to be a better starting point for the preparation of nitramino-alcohol than the methyl ester. Poured into real nitric acid it at once yields quantitatively a mononitroderivative which is not further acted upon by nitric acid, so that it may be evaporated with four times its weight of this acid to dryness on the waterbath without suffering any decomposition; the same has been previously stated for hydantoine and its derivatives. This mononitroderivative is more soluble in hot benzene than the internal ester and crystallises on cooling in beautiful, long, lustrous needles which melt at  $111^{\circ}$ .

This nitrocompound in which the nitro-group is undoubtedly linked to the nitrogen yields on boiling with water quantitatively  $\text{CO}_2$  and *nitramino-ethanol* (oxethylnitramine) the desired nitramino-alcohol, according to the equation:



The product which remains dissolved in the water is obtained on evaporation as a syrupy liquid. On boiling the aqueous solution with mercuric oxide a mercury salt was prepared which is but very sparingly soluble in cold water and crystallises in fine needles. A silver salt was obtained in beautiful, nacreous plates by heating the aqueous solution with silver carbonate. Both salts have been analysed. On heating they explode, the mercury salt more violently than the silver compound. The mercury salt is not decomposed by boiling with water but the silver salt is reduced. We have prepared both these salts because there is then no danger that the alcoholic OH-group will yield a metallic derivative. Nitramino-ethanol does not produce at once a precipitate in a solution of silver nitrate as is the case with methylnitramine and also ethylnitramine, thence the preparation of the silver salt with silver carbonate.

Boiled with dilute sulphuric acid of, say, 5 percent strength, nitramino-ethanol yields quantitatively  $N_2O$  according to the equation:

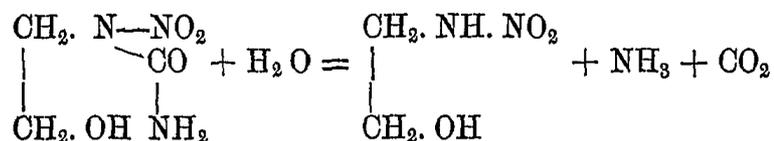


Presumably there is also formed some glycol, but at all events no ethylene, no ethylene oxide or aldehyde; but after removal of the sulphuric acid the solution gives with copper sulphate and potassium hydroxide a dark blue liquid like the polyhydric alcohols.

We are now engaged in preparing the nearest homologue and will then try to state the other properties of the nitramino-alcohols.

Nitramino-ethanol is perhaps formed from the nitroderivative of the internal ester of oxethylaminoformic acid by another process which is not so simple but not less important on account of the intermediate products. If dry  $NH_3$  is passed through a cold 1 pCt. solution in benzene a white precipitate is formed which to judge from its behaviour, is a  $NH_3$  compound of nitro-ureo-ethanol (oxethylnitro-urea). This compound when boiled with absolute alcohol, in which it is but little soluble, parts with its  $NH_3$ , which as we know from experience happens in the case of all compounds of nitramines with  $NH_3$ , and on evaporating the solution nitro-ureo-ethanol is obtained which is very soluble in water and alcohol and very slightly so in benzene and chloroform. From these solutions it crystallises in beautiful thin glossy plates which melt at  $86^\circ$ . The aqueous solution gives like urea itself immediately a white precipitate with mercuric nitrate but not with mercuric chloride or silver nitrate unless an alkali is added.

Nitro-ureo-ethanol which, as has been stated above, I had tried in vain to obtain from ureo-ethanol, yields on boiling with barium hydroxide  $NH_3$  and  $CO_2$ . Perhaps nitramino-ethanol is formed simultaneously according to the equation:



unless nitrous acid is formed first from the nitro-urea derivative as is the case with nitrohydantoïne, but no certainty exists on this point.

Attention must also be called to the acid character of nitro-ureo-ethanol which not only yields a compound with  $\text{NH}_3$  but may be readily titrated in aqueous solution with potassium hydroxide, using phenolphthalein as indicator. It then saturates one mol. of potassium hydroxide and consequently behaves, apparently, like a monobasic acid, such as nitrohydantoïne for instance. If we do not wish to assume that the hydrogen of the group  $\text{CH}_2$  is replaceable by metals under the influence of the negative group  $-\text{N} < \begin{matrix} \text{NO}_2 \\ \text{CO} \end{matrix}$ , or in other words, that it causes the acid character of the substance, then similar substances and also nitrohydantoïne, ethylenedinitro-ureïne etc. would have a structure totally different from that of the nitramines, which from the manner in which they are prepared have one hydrogen atom linked to the nitrogen. When in these substances the presence of the group  $-\text{N}-\text{NOH}$  is assumed, instead of  $-\text{NHNO}_2$ , nitrohydantoïne etc. ought to contain the group  $-\text{CH}-\text{N}-\text{NOH}$  unless, as has been rendered highly probable in the case of nitrohydantoïne, the alkali simply forms and eliminates one mol. of nitrous acid. Should oxethylnitro-urea prove to be better suited than nitrohydantoïne to settle this point we will not neglect to have this matter further investigated.

**Chemistry.** — Professor FRANCHIMONT reads a paper from Miss E. VAN AKEN on: "*The oxidation of organic nitrogen-compounds and the estimation of the carbon and nitrogen therein by the moist process.*"

The oxidation of organic nitrogen compounds is a subject about which a good deal has already been and is still being written. The knowledge thereof is also of practical importance as it is applied not only to the quantitative determination of the nitrogen but also to that of the carbon and nitrogen. The result is that the nitrogen is either liberated or converted into ammonia. This does not only depend on the nature of the oxidizer and the circumstances under which the oxidation takes place, but also, if not in the first place, on the chemical structure of the nitrogen compound. Thence it follows that none of the methods for the quantitative determination of the nitrogen can be applied in every case and even the method of DUMAS, which