

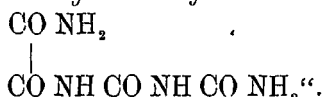
Citation:

Bornwater, J. Th., On the synthesis of amido-oxalybiuret, in:
KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 198-200

by the size and the thickness of the membrane, which is quite a natural thing, considering that the membrane vibrates all over ("en masse") with the greatest excursion in the centre. The technique damps it to a certain extent in various degrees of efficiency (damping caused by air and by induction). In circuit with this telephone is the microphone varying considerably as to the number and the size of the carbon granules. Without exception I used for the microphones coal-membranes tuning with the telephone diaphragm selected beforehand, and I regulated the damping by selecting granules of a particular size. This can easily be managed, so that harmony for a broad zone may readily be effected, which is requisite for a proper reinforcement and audibility to be guaranteed by the circuit.

The graphic representations show, that much can be attained in the indicated way even with the present means. If the technique could be improved so as to enable us to apply the principles here brought forward, I doubt not but telephony in private houses, in churches and in assembly-rooms would be made subservient to a much greater number of pathological organs of hearing than the attainable means allow, seeing that hitherto only reinforcement was the object of experimenters and that a reinforcement not always in a zone of sufficient breadth. A new field of research opens up when the zones of reinforcement are extended to different portions of the speechzone a_1 to e_3 . Every ear will then be able to select an apparatus complementary to what it lacks.

Chemistry. — "*On the synthesis of amido-oxalybiuret*"



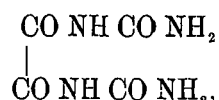
By DR. J. TH. BORNWATER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of June 28, 1913).

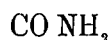
In 1911, I showed that oxalyldiureid is not identical with the compound obtained by GRIMAU (Bull. 32 (1879) p. 120) on heating parabanic acid with urea and which in the German literature is called wrongly oxalyldiureid, although GRIMAU rightly calls it "amide d'un acide oxalybiurétique".

The substance of GRIMAUx shows biuret reaction and, after being dissolved in dilute potassium hydroxide solution evolves ammonia in the cold and yields on acidifying with acetic acid a crystalline precipitate.

In the *Berichte der Deutschen chemischen Gesellschaft* **46** p. 1404, H. BILTZ and E. TOPP discuss this oxalyldiureid



obtained by the interaction of oxalylchloride with urea and consider this identical with the "amide d'un acide oxalylbiurétique"



of GRIMAUx. I have now tried to prepare this

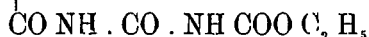


compound synthetically in order to be able to show that this substance is different from the true oxalyldiureid.

As has been shown previously, on boiling in dry benzene there are formed in the interaction of oxalylchloride with amides and with similar substances possessing a primary amide function, in most cases the corresponding carbonyl derivatives. On the ground of this experience it was to be expected that, if we allow in the same manner oxaminic acid ethylester and ethylurethane to react in equimolecular quantities a substance might form of the composition



which might be called *a. carbethoxyl*



b. oxalylethoxyl urea. This substance indeed formed to the extent of 10% of the theoretical quantity in the presence of other products and after repeated recrystallisations from dry ethyl acetate it crystallised in beautiful glittering needles melting at 152°, the analyses of which were quite in accordance with the theoretical results.

It could not be recrystallised from water as this causes a decomposition to set in with formation of oxaluric acid.

When this substance was dissolved in absolute alcohol and a current of dry gaseous ammonia passed through the solution while cooling in ice, a fine pulverulent substance was deposited which on account of its mode of formation and analysis could be considered to be the amido-oxalylbiuret and in properties agreed entirely with the "amide d'un acide oxalylbiurétique" of GRIMAUx.

This amido-oxalylbiuret also showed the so-called biuret reaction, dissolved in alkali with evolution of ammonia and then gave with acetic acid a crystalline precipitate either as stated by PONOMAREW

(Ber. d. D. ch. G. **18** p. 982) of the acid potassium salt of allantoic acid or, according to BILTZ and TOPP of the potassium salt of oxaluric acid. For want of sufficient material this could not be further elucidated.

From this it may therefore be concluded that the substance obtained by GRIMAUX and the synthetically prepared amido-oxalyl biuret may be considered as identical.

In order to obtain the so-called biuret reaction it seems to me desirable to first add the highly diluted copper sulphate solution and then a solution containing at most 15% of KOH.

BILTZ and TOPP carry out this reaction in the reverse way so that there is a possibility that the substance is already undergoing a partial decomposition before the copper sulphate is added, thus interfering with the biuret reaction. Moreover, they use a KOH solution D. 1.3 which will cause a more rapid decomposition. I have, therefore, mutually compared the reaction obtained with biuret itself, with the amido-oxalylbiuret prepared by my process and with the substance obtained by GRIMAUX and have also compared the colouring with that of the "Code des couleurs" of KLINCKSTECK and VALETTE.

On adding the different reagents rapidly the violet-red colouring 596 was always obtained in all three cases even when the KOH solution was added previous to the copper sulphate. In the latter case, however, the colouring had changed after 5 minutes; with amido-oxalylbiuret and KOH D. 1.1 to 566, with KOH D. 1.3 to 541; with GRIMAUX's substance and KOH D. 1.1 to 561, with KOH D. 1.3 to 528 D, whereas in the first case (CuSO₄ first, KOH afterwards) — with my own preparation as well as with that of GRIMAUX — a change took place, after 5 minutes, to 571 when using KOH D. 1.1 and to 564 with KOH D. 1.3.

In conclusion I wish to call attention to the difference in results obtained by BILTZ and TOPP in the reduction with hydrogen iodide. With oxalyldiureid they obtained hydantoine, with GRIMAUX's substance a compound of the empirical composition C₄H₆O₃N₂ of which they have not been able to give a definite structure. However, it is not impossible that they were dealing here with uramil which has the same empirical composition, begins to decompose above 270° and also forms so-called salts. If we attribute to GRIMAUX's substance the formula of amido-oxalylbiuret the formation of uramil is explained quite as readily as the formation of hydantoine from oxalyldiureid.