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.

very little had crystallized out and a further trifling quantity was recovered by distilling off the benzene The distillate had a strong odour of *iso*butyric nitrile and evolved much ammonia when boiled with potassiumhydroxide, it did not contain any previously. Boiling with strong hydrochloric acid first and then with potassiumhydroxide also yielded ammonia which likewise points to the presence of the said nitrile. The solid product was but little soluble in cold water or ether; after being extracted with both it was recrystallized a few times from alcohol and then melted at 160°. When heated with aqueous potassium hydroxide it gave oxalic acid. On analysis were obtained figures corresponding with those required by *oxalylbisiso-*

$$\begin{matrix} CO\text{-}NH\text{-}CO\text{-}C_3H_7 \\ | \\ CO\text{-}NH\text{-}CO\text{-}C_3H_7 \end{matrix}$$

butyrylamide. Hence there was obtained, not as was expected from the results obtained by BORNWATER with other amides, a *carbonyl*, but an *oxalyl* derivative, whilst the greater part of the amide had been converted into nitrile. Hence, the oxalylchloride had acted to a large extent as other acid chlorides and anhydrides do sometimes, namely caused formation of water. Perhaps this happens also with other amides and to this might be attributed the frequent bad yield. Why no carbonylderivative but an oxalyl derivative has formed here remains for the moment obscure.

As *isobutyrylmethylamide* $C_3H_7 \cdot CO\text{-}NH\text{-}CH_3$ was not known, I have prepared this also and I found again confirmed the regularity, to which I have pointed previously [1]), that methylamides have a lower melting point than the amides. It was prepared from *iso*butyryl chloride and methylamine in ethereal solution at a low temperature and distilled under a diminished pressure. At 17 m.m. it passed over constantly at 110° as a colourless liquid. On cooling it crystallized and again melted at fully 20°. The analysis showed its purity. In supermelted condition at 16° the sp. gr. was 0,9089.

The ethanesulphonamide, obtained by JAMES from the chloride with ammonia in ether, was prepared by me in the same manner; only the melting point I found a little higher (60°) and not 58°. From benzene in which it is little soluble it crystallizes in long delicate needles, from ether, in which it is more soluble, in thick prisms, likewise from acetic ether and acetone in which it is freely soluble. Boiled for seven hours with oxalylchloride in benzene it deposited a solid substance, whilst in the benzene was dissolved but little of a brown syrupy mass, which was left on distillation. It may be recrystallized both from water and alcohol, although it is decom-

[1]) Rec. d. tr. ch. d. P. B. T. XVI. p. 128.

posed on boiling with water. It melts at 224°; its solutions have an acid reaction. The analysis gave figures agreeing with those required

$$\begin{matrix} CO\text{-}NH\text{-}SO_2\text{-}C_2H_5 \\ | \\ CO\text{-}NH\text{-}SO_2\text{-}C_2H_5 \end{matrix}$$

by *oxalylbiethanesulphonamide*. On boiling with water oxalic acid may be already detected therein.

Hence, ethanesulfonamide like benzenesulphonamide yields with oxalylchloride an oxalylderivative.

I now prepared *ethanesulphonmethylamide*, obtained already in 1886 by me and KLOBBIE from the chloride with methylamine in ether, from the chloride by means of an aqueous 33 % solution of methylamine; the chloride was diluted with ether. After being dried it was distilled under diminished pressure. On strong undercooling by liquid air it crystallized and even remained solid above 0°; the melting point which was not yet determined accurately, lies presumably between 3° and 7°. Hence, it melts again lower than the ethylsulfonamide, in harmony with the above-mentioned regularity.

Boiled with oxalylchloride in benzene an evolution of hydrogen chloride only started on warming and had not yet ceased after 10 hours boiling. The benzene was now distilled off when the residue became crystalline. It was washed with water and with ether in which, as in alcohol, it is but little soluble and after careful drying crystallized from boiling benzene, when it forms beautiful thick crystals which melt at 144°. In chloroform it is also freely soluble. It is not decomposed on boiling with water but when boiled with aqueous potassium hydroxide it yields oxalic acid. The analysis gave figures required for *oxalylbisethanesulphonmethylamide*

$$\begin{matrix} CO—N(CH_3)—SO_2.C_2H_5 \\ | \\ CO—N(CH_3)—SO_2.C_2H_5 \end{matrix}$$

A nitroderivative from ethanesulphonmethylamide had been obtained previously by me and KLOBBIE by the action of absolute nitric acid, but neither the ethanesulphonamide nor the *iso*butyrylamide had as yet been treated with nitric acid. I have now supplemented this void and also treated the sulphon-*iso*butyricdiamide of MOLL VAN CHARANTE in the same manner.

The *iso*butyrylamide placed in cooled absolute nitric acid yields, when the solution attains the ordinary temperature, slowly and in theoretical quantity nitrous oxide like all simple amides.

Ethanesulphonamide when placed in absolute nitric acid causes a sudden and rapid (explosive like) evolution of gas; on cooling to —18° the evolution is quiet but yet it ceases within an hour. The gas is nitrous oxide.

Benzenesulphonamide when cooled in ice and salt gives with absolute nitric acid but little gas but this increases on elevation of temperature.

The sulphon*iso*butyric diamide of MOLL VAN CHARANTE dissolves slowly in absolute nitric acid without evolution of gas even after two days and is reprecipitated unchanged by addition of water particularly on neutralising the acid.

Hence also in regard to absolute nitric acid this substance behaves quite differently than was to be expected from the diamide.

Finally, it may be mentioned here that just as HINSBERG prepared benzenesulphonnitramide from benzenesulphamide by means of nitric and sulphuric acid at low temperatures, ethylsulphonnitramide is to be obtained also from ethanesulphonamide in this manner, though with a poor yield, as a substance crystallizing beautifully from benzene in which it is fairly soluble and melting at ± 70°.

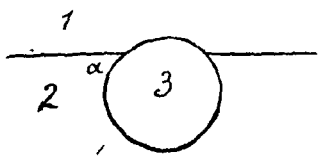
Chemistry. — "*The distribution of a colloidally dissolved substance over two layers*". By Prof. W. REINDERS. (Communicated by Prof. SCHREINEMAKERS).

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

1. When three non-miscible liquids meet, three things may happen depending on the values of the contact surface tensions $\sigma_{1,2}$, $\sigma_{2,3}$ and $\sigma_{3,1}$, apart from the action of the gravitation; either the three phases meet in one common side or one of them expands between the other two and prevents these from coming into contact.

The first will happen if none of the three contact surface tensions is greater than the sum of the other two; the second if this should be the case. If, for instance $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$, 3 will expand between 1 and 2 [1]).

2. If one of the phases (3 for instance) is solid and the other two liquid we can again distinguish the same two cases with this difference, however, that when $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$, the expansion of 3 between 1 and 2 is not possible. Phase 3 will then arrive at the contact surface of 1 and 2.



Let us now suppose the phase 3 to be in the form of a small globule. There will then be an equilibrium if $\sigma_{1,3} = \sigma_{2,3} + \sigma_{1,2} \cos \alpha$. If $\sigma_{1,3} > \sigma_{2,3}$, $\cos \alpha$ will be positive and $\alpha < 90°$. The greater part

[1]) QUINCKE. Consult the test-books, for instance BOSSCHA-KUENEN II, 658.