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

I may, however, state provisionally that this glucoside is either insoluble or at most very slightly soluble in cold alcohol. When the leaves, after being dried in an airbath at 80°, and then powdered, were extracted with cold alcohol, no HCN and acetone could be obtained by enzyme-action from the alcoholic residue.

When the extracted powder after being dried was mixed with water, and then brought in contact with the enzyme, the aqueous distillate showed abundant evidence of the presence of HCN and acetone.

Utrecht, September 25, 1905.

Chemistry. — Prof. P. VAN ROMBURGH presents a communication: *"On the action of ammonia and amines on formic esters of glycols and glycerol"* (II).

As the action of ammonia and amines on allyl formate (Proc. June 24 '05) had yielded such good results to me, I have also included in my research other formic esters, and I now communicate, briefly, the results obtained with the formates of some polyhydric alcohols.

If gaseous ammonia is allowed to act on the diformate of glycol it is first absorbed slowly with evolution of heat. If, when the action is over, the liquid is distilled, nothing passes over at the boiling point of the diformate (174°), but the temperature rises at once to the boiling point of glycol, and then gradually to that of formamide. A complete separation of the two substances, whose boiling point only differs about 20°, does not succeed with small quantities, and although it has been proved that the reaction takes place readily and almost quantitatively, formamide cannot be obtained pure in this way.

One gram of the diformate when mixed with 2 grams of dipropylamine gave a slow rise from 18° to 42°. The liquid being distilled the formate again seemed to have disappeared, and a fraction could be obtained at the boiling point of the glycol, and another at that of dipropylformamide.

With 1.8 gram of benzylamine, 1 gram of glycol diformate gave a slow rise from 18° to 80°. On distillation, the formate seemed to have disappeared and the glycol being distilled off, nearly the theoretical amount of benzylformamide was left in a pure condition.

If gaseous ammonia is allowed to act on the diformate of propanediol (1. 2), which I prepared by heating this glycol with formic acid, phenomena are noticed analogous to those in the case of glycol

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diformate. After the action is over the ester has again disappeared, and a mixture of propanediol (1. 2) and formamide has formed.

7 grams of this diformate being mixed with 10 grams of piperidine the temperature rose from 20° to 120° and on fractionation it again appeared that the ester had been completely converted into propanediol, whilst the formylpiperidine, after a few distillations, could be separated in a fairly pure condition. The boiling point was a little too low, probably owing to traces of the glycol.

With 7 grams of benzylamine, the diformate of propanediol (1. 2.) gave a rise from 20° to 110°. On distillation the formed glycol passed over at about 190°. The residue which had been heated to about 250° (thermometer immersed in the liquid) solidified on cooling, and consisted of nearly pure benzylformamide. It may be distilled at about 295° with only slight decomposition. The distilled product had a faint odour of carbylamine, and melted at 59°. By recrystallisation the melting point rose to 61°.

If gaseous ammonia is passed into a mixture of formines of glycerol, such as is obtained for instance by boiling glycerol with formic acid, or heating with oxalic acid, and then removing the free formic acid by distillation in vacuo, it is absorbed with great evolution of heat. After expelling the excess of ammonia and distilling in vacuo a rich yield of almost pure formamide is obtained.

In one of my experiments 66 grams of formine (yielding 65 % of formic acid on saponification) was saturated with ammonia. In the first distillation 22 grams of formamide m.p. 0° and 17 grams dito m.p. — 2° were separated whilst 40 grams of glycerol remained in the distilling flask. The yield was therefore practically the theoretical one so that this method may be recommended for the rapid preparation of formamide in large quantities.

With pure triformine [1]) the action of ammonia is slower than with the above mentioned mixture. Triformine of glycerol eagerly absorbs gaseous dimethylamine with strong evolution of heat, and on distillation in vacuo a good yield of the dimethylformamide b. p. 153° is obtained. Piperidine gives with triformine a considerable rise in temperature (from 20° to 70).

Dipropylamine forms with triformine, at first, two layers. After a little shaking (the temperature rose from 18° to 77°) the liquid becomes homogeneous, and by distillation in vacuo a good yield of the dipropylformamide formed could be readily obtained.

With diisobutylamine, triformine also gives two layers which do

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[1]) I hope to communicate about this substance, shortly.

not disappear on shaking for a while, but if the liquid was allowed to stand over night it became homogeneous, and on distillation in vacuo yielded diisobutylformamide.

Formic esters of unsaturated glycols also seem to react readily with amines, at least Mr. W. VAN DORSSEN, who is engaged in the Utrecht laboratory upon the study of the 3.4-dihydroxy-1.5-hexadiene

$$CH_2 = CH - CH.OH$$
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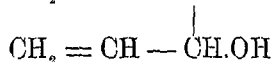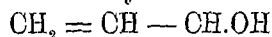
obtained, on mixing 1 gram of the diformate of this glycol with 1.3 gram of benzylamine, a rise in temperature from 18° to 65°, and after distilling off the glycol could readily isolate benzylformamide m. p. 61°.

Mathematics. — *"A local probability problem"*. By Prof. J. C. KLUYVER.

The following problem was lately (Nature, July 27) proposed by Prof. PEARSON :

"A man starts from a point O, and walks l yards in a straight line; he then turns through any angle whatever, and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r + dr$ from his starting point O." [1])

I find that the general solution of this problem depends upon the theory of BESSEL's functions, especially that in some particular cases it leads to the evaluation of certain definite integrals, involving these functions.
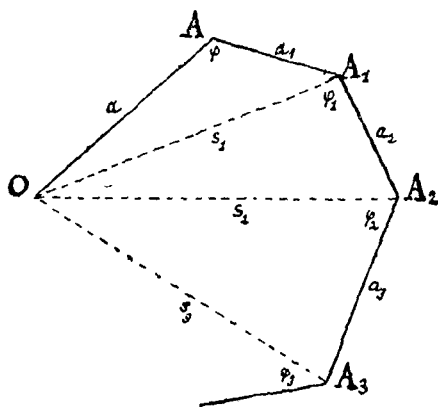
Let $OAA_1A_2A_3 \ldots A_{n-1}$ be the broken line, the n stretches of which need not be all of the same length. Then the shape of the figure, not its orientation in the plane, is wholly determined by the lengths $a, a_1, a_2, \ldots, a_{n-1}$ of the stretches, and by the magnitudes of the angles $\varphi, \varphi_1, \ldots, \varphi_{n-2}$, formed at the origin of each stretch a_k by the stretch itself and by the radius vector s_{k-1}.

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[1]) Recently (Nature, August 10) Prof. PEARSON stated, that the solution for n very large was already virtually contained in a memoir on sound by Lord RAYLEIGH.