

*Citation:*

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rodentia and primates (man), must probably be regarded as a more advanced differentiation, and will have more to do with special biological functions than in general with the position of the animals in question upon the phyletical scale.

6. Regarding the functions of the mesenc. quintus nucleus, nothing is to be deduced with certainty from comparative anatomical investigations, although the dorsal entrance of the radix mesencephalica in regard to the motor root might suggest a sensory function. But as in teleostei the motor V root also does not leave the oblongata ventrally to the sensory one, and in all animals e. g. the nerv. trochlearis passes quite dorsally outside the brain-stem, no positive conclusions are to be deduced from the above anatomical fact.

The same may be said of the dorsal position of the nucleus, in view e. g. of the dorsal position of the trochlear nucleus in cyclostomes (ammocoetes and petromyzon).

The problem of the significance of the mesenc. part of the nervus trigeminus is thus still unsolved.

**Chemistry.** — "*On the action of Oxalyl chloride on amines and amides.*" By Dr. J. TH. BORNWATER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of April 28, 1911).

It is well known that acid-chlorides act not only on ammonia, but also on primary and secondary amines with formation of primary mono- and dialkylamides, and on primary simple amides and alkyl-amides with formation of secondary simple and alkylamides.

But with the chloride of oxalic acid (oxalylchloride), however, very few experiments have, as yet, been made, although this is now a reliable commercial article. STAUDINGER casually remarks that oxalylchloride forms with amines oxamides and cites as an instance aniline, which he uses for the quantitative determination of oxalyl chloride. TASKER and JONES only mention that oxalylchloride has a powerful action on primary and secondary amines.

At the request of Prof. FRANCHIMONT I have convinced myself, in the case of a number of amines and amides, that the action takes place sometimes readily, sometimes with difficulty; in some cases it does not take place at all or takes another direction so that instead of oxalyl derivatives carbonyl derivatives are formed.

With piperidine in ethereal solution I obtained at the ordinary

temperature oxalylpiperidide, with aniline oxanilide, with *o*-nitraniline oxalyldi(*o*-nitraniline), with *m*-nitraniline oxalyldi(*m*-nitraniline) and with *p*-nitraniline oxalyldi(*p*-nitraniline).

With 1.2.4 dinitraniline no action was noticed at the ordinary temperature; here it was necessary to boil and benzene was used as solvent. This led to the formation of oxalyldi (1.2.4 dinitraniline). In these circumstances, no reaction was obtained with trinitraniline.

It was further shown that in the case of oxalylchloride we can also work according to the method of HARTWIG FRANZEN and make use of the hydrochlorides of the amines. On boiling these in benzene with oxalylchloride until the evolution of hydrogenchloride ceases oxalylderivatives are readily obtained. Apart from the advantage that the hydrochlorides are more readily procurable, this method is also more convenient in so far as that less of the amine is required and that the reaction proceeds quietly and no special precautions are necessary.

I noticed this with the hydrochloride of aniline which gave oxanilide and with that of piperidine which gave oxalylpiperidide.

To the amines belong also the esters of the amino-acids and I endeavoured to obtain<sup>1)</sup> oxalylderivatives from their hydrochloric compounds by the last mentioned method which succeeded very readily, for instance with the hydrochloride of glycollethylester

when oxalyldiglycollethylester  $\begin{array}{c} \text{CONH CH}_2\text{COOC}_2\text{H}_5 \\ | \\ \text{CONH CH}_2\text{COOC}_2\text{H}_5 \end{array}$  was obtained

in beautiful needles melting at 143°. A similar result was obtained with the hydrochloride of glycylglycinethylester. This yielded

oxalyldi(glycylglycinethylester)  $\begin{array}{c} \text{CO NH CH}_2\text{CO NH CH}_2\text{COOC}_2\text{H}_5 \\ | \\ \text{CO NH CH}_2\text{CO NH CH}_2\text{COOC}_2\text{H}_5 \end{array}$  in

beautiful lustrous leaflets melting at 250°, which exhibit the so-called biuretreaction.

Already a few other hydrochloric compounds of the amino-acid esters have been treated in the same manner with an equally good result. Such as that of the methylester of  $\alpha$ -aminopropionic acid

<sup>1)</sup> The above mentioned method of HARTWIG FRANZEN could also be successfully applied to the preparation of the chloroacetyl derivatives of the esters of the amino-acids. On boiling chloroacetylchloride dissolved in benzene with the hydrochloride of glycollester I obtained chloroacetylglycinethylester and with the hydrochloride of glycylglycinethylester chloroacetylglycylglycinethylester. Both with a very good yield so that this method deserves the preference to that employed by FISCHER for obtaining the chloroacetyl derivatives of the polypeptides as well on account of the better yield as of the less complicated method of working.

when oxalyldi( $\alpha$ -aminopropionic [methylester])

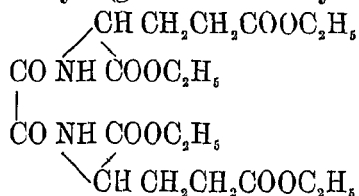
$$\begin{array}{c} \text{CH}_3\text{CH}(\text{NH})\text{COOCH}_3 \\ | \\ \text{CO} \\ | \\ \text{CO} \\ | \\ \text{CH}_3\text{CH}(\text{NH})\text{COOCH}_3 \end{array}$$

was obtained in delicate white needles. Further that of diglycylglycinethylester when oxalyldi(diglycylglycinethylester)

$$\begin{array}{c} \text{CO NH CH}_2\text{CO NH CH}_2\text{CO NH CH}_2\text{COOC}_2\text{H}_5 \\ | \\ \text{CO NH CH}_2\text{CO NH CH}_2\text{CO NH CH}_2\text{COOC}_2\text{H}_5 \end{array}$$

was formed as silky delicate needles with a melting or decomposition point at  $302^\circ$ . They give a red violet biuret reaction.

An example was also taken from the aminoderivatives of the dibasic acids, namely the hydrochloride of the diethylester of glutaminic acid which yielded oxalyldi(glutaminic diethylester)



as exceedingly fine hair-like crystals m. p.  $94^\circ.5$ .

The compounds obtained might probably become of interest as regards the knowledge of the albumenoids. It is known that more than forty years ago SCHÜTZENBERGER obtained oxalic acid from all albumenoids by resolving these with barium hydroxide. For instance from :

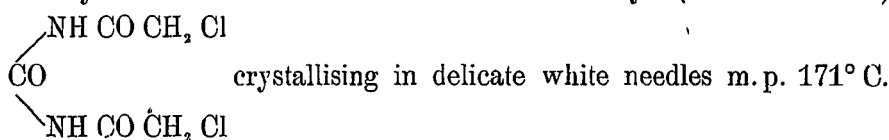
	5,7 %	barium oxalate	= 2,22 %	oxalic acid
Egg albumen				
"    "	12,5	"	4,87	"
Casein	17,5	"	6,82	"
Serum (from horse's blood)	16,5	"	6,43	"
Fibrin (from horse's blood)	11,5	"	4,48	"
Hemiprotein	14,7	"	5,73	"
Vegetable fibrin (gluten)	8,0	"	3,12	"
Ossein	5,0	"	1,95	"
Wool	20,4	"	8,14	"
Hair	19,4	"	7,74	"
Fish-glue	11,3	"	4,50	"
Fibroin from silk	8,1	"	3,23	"
Chondrin	11,4	"	4,44	"
Gelatin	8,9	"	3,55	"

No further attention has been paid of late to this production of oxalic acid, which might most likely be obtained from substances other than oxalylderivatives, for instance, mesoxalic acid derivatives.

As the above reaction appears to take place with all the hydrochlorides of aminoesters as yet examined, it may be expected that similar oxalylcompounds will be obtained from the polypeptides in general, which might be looked on as building stones of the proteid molecule.

But little attention is also paid to the production of carbon dioxide in the resolution of the albumenoids and yet — like the oxalylcompounds of the polypeptides — their carbonyl compounds might also be building stones of the proteid molecule. Provisional experiments with simple amides showed that by the action of oxaly chloride no oxaly-, but carbonylderivatives were obtained because oxalychloride behaves in some cases as a source of carbonylchloride.

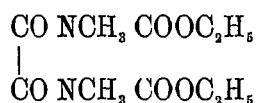
With acetamide (boiling in benzene) I obtained in this way diacetylurea and with chloroacetamide carbonyldi(chloroacetamide)



With benzamide dibenzoylurea was formed but with benzanilide,  $\text{CO NC}_6\text{H}_5 \text{ COC}_6\text{H}_5$  on the otherhand, oxalyldi(benzanilide)  $\begin{array}{c} \text{CO NC}_6\text{H}_5 \text{ COC}_6\text{H}_5 \\ | \\ \text{CO NC}_6\text{H}_5 \text{ COC}_6\text{H}_5 \end{array}$  was obtained in beautiful needles melting at  $210^\circ \text{C}$ .

Acetethylamide gave oxalyldi(acetethylamide)  $\begin{array}{c} \text{CO N(C}_2\text{H}_5) \text{ CO CH}_3 \\ | \\ \text{CO N(C}_2\text{H}_5) \text{ CO CH}_3 \end{array}$  in beautiful crystals melting at  $130^\circ \text{C}$ .

Whereas ethylurethane yielded carbonyldi(ethylurethane) I obtained with methylethylurethane oxalyldi(methylethylurethane)



in clear white needles m.p.  $67^\circ \text{C}$ .

It thus appears that with mono-alkylamides the reaction leads to oxalylderivatives but with simple amides to carbonylderivatives.

With urea, which may also be classed among the amides were obtained (in ether at the ordinary temperature) parabanic acid and presumably, the true oxalyldiureid  $\begin{array}{c} \text{CO NH CO NH}_2 \\ | \\ \text{CO NH CO NH}_2 \end{array}$  different from the

"amide d'un acide oxalylbiurétique" prepared by GRIMAUZ which in the German literature is wrongly called oxalyldiureid. The oxalyldiureid obtained by me not only shows complete insolubility in all the ordinary solvents, but also gives no biuret reaction.

Symmetric dimethylurea whether in ether at the ordinary temperature or in boiling benzene gave the well-known cholestrophane, whereas with asymmetric dimethylurea, when boiled in benzene, carbonyl-

di-(as. dimethylurea)  $\begin{array}{c} \text{NH CO N (CH}_3\text{)}_2 \\ \diagup \text{CO} \\ \diagdown \text{NH CO N (CH}_3\text{)}_2 \end{array}$  .  $\frac{1}{2}$  H<sub>2</sub>O is obtained in particularly beautifully formed prismatic crystals melting at 140° C.

**Chemistry.** — "*Additive compounds of m. Dinitrobenzene.*" By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of April 28, 1911).

The increased interest taken in the coloured compounds of polynitro-substances with aromatic amines induces me to call attention again to the fact that m. dinitrobenzene is also capable of yielding with different amines beautifully coloured crystallised compounds as I mentioned casually many years ago <sup>1)</sup>.

Generally speaking, these compounds are obtained less readily, and many are less stable than those of s. trinitrobenzene. This probably explains why NOELTING and SOMMERHOFF <sup>2)</sup> have not succeeded in isolating such products. KREMANN <sup>3)</sup> has studied the equilibrium between aniline and m. dinitrobenzene and states that no data occur in the literature as to the existence of a compound between these substances although I had already mentioned having isolated the same.

If we dissolve m. dinitrobenzene in aniline the liquid turns intensely red on warming and when cold, a beautiful red compound crystallises in large crystals, which melt at 41°—42° (in a capillary tube). According to KREMANN the melting point lies at 40°. The compound consists of an equal number of molecules of the components. On exposure to the air, the crystals lose the aniline.

Analysis: Found 64.1% C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>. Calculated 64.3%.

Dimethyl p. toluidine when heated with m. dinitrobenzene gives an intensely coloured solution from which, on cooling, crystallises a

<sup>1)</sup> R. 6, 366 (1887).

<sup>2)</sup> B. 39, 76 (1906).

<sup>3)</sup> M. 25, 1298 (1904).