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T ...	„	tetrahedron,
C	„	hexahedron (cube),
O	„	octahedron,
C ₅ ...	„	fourdimensional five-cell,
C ₁₆	„	„ sixteen-cell,
C ₂₄	„	„ twinty four-cell,
S _n	„	n-dimensional simplex,
Cr _n	„	„ cross polytope.

The cases in which we have to deal with a half characteristic are also indicated in this table. So e.g. the first polytope of the table is limited by equilateral triangles of two different kinds, presenting themselves in the numbers 10 and 20.

Meppel, June, 1912.

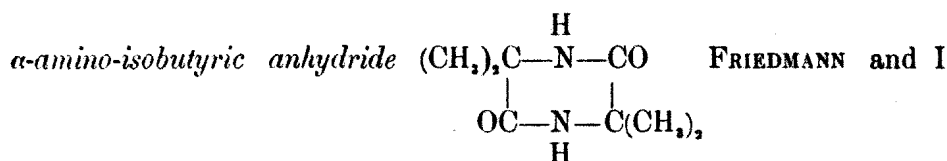
Chemistry. — “*Contribution to the knowledge of the direct nitration of aliphatic imino compounds*”. By Prof. A. P. N. FRANCHIMONT and Dr. J. V. DUBSKY.

In the January meeting 1907 I had the honour to give a survey of the action of absolute nitric acid on saturated heterocyclic compounds whose ring consists of C and N atoms. This originated in the fact observed and described by Dr. DONK, that the so-called

glycocollanhydride
$$\begin{array}{c} \text{H} \\ | \\ \text{H}_2\text{C}-\text{N}-\text{CO} \\ | \quad | \\ \text{OC}-\text{N}-\text{CH}_2 \\ | \\ \text{H} \end{array}$$
 in which the group NH is placed

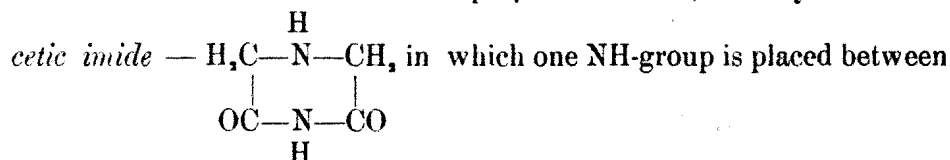
between CO and CH₂, nitrated with difficulty, with much more difficulty than I had expected because a number of other heterocyclic compounds with rings of five or six atoms in which the group NH is placed in the same manner may be readily nitrated with absolute nitric acid at the ordinary temperature. This was not the case here; only a treatment of the nitrate with acetic anhydride or, as I showed with Dr. FRIEDMANN, of the glycocoll anhydride with acetic anhydride and nitric acid gave a mono- and a dinitroderivative.

With the so-called alanine anhydride
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{HC}-\text{N}-\text{CO} \\ | \quad | \\ \text{OC}-\text{N}-\text{CH} \\ | \quad | \\ \text{H} \quad \text{CH}_3 \end{array}$$
 and with the



found something similar, with this understanding, however, that the nitration always took place with more difficulty, which can be attributed to sterical influence.

At the same meeting, I also called attention to the fact previously noticed by me that the group NH placed in a ring between two groups CO cannot be nitrated with absolute nitric acid, neither when it is placed between two saturated hydrocarbon groups. The expectation that one of the eleven isomers of the so-called glycocoll anhydride which Dr. JONGKEES had prepared for me, namely *iminodiacetic imide* —



two CO-groups and the other one between two CH_2 -groups, would not be capable of direct nitration by absolute nitric acid, was not realised in so far that it appeared indeed to give a nitroderivative but with some properties differing from those observed up to the present with nitramines and nitramides, so that it was questionable whether the nitrogroup is attached to the nitrogen or to the carbon.

Owing to the peculiar properties of the nitroderivative the chance of answering that question in a direct manner, for instance by reduction to hydrazine, was but a very slight one.

Moreover, the starting material, the imide, is obtained with difficulty and then only in small yield so that a great economy is necessary in the research. Two indirect ways could, however, be pursued, namely by starting from substances in which either the hydrogen at the N, or that at the C is replaced by other groups and to test these compounds $\text{RN}(\text{CH}_2-\text{CO})_2\text{NH}$ and $\text{HN}(\text{C}(\text{R})_2-\text{CO})_2\text{NH}$ as to their behaviour on nitration.

The last way is undoubtedly the best although even there we may meet with difficulties, for instance a difficult nitration owing to sterical hindrance as has already been demonstrated by me and FRIEDMANN.

Of the first process a few examples will be given here, namely acetyl and methyl derivatives, which, however, do not justify a final conclusion. The surmise that the NO_2 -group is placed at the N can be supported somewhat by the results of the nitration of the

acyclic compounds from which the imide is derived, such as iminodiacetonitrile, iminodiacetic acid, its ester and imide. This at the same time also furnishes a contribution to our knowledge of the nitration of acyclic imino compounds from which it is again evident that the nitration of one NH-group placed between two CH_2 -groups (residues of saturated hydrocarbons) depends also on other constituents attached to these hydrocarbon residues.

The results obtained are as follows:

Iminodiacetonitrile $\text{HN}(\text{CH}_2\text{CN})_2$ yields with ordinary nitric acid a nitrate in beautiful glittering needles which melt at $138\text{--}140^\circ$ with decomposition. The formula was determined by analysis and titration of the nitric acid. It is readily soluble in cold water, soluble in hot methyl alcohol, ethyl alcohol and benzene. On slowly cooling a hot alcoholic solution it yields very beautiful crystals. If this nitrate is dissolved in absolute nitric acid (which is accompanied by a slight evolution of heat) and the acid is allowed to evaporate in vacuo over lime, the residue when triturated with absolute alcohol gives a crystal-paste which, after being dried and recrystallised from dry benzene, forms splendid snow-white needles melting at $100\text{--}101^\circ$. Their analysis points to the nitro-derivate $\text{NO}_2\text{N}(\text{CH}_2\text{CN})_2$, *nitro-iminodiacetonitrile*. It gives the reaction of the nitramines with zinc and an acetic acid solution of α -naphthylamine. On warming with water decomposition sets in.

Iminodiacetic acid $\text{HN}(\text{CH}_2\text{CO}_2\text{H})_2$ gives a nitrate already described in 1865 by HEINTZ. When this nitrate is dissolved in absolute nitric acid and evaporated in vacuo over lime it is recovered unchanged. It is insoluble in ether, benzene and acetic ether. If, however, the nitric acid solution is heated to boiling a nitroderivative $\text{NO}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, *nitroiminodiacetic acid* is formed, which is left behind after evaporation of the nitric acid in vacuo over lime. It is soluble in methyl and ethyl alcohol in acetone and acetic ether, also in cold water. Crystallised from acetic ether it forms broad, flat needles mutually joined like a fan. Its melting, or rather decomposition point appears to lie at about 153° . Its aqueous solution is strongly acid and gives the above nitramine reaction. A neutral potassium salt was prepared which readily crystallises on addition of absolute alcohol to the watery solution; it is decomposed at about 195° with explosion. The acid potassium salt which is not easily soluble in alcohol and yields beautiful crystals was also prepared. From the ethyl ester of iminodiacetic acid described by Mr. JONGKEES there was also prepared a nitrate, which is very little soluble in alcohol and crystallises in silky needles, which melt at

198—199°. By treating this nitrate, in the manner described, with absolute nitric acid in the cold it is recovered unchanged but if the solution is heated to boiling the nitroderivative $\text{NO}_2\text{N}(\text{CH}_2\text{CO}_2\text{CH}_3)_2$ is formed which is not, or but little, soluble in cold water so that it may be precipitated by pouring the nitric acid solution into cold water. From acetic ether, in which it is soluble, it is obtained in silky delicate scales which melt at $63^\circ.5$.

Iminodiacetamide $\text{HN}(\text{CH}_2-\text{CONH}_2)_2$ gave with one mol. of NO_2H a nitrate which was obtained from the aqueous solution, by addition of absolute alcohol, in beautiful lustrous leaflets which melt at 206° with decomposition. If this nitrate is placed in absolute nitric acid, an evolution of gas takes place after a short time, as in the case of all amides of N_2O ; when this has ceased, or has been accelerated by warming, the nitro-iminodiacetic acid is obtained.

Iminodiacetimide $\text{HN}(\text{CH}_2\text{CO})_2\text{NH}$, which was made according to the directions of JONGKEES, also gave compounds with acids. We prepared: (1) the HCl compound in lustrous, beautiful crystals which are decomposed on heating above 180° ; (2) the NO_2H compound, also white crystals with a strong lustre, which when heated above 180° , are decomposed and turn a bluish-green. Both compounds contain one mol. of acid.

When iminodiacetimide or its nitrate is dissolved in absolute nitric acid and the solution evaporated in vacuo over lime a crystal-cake is obtained which may be recrystallised from boiling dry chloroform in which it is very little soluble. It then forms beautiful colourless needles which have the empirical composition of a mononitroderivative. This *nitroiminodiacetimide* $\text{NO}_2\text{N}(\text{CH}_2\text{CO})\text{NH}$ spontaneously turns a dark blue, especially in not quite dry air and its aqueous solution on warming first turns green, then blue and deposits an almost black amorphous substance soluble only in strong sulphuric acid with an indigo-blue colour.

In order to render it more probable still that the nitro-group is attached to the nitrogen situated between the CH_2 -groups, the *acetylminodiacetimide* $\text{CH}_3\text{CON}(\text{CH}_2\text{CO})_2\text{NH}$ was prepared first of all by subliming in vacuo acetylminodiacetamide, which according to JONGKEES decomposes at 203° . On recrystallising the sublimate from methylalcohol splendid small crystals were obtained which melt at $167-168^\circ$ and according to analysis, have the empirical composition of acetylminodiacetimide. They are insoluble in benzene, petroleum ether and acetic ether. The same substance was prepared by boiling iminodiacetimide with acetic anhydride. This acetyl derivative was dissolved in absolute nitric acid and the solution evaporated in vacuo

over lime. The residual crystalline mass, after being recrystallised from methyl alcohol, proved to consist mainly of unchanged acetyl derivative. The mother liquor, however, exhibited colour phenomena which may raise a suspicion that a small fraction of the acetyl group has been replaced by the nitro-group.

Finally, also a few derivatives of *methyliminodiacetic acid* $\text{CH}_3\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ were made, in which the hydrogen atom of the NH-group which is placed between 2 CH_2 has been replaced by methyl. First of all the *diamide* by acting on the methyl ester of the said acid for some time, with NH_3 in methyl alcoholic solution. This diamide $\text{CH}_3\text{N}(\text{CH}_2\text{CONH}_2)_2$ forms beautiful, large crystals melting at 162—163°; it is readily soluble in cold water, methyl- and ethyl alcohol, very little so in acetic ether, acetone, ether, petroleum ether, chloroform and benzene. It was recrystallised from boiling methyl alcohol.

From the diamide the *imide* was prepared by sublimation under a pressure of 17—18 m.m. at 200—220°. The *methyliminodiacetimide* $\text{CH}_3\text{N}(\text{CH}_2\text{CO})_2\text{NH}$ thus obtained was first recrystallised from boiling acetic ether in which the amide is practically insoluble, then from boiling acetone and finally from a little boiling methyl alcohol. It then forms white, glittering crystals which melt at 106°. This imide gives crystallised compounds with one mol. of HCl or NO_2H . The first is decomposed by heating above 235°; the second by heating above 130°; treated with absolute nitric acid an oxidation seems to take place slowly at the ordinary temperature, at least after being some time in vacuo over lime a decidedly strong evolution of red fumes took place and from the residual swollen mass no well-defined product could, as yet, be isolated.

Although the question as to the position of the nitro-group in nitroiminodiacetimide is not yet quite solved, as this position will be determined fully only then when the analogous isobutyric acid derivative $\text{HN}(\text{C}(\text{CH}_3)_2\text{CO})_2\text{NH}$ has also been tested as to its behaviour on nitration, yet it has been rendered very probable by the results obtained, the publication of which was rendered desirable owing to the departure of Dr. DUBSKY.

The direct nitration capacity of the above acyclic aliphatic amino-compounds, also the differences in the readiness of this nitration point to a connection with what has been found in the case of aromatic N-compounds where the nitration capacity, or otherwise the formation, of nitramines by direct nitration, has been first shown by VAN ROMBURGH.

This connection is quite in harmony with what I have demonstrated

previously as to the direct nitration capacity of aliphatic carbon compounds, by nitrating malonic acid and its esters, methylenetricarboxylic ester etc. from which it follows that the direct nitration capacity is caused by the adjacency of so-called negative groups of definite strength.

In this manner were also discovered the aliphatic nitramines and nitramides, by nitrating the amides wherein occurs also a negative group and it now appears that an aliphatic secondary amine (dimethylamine) may also undergo direct nitration when in the alkyl groups are present the group CN or CO₂H, so distinctly negative groups.

I, therefore, put to myself the question whether the phenyl or nitrophenyl-group would also be able to give the same result as CN or CO₂H. This, however, does not seem to be the case, for dibenzylamine HN(CH₂C₆H₅)₂ yielded only dinitrodibenzylamine nitrate, but no nitramine on boiling with absolute nitric acid.

The ready nitration capacity of iminodiacetonitrile and of iminodiacetic acid and its derivatives is striking especially when we compare it with that of other substances as shown in the subjoined list.

CH ₃ .NH.CH ₃	not	CN.CH ₂ .NH.CH ₂ .CN	readily
CH ₃ .NH.CO.CH ₃	readily	CO ₂ H.CH ₂ .NH.CH ₂ .CO ₂ H	readily
CH ₃ .CO.NH.COCH ₃	readily	CO ₂ .CH ₃ .CH ₂ .NH.CH ₂ .CO ₂ .CH ₃	readily
CH ₃ .NH.CO ₂ CH ₃	readily	C ₆ H ₄ (NO ₂)CH ₂ .NH.CH ₂ .C ₆ H ₄ NO ₂	not
CH ₃ .CO.NH.CO ₂ CH ₃	readily	C ₆ H ₂ (NO ₂) ₃ .NH.CH ₃	readily
CH ₃ .CO ₂ .NH.CO ₂ CH ₃	not	C ₆ H ₂ (NO ₂) ₃ .NH.C ₆ H ₂ (NO ₂) ₃	not

Biochemistry. — “*A biochemical method of preparation of l-Tartaric acid.*” By Prof. J. BÖESEKEN and Mr. H. J. WATERMAN. (Communicated by Prof. BEIJERINCK).

In our investigations on the assimilation of carbon nutriment by different kinds of mould it was found necessary to get some more information as to the manner in which the carbon was retained in the body of the plant either temporarily or permanently.

For this purpose one of us (H. J. W.) carried out a large number