ON THE SO-CALLED DIETHYL DICYANOGLUTACONATE AND SOME OF ITS DERIVATIVES.

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The diethyl dicyanoglutaconate was first prepared by G. Errera⁽¹⁾ and by Ruhemann and Browning⁽²⁾ independently, by the action of ethyl cyanoacetate, sodium ethylate, and chloroform, the sodium derivative being formed intermediately. The formula I was given to the ester and II to the sodium derivative.

$$C_2H_5OOC—C(CN)=CH—CH(CN)—COOC_2H_5 \qquad I.$$
$$C_2H_5OOC—C(CN)=CH—CNa(CN)—COOC_2H_5 \qquad II.$$

Errera's observations are as follows: The diethyl sodio-dicyanoglutaconate is light yellow, glittering needles, has two molecules of water of crystallisation, when it is crystallised from water, and melts at about 265°C. By acidifying a warm aqueous solution of this sodium compound a yellow substance is precipitated, which is recrystallised from benzene and found to be pure diethyl dicyanoglutaconate.

(Found: $C=55.52$; $H=5.59$; $H=11.59$. $C_{11}H_{12}O_4N_2$ requires $C=55.93$; $H=5.08$; $N=11.86\%$)

The diethyl dicyanoglutaconate melts at 178–179°, is difficultly soluble even in hot benzene, easily soluble in alcohol but *decomposed*. By boiling the spirit solution, the diethyl dicyanoglutaconate is changed into another substance of the formula $C_{11}H_{16}O_6N_2$.

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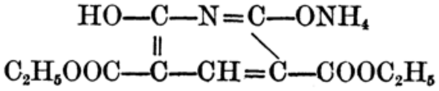
(1) *Ber.*, **31** (1898), 1241.

(2) *J. Chem. Soc.*, **73** (1898), 280.

He thought this substance was the diamide of the dicarboxyglutaconic ester but M. Guthzeit(1) showed that it was the ammonium salt of the diethyl dihydroxydinicotinate of the formula III.



III.

Ruhemann and Browning made similar observations and also obtained some pyridine derivatives. They state as follows:

"Ethylic dicyanoglutaconate dissolves readily in hot acetone, and crystallises from it in yellow, glittering plates which melt and decompose at 187–188°. It was found to contain a small quantity of another substance *which was not removed by repeated recrystallisation.* The following analytical results show that the percentage of carbon in different specimens of the product varies from the theoretical number by one to two percent."

(Found: C=54.07, 54.42, 55.22, 54.65; H=5.55, 5.38, 5.46, 5.42; N=11.50, 11.70 %).

By the action of ethyl cyanoacetate, sodium ethylate and carbon tetrachloride, Otto Dimroth(2) also obtained the same yellow sodium derivative, and from it the free ester melting at 181–183°. He observed that this substance showed a varying melting point according to the mode of heating. His analytical data is N=11.51 %.

G. Errera and F. Perciabosco(3) obtained the same yellow sodium compound by a long boiling of the triethyl sodio-dicyanoaconitate.

A Corrected Idea on the So-called Diethyl Dicyanoglutaconate. This compound was often prepared by the author according to the method of Errera for the purpose of obtaining any brominated derivatives by the action of bromine. The sodium derivative several times recrystallised from hot water was yellow needles, and its properties as well as those of the free ester agreed with the literatures.

After the obtainment of some new derivatives the starting substance, e.i. the diethyl dicyanoglutaconate seemed very doubtful in its chemical composition and constitution.

Preparation of Pure Substance. The diethyl dicyanoglutaconate precipitated from a hot aqueous solution of repeatedly recrystallised sodium derivative, washed with water, and dried, was dissolved in boiling absolute alcohol, filtered while hot and then cooled. The deposited crystals were collected, washed with ether, and dried.

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(1) *Ber.*, 32 (1899), 779.

(2) *Ber.*, 35 (1902), 2881.

(3) *Ber.*, 34 (1901), 3707.

0.2873 gr of subst. gave 29.2 c.c. of N_2 at 24° and 758 mm. (Found: N = 11.31. $C_{11}H_{12}O_4N_2$ requires N=11.86 %.)

This was again recrystallised from pure acetone, and gave the following analytical result. 0.2616 gr. of subst. gave 26.5 c.c. of N_2 at 22° and 755 mm. (Found: N=11.34 %.)

Once more recrystallised from acetone (that is once from alcohol and twice from acetone). 0.2014 gr. of subst. gave 20.0 c.c. of N_2 at 19.5° and 763 mm. (Found: N=11.38 %).

Each time the taken substance was dried at 100° for half an hour in the stream of dry air, and weighed. After this treatment the yellow colour of the crystals became slightly deeper than before. Errera found in the substance crystallised from alcohol a carbon content too small by one to two percent, which he attributed to decomposition. Thus the determination of nitrogen seemed to lead to the same conclusion.

Another attempt of obtaining a pure substance was made by the replacement of chloroform with iodoform. The author found formerly that the tetraethyl sodio-dicarboxyglutaconate was obtainable in a purer state by using iodoform than by chloroform, and had lighter colour and somewhat higher melting point. In the case of the diethyl dicyanoglutaconate the same result was expected.

The sodium compound formed by using iodoform, after removing the usual red-coloured by-product by repeated recrystallisation from hot water, became nearly *colourless* crystals, melting at about 265°. On heating over 100° it turned yellow. With chloroform a *yellow* substance was always obtained, and thus it was ascertained that the colour was not essential, but caused by impurities. Between the melting point of the two kinds of preparations no remarkable difference was observed.

This colourless sodium compound was converted into the free ester by the ordinary procedure. The yellow crystals precipitated by hydrochloric acid were washed with water, dried, and recrystallised from pure acetone. This purified substance melted at 183° (corr.) and gave the following analytical result.

0.1495 gr. of substance dried at 100° gave 14.9 c.c. of N_2 at 20° and 766 mm. (Found: N=11.43 %.)

This corresponds to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$, which requires N=11.43 %.

Composition of the So-called Diethyl Dicyanoglutaconate. The following facts suggest a great doubtfulness in the nature of this compound. (I) Its yellow colour, whilst the sodium derivative was ascertained to be colourless. cf. The tetraethyl dicarboxyglutaconate, which is colourless liquid and its sodium derivative is light yellow crystals. (2) Its high melting point, whilst the tetraethyl dicarboxyglutaconate and the triethyl α-cyano-γ-carboxyglutaconate are both liquid at the ordinary temperature. (3) When an aqueous solution of the sodium compound is acidified, the free ester separates out only after a while, not immediately. (4) Its small solubilities in various solvents. It is practically insoluble in benzene and ether, and only slightly soluble in cold alcohol and cold acetone. (5) The low value of nitrogen content. In both Errera's and Ruhemann's analytical data, the sodium derivative shows satisfactory numbers, while the free ester, obtainable by a simple treatment from the former, varies from the theoretical number by an impermissible amount.

The purest specimen obtained by using iodoform and recrystallised from acetone, contained 11.43 % of nitrogen as mentioned above, which corresponded to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$. The contents of carbon and hydrogen were determined.

0.1959 gr. of substance dried at 100° gave 0.3868 gr. CO_2 and 0.0928 gr. H_2O. (Found: C=53.87; H=5.30. $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$ requires C=53.88; H=5.31 %.)

There can be no hesitation in giving the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$ to the diethyl dicyanoglutaconate.

Errera and Ruhemann got probably only impure substances and calculated by an incorrect formula. One of Ruhemann's specimens, that showed the smallest contents of carbon (54.07 %) and nitrogen (11.50 %), although there is no knowing if the substances for both determinations belonged to the same specimen or not, may really be the purest, which he might considered as the least pure. Errera observed that the crystals from alcohol contained too small carbon, but did not noticed the presence of half a molecule of water. Ruhemann obtained an ammonia derivative of the formula $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot \frac{1}{2} H_2O$, but did not detect half a molecule of water contained in the original ester.

Constitution of the Diethyl Dicyanoglutaconate. The triethyl dicyanoaconitate [145–146°], $C_2H_5OOC{-}C(CN){=}C(COOC_2H_5){-}CH(CN){-}COOC_2H_5 + \frac{1}{2} H_2O$⁽¹⁾, and the methenylbismalonitrile imidether [244°], $(CN)_2C{=}CH{-}CH(CN){-}C(NH){-}OC_2H_5 + \frac{1}{2} H_2O$⁽²⁾, obtained from the corresponding sodium derivatives by acidifying their aqueous solutions have also half a molecule of water. In both cases it was not determined whether the half molecule of water was the water of crystallisation or combined constitutionally. The present author made no close investigation of these two substances, but if such derivatives of the dinitrile of the glutaconic acid usually have half a

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(1) G. Errera und F. Perciabosco, *Ber.*, **34** (1901), 3704.

(2) W. Zoernig, *J. prakt. Chem.*, **74** (1906), 435.

molecule of water when they are formed from the sodium derivatives by acidifying their aqueous solutions, it will not, probably, be a water of crystallisation.

Dehydration of the Ester. A substance dried in the desiccator at the ordinary temperature showed practically no decrease in weight on heating half an hour at 100° in the stream of dry air. 0.3114 gr. of the substance dried at 100° weighed 0.3108 gr. after one hour heating at about 130°, and 0.3104 gr. after more one hour heating at 150°, in the stream of dry air. The water in the diethyl dicyanoglutaconate was unremovable even by heating at 150°

Molecular Weight. Although the ester is not sufficiently soluble in boiling acetone, and the elevation of the boiling point is small, an ebullioscopic determination in this solvent was tried. The number 406 was obtained as the molecular weight, and it seemed that the diethyl dicyanoglutaconate had the molecular formula $(C_{11}H_{12}O_4N_2)_2H_2O$.

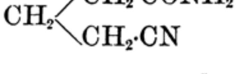
Chemical Properties. The sodium derivative of the diethyl dicyanoglutaconate does not evolve ammonia on heating with caustic alkali, but when the free ester is heated with caustic alkali, the ammoniacal odour is evidently perceived. Some of the nitrogen atoms in the free ester are more easily detached by alkali than those in the sodium compound. This indicates an undeniable difference in the constitution of these two compounds.

All these facts and the investigation of the bromine addition compound, which will be described later, show that the constitution of the diethyl dicyanoglutaconate will probably be represented by one of the following formulæ.

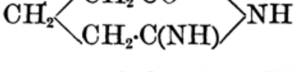
$$(C_{10}H_{12}O_4N)\text{—}C(NH)\text{—}O\text{—}C(NH)\text{—}(C_{10}H_{12}O_4N) \qquad \text{IV.}$$

$$(C_{10}H_{12}O_4N)\text{—}CO\text{—}NH\text{—}C(NH)\text{—}(C_{10}H_{12}O_4N) \qquad \text{V.}$$

J. F. Thorpe⁽¹⁾ indicated that a nitrile of the formula VI would pass into an imino piperidine of the formula VII.



VI.



VII.

In the present case the formula V is also more probable than IV, for it can be supposed that this compound would be formed by the condensation of a monoamide-mononitrile and a dinitrile.

This assumption is not contradictory to the fact that some pyridine derivatives were obtained from the ester, for a compound with such a constitution will easily be split into two similar molecules.

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(1) *J. Chem. Soc.*, **99** (1911), 422. Further cf. *J. Chem. Soc.*, **99** (1911), 1684; **115** (1919), 686; **117** (1920), 1465.

It is supposed that an analogous discussion may be made on the triethyl dicyanoaconitate and the methenylbismalonitrile imidether.

Action of Bromine on the Diethyl Dicyanoglutaconate. The diethyl dicyanoglutaconate was introduced in pure chloroform (about ten times in weight), and bromine (dehydrated by shaking with concentrated sulphuric acid) was added drop by drop. By the time when the quantity of bromine reached to four atoms to one molecule of the ester (refered to the formula $(C_{11}H_{12}O_4N_2)_2 H_2O$), the solid entered completely into solution, and during the addition of further four atoms of bromine, brick-red crystals were separating out. (In the dark the appearance of the crystals was somewhat delayed.) When the increase in amount of the crystals ceased, they were collected, washed with pure benzene (dehydrated on sodium) and dried in vacuum. When the brominated product was left in its mother liquor for a long time, it was accompanied by another substance, which also crystallised from the filtrate of the former and was considered to be the product of a secondary change.

This experiment was often repeated, and specimens of various purities were obtained. This substance melts at 146–149°, has a large proportion of free bromine, and is so unstable that it is decomposed in ether, alcohol, and water, but crystallises unchanged from a hot pure benzene solution on cooling. As shown in the following pages, this substance is transformed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2 \cdot HBr$ and then into the picrate, $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, which indicates that it is merely a molecular addition compound.

0.2247, 0.2028, 0.2960, 0.2750, 0.1199 gr. subst. (each belonging to a different specimen), gave 0.2809, 0.2483, 0.3730, 0.3457, 0.1520 gr. AgBr respectively. 0.1701, 0.6071, 0.4638 gr. subst. gave 19.8 (26.5°, 760 mm.), 29.4 (29°, 758 mm.), 24.4 c.c. (31°, 751 mm.) nitrogen respectively. (Found: Br=53.6, 52.10, 53.63, 53.50, 53.95; N=5.27, 5.24, 5.57 %).

Determination of Free Bromine. The iodometry was not successful in this case, for the liberation of iodine was incomplete. The method of analysis was as follows. The substance was weighed in a watch glass and placed in a beaker. A freshly prepared aqueous solution of sulphur dioxide, which should be free from sulphuric acid, was poured in the beaker and heated on the water bath. The crystals were dissolved to a colourless solution. Most of the excess of sulphur dioxide was then expelled by adding hydrochloric acid and heating. The formed sulphuric acid was determined as barium sulphate by the ordinary method. From the mother liquor of the barium sulphate a white substance crystallised out, which was identified with the diethyl dihydroxydinicotinate by its melting point (about 200°), and its reddish coloration on adding ferric chloride, the experimental fact described on p. 34 and 35 being taken into consideration. One molecule of barium sulphate corresponds to two atoms of bromine.

0.5004, 0.2887, 0.3617 gr. subst. gave 0.3287, 0.1910, 0.2397 gr. $BaSO_4$ respectively. (Found: Free Br=45.0, 45.3, 45.4. $(C_{11}H_{12}O_4N_2)_2H_2O.HBr.Br_6$ requires, total Br=53.3; free Br=45.7; N=5.33 %).

H. L. Wheeler and D. T. Walden⁽¹⁾ obtained many addition compounds of the general formula $(C_6H_5NHCOCH_3$ or derivative$)_2.HX.X_{2n}$, where X represents Br or I, for instance, $(m\text{-}NO_2C_6H_4NHCOCH_3)_2HBr.Br_6$. At first they obtained some compounds of this series by the action of bromine on the meta-nitroacetanilide in chloroform. If the bromine was free from hydrogen bromide and the solvent was not attacked by bromine, no addition took place. Thus in carbon bisulphide they could not get the addition compounds. The present author also ascertained that the diethyl dicyanoglutaconate gave no addition compound in carbon bisulphide. But a long standing caused a substitution in a part of the substance and some brominated product separated out. The formula with two imino-groups given to the diethyl dicyanoglutaconate seems to be quite correct.

The Diamide Hydrobromide. When the bromine addition compound was introduced in commercial ether it changed into a white crystalline compound. This transformation was neither realised in absolute ether, nor in the presence of an excess of bromine, but promoted by light. Hence this reaction proceeded by liberating bromine and combining with water, and required more hydrogen bromide than the bromine addition compound originally contained. The ether in which the new substance was formed, was brown with bromine and left nearly no residue on evaporation. For the purpose of preparation it is better to use a sufficient amount of ether saturated with water. After the disappearance of the original brown crystals, the product is collected, washed with ether and dried. (The yield is theoretical, see under).

0.1369, 0.2952, 0.2206, 0.1460 gr. subst. gave 0.0733, 0.1587, 0.1173, 0.0785 gr. AgBr respectively. 0.1982, 0.2856 gr. subst. gave 14.3 (30°, 750 mm.), 20.7 c.c. (29°, 756 mm.) nitrogen respectively. (Found: Br=22.79, 22.88, 22.63, 22.88; N=7.73, 7.83. $C_{11}H_{12}O_4N_2.2H_2O.HBr$ requires Br=22.79; N=7.96 %).

This compound forms light, silky, white needles, does not show a sharp melting point, but decomposes to a dark red liquid when heated near 180°. It is soluble in water and alcohol, much more when heated, but insoluble in ether. The alcoholic solution is slightly fluorescent, and gives no coloration on adding ferric chloride. From a hot concentrated solution in water or

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(1) *Am. Chem. J.*, 18 (1896), 86.

alcohol the unchanged substance crystallises out on cooling. It dissolves also in hot concentrated hydrobromic acid (ca. 40 %) and crystallises from it unchanged. This substance does not liberate ammonia when boiled with caustic alkali, and only a long boiling with strong alkali decomposes it into ammonia and other substances. The aqueous solution is acidic and precipitates silver bromide on adding silver nitrate.

In every point it does not resemble(1) with the ammonium salt of the diethyl dihydroxydinicotinate, which was formed by adding two molecules of water to the diethyl dicyanoglutaconate in spirit solution but possesses a great likeliness for being a hydrobromide of an acid amide. Many acid amides give molecular compounds of the formula $2R.CONH_2.HX$ with hydrogen halide. Comparison of their properties with those of the present substance indicates that it belongs to the compound of this type, and it has two amide-groups in one molecule. The hydrohalides of amides are easily formed from nitriles in various reactions, where necessary water, or such substances as to give water by reaction, and hydrogen halide are present.(2)

The diethyl dicyanoglutaconate gave directly a slightly yellowish compound containing bromine and 7.86% of nitrogen, by the action of ether shaken with concentrated hydrobromic acid.

Moreover the hydrobromide gives the picrate of the formula $C_{11}H_{16}O_6N_2.C_6H_2(NO_2)_3OH$ which will be described in details in the following paragraphs.

Picrate of the Diamide. When the diamide hydrobromide was mixed with the picric acid both in alcoholic solutions, yellow, glittering needles separated out, which were collected, washed with alcohol several times and dried in the air-bath. This picrate melted at 196–197° (corr.) and contained no bromine, whilst the mother liquor showed the reaction of the bromine ions.

0.2214, 0.2189 gr. subst. gave 28.0 (26°, 754 mm.), 27.8 c.c. (25.5°, 755 mm.) nitrogen respectively. (Found: N=13.85, 13.97. $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$ requires N=13.97%).

The value of carbon and hydrogen did not exactly agree with the formula, but was sufficient to exclude such a formula as $(C_{11}H_{12}O_4N_2)_2C_6H_2(NO_2)_3OH$, which requires N=14%.(3)

	Found	$C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$	$(C_{11}H_{12}O_4N_2)_2 \cdot C_6H_2(NO_2)_3OH$
C	41.9%	40.7%	46.8%
H	3.5%	3.8%	3.9%

0.2146 gr. of the picrate weighed 0.2141 gr. after heating at 150° for half

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(1) See page 35.

(2) Colson, *Bull. soc. chim.*, [3] 17 (1897), 57. A. Pinner und Fr. Klein, *Ber.*, 10 (1877), 1896. F. Henle und G. Shupp, *Ber.*, 38 (1905), 1370.

(3) Nitro-compounds often give deviated results in analysis, unless a special care is taken.

an hour in the stream of dry air. Therefore the two molecules of water which came from the hydrobromide were not a water of crystallisation but combined constitutionally. The picrate agreed in appearance very closely with the picrates of the acetamide and formamide. The picric acid almost always gives the binary molecular compounds, when it enters into so-called picrates, whatever the constitution of the other substances may be. In this case the diamide also produced a binary compound, like the acetamide. The picrate is difficultly soluble in absolute alcohol, but easily soluble in hot spirit. It is not decomposed by, and when the two components are present also formed in, a moderately strong hydrobromic acid.

The same picrate was formed when the diethyl dicyanoglutaconate was mixed with the picric acid in alcohol containing some water. When the solutions of the diethyl dicyanoglutaconate and of the picric acid both in absolute alcohol were mixed, a brown clear solution resulted. On adding a few drops of water to this solution the picrate separated out in fine crystals immediately, whilst this picrate is more soluble in alcohol containing water than in absolute alcohol. Without the addition of water the picrate crystallised slowly taking water from surroundings.

0.1034 gr. of substance gave 13.0 c.c. of N_2 at 24.5° and 758 mm. (Found: $N=13.95\%$.) Melting point: 196.5°. The substance mixed with the picrate from the hydrobromide melted at 195.5°.

Finally the same picrate was formed when the bromine addition compound of the diethyl dicyanoglutaconate was mixed with the picric acid in alcoholic solution. Melting point: 195.5°. The substance mixed with the picrate from the hydrobromide melted at 196°.

The three compounds, diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide gave the same picrate.

Transformation of the Diamide Hydrobromide into the Diethyl Dihydroxydinicotinate. The diamide hydrobromide was boiled with dilute hydrobromic acid. It entered into solution at first, and in the course of a few minutes a solid separated, which rapidly increased in quantity. When cold this was collected. The mother liquor gave ammonia on heating with alkali. This substance was treated with cold concentrated hydrochloric acid. After adding water the solid was collected, washed and dried.

For comparison, the diethyl dihydroxydinicotinate was prepared by Ruhemann's method.⑴ The substance obtained by the hydrolysis of the diethyl dicyanoglutaconate with dilute hydrobromic acid was not already the ammonium salt but the free diethyl dihydroxydinicotinate, for it gave no ammonia on heating with alkali, and the mother liquor gave it. But to

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(1) *J. Chem. Soc.*, 73 (1898), 284.

complete the reaction the solid was treated with cold concentrated hydrochloric acid, as described by Ruhemann. The substance obtained from the hydrobromide was compared with that from the diethyl dicyanoglutaconate, and found to be identical. The former, as well as the latter, was readily soluble in chloroform, gave the red coloration on adding ferric chloride, and melted at the same point (199° not corr.) The three compounds, the diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide, are all changeable into the diethyl dihydroxydinicotinate.

The ammonium salt of the diethyl dihydroxydinicotinate was prepared according to Errera's method⁽¹⁾ by the hydrolysis of the diethyl dicyanoglutaconate in spirit. On boiling, the solution of the diethyl dicyanoglutaconate in spirit became gradually colourless and a solid separated out, the mother liquor remaining colourless, whilst Errera observed that the mother liquor became intensively yellow, which was probably due to impurities.

This ammonium salt gave no product with picric acid in alcohol. By heating with caustic alkali it liberated ammnonia. By a dilute acid it was changed into the free ester, for by Ruhemann's method the ammonium salt was not obtained. On adding a ferric chloride solution to the substance suspended (not dissolved) in alcohol, at first no coloration, and then gradually reddish violet coloration occurred, which shows that the ammonium salt was transformed into the free ester by the ferric chloride solution.

The compound $C_{11}H_{16}O_6N_2$, which was obtained as its hydrobromide $C_{11}H_{16}O_6N_2\cdot HBr$ and picrate $C_{11}H_{16}O_6N_2\cdot C_6H_2(NO_2)_3OH$, differs from the ammonium salt of the diethyl dihydroxydinicotinate with the same composition and obtainable from the same mother substance, and is changeable into the diethyl dihydroxydinicotinate. Hence it can be no other compound than the diamide of the dicarboxyglutaconic ester, which corresponds to the formula $NH_2CO{-}C(COOC_2H_5){=}CH{-}CH(COOC_2H_5){-}CONH_2$ and should be called the " diethyl $\alpha\gamma$-dicarbamylglutaconate." No amide of this type has ever been obtained, and in cases where such amides should be formed, a ring formation or splitting into a propene chain took place.⁽²⁾

In those reactions producing the bromine addition compound of the diethyl dicyanoglutaconate, the diamide hydrobromide, and the picrate, no heat was applied. All the transformations proceeded at the ordinary temperature. Hence it is natural to suppose that there took place no extraor-

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(1) *Ber.*, 31 (1898), 1241.

(2) See page 27 and Errera, *Ber.*, 33 (1900), 2973; Ruhemann and Morrell, *J. Chem. Soc.*, 59 (1891), 743; ibid., 61 (1892), 791; ibid., 63 (1893), 874; Guthzeit und Laska, *J. prakt. Chem.*, 58 (1898), 419; Guthzeit und Haussmann, *Ann.*. 285 (1895), 61 u. 97. Further cf., J. F. Thorpe and his collaborators, *J. Chem. Soc.*, 85–117 (1904–1920), "The Formation and Reactions of Imino Compounds. Part I-Part XX".

dinary change as the ring formation. The free diamide has not yet been isolated.

The author expresses his hearty thanks to Prof. K. Matsubara, who gave kind suggestions and in whose laboratory these experiments were carried out.

Summary.

1. The so-called diethyl dicyanoglutaconate has the composition $(C_{11}H_{12}O_4N_2)_2H_2O$ and the constitution is considered to be represented by the formula $(C_{10}H_{12}O_4N)$–CO–NH–C(NH)–$(C_{10}H_{12}O_4N)$.
2. The diethyl sodiodicyanoglutaconate is colourless when pure.
3. By the action of bromine on the so-called diethyl dicyanoglutaconate an addition product is obtained, which has the composition $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O \cdot HBr \cdot Br_6$. This is changed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2 \cdot HBr$, in ether containing water.
4. The picrate of the diamide, $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, is obtained from the diamide hydrobromide, from the bromine addition compound, and from the so-called diethyl dicyanoglutaconate. These three compounds are all changeable into the diethyl dihydroxydinicotinate.

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