3-Iodononane.—This was obtained from 3-nonanol by the usual procedure for the conversion of alcohols into iodides. In a typical experiment 40 g. of 3-nonanol were mixed with 4 g. of red phosphorus and 36 g. of iodide. The mixture, which at first was artificially cooled, was later heated for two hours on the steam bath, then filtered to remove unchanged red phosphorus, washed with water to remove acids of phosphorus, and without further purification was converted into nonylene.

Normal Nonylene.—The above 3-iodononane was refluxed with excess of strong alcoholic potash for about an hour. The liquid in the reaction flask was distilled, and yielded a solution of nonylene and alcohol, these forming a mixture of minimum boiling point. On the addition of much water, the hydrocarbon separated as a floating layer, which was removed, washed with water, dried with calcium chloride and distilled from metallic sodium. On subsequent fractionation, the main portion boiled at 149.4–149.9°.

Properties.—Colorless liquid, very mobile, pleasant petroleum-like odor. It boils at 149.4–149.9° and has at 15° the specific gravity 0.7540 compared to water at 15°.

Calculated for C_9H_{18}: C, 85.7; H, 14.3. Found: C, 85.3; H, 14.2.

Normal Nonane.—Normal nonylene was reduced to normal nonane by passing the vapor of the former, together with hydrogen, over freshly reduced nickel at a temperature of 160°.[1]

Properties.—Colorless, very mobile liquid, with a very slight "sweetish" odor. B. p. 150.4–150.6° at 759 mm. The specific gravity at 15° compared to water at 15° is 0.7219. The index of refraction $n_D^{25°}$ = 1.4025. It is miscible with the common organic solvents.

Calculated for C_9H_{20}: C, 84.4; H, 15.6. Found: C, 84.1; H, 15.7.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF THE NITRO-α-CARBOPYRROLIC ACIDS.[2]

BY WILLIAM J. HALE AND WILLIAM V. HOYT.

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In 1882 Weidel and Ciamician[3] prepared the first nitro derivative of the pyrrole ring in the form of a nitrocarbopyrrolic acid. The dry distillation of gelatin yielded pyrocoll, and this product, upon careful nitra-

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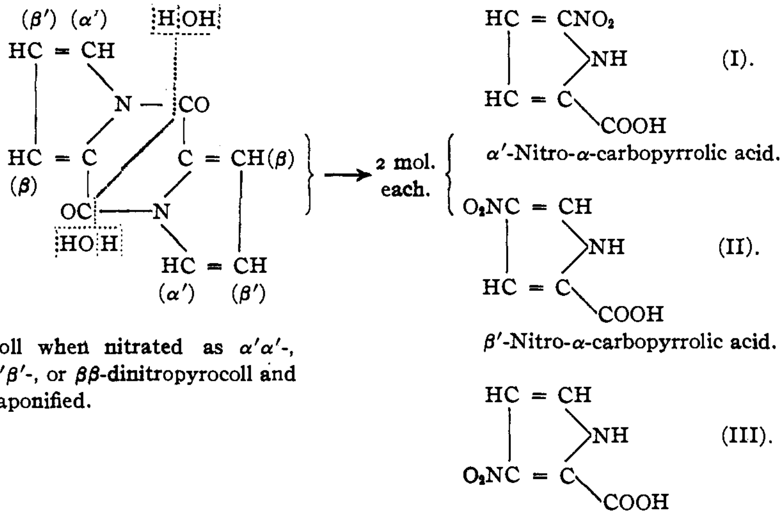
[1] The exact procedure may be found in an article by Clarke and Beggs, THIS JOURNAL, 34, 59 (1912).

[2] The work described in this article forms part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan by William V. Hoyt.

[3] *Gazz. chim. ital.*, 12, 39 (1882).

tion with fuming nitric acid, was converted into a dinitropyrocoll, which was in turn readily saponified by cold alkali into a nitro-α-carbopyrrolic acid (m. p. 144–6°). These investigators had previously established the constitution of pyrocoll[1] by a study of its decomposition products—its hydrolysis, for example, gave only α-carbopyrrolic acid. Later Ciamician and Silber[2] synthesized pyrocoll by the action of acetic anhydride upon α-carbopyrrolic acid, thus leaving no room for doubt as to the constitution of this crystalline product.

With the production of this nitro-α-carbopyrrolic acid alone, through the nitration of pyrocoll, Weidel and Ciamician correctly assumed that the nitration must have proceeded symmetrically in respect to the two pyrrole nuclei in the pyrocoll molecule. Three distinct symmetrical dinitro derivatives (α'α'-, β'β'-, ββ-) of pyrocoll are possible. These therefore must yield by hydrolysis three distinct (α'-, β'- and β-) nitro-α-carbopyrrolic acids as here shown.



Pyrocoll when nitrated as α'α'-, β'β'-, or ββ-dinitropyrocoll and saponified.

(I). α'-Nitro-α-carbopyrrolic acid.

(II). β'-Nitro-α-carbopyrrolic acid.

(III). β-Nitro-α-carbopyrrolic acid.

Although Ciamician and Silber had succeeded in obtaining only this one nitro-α-carbopyrrolic acid melting at 146°, they made many attempts to prepare the other two isomers. Their attempts, however, resulted in failures.[3] They found, for example, that the action of nitric acid upon α-carbopyrrolic acid led to decomposition into dinitropyrroles and carbon dioxide. Anderlini,[4] on the other hand, was able to introduce the nitro group into the methyl ester of α-carbopyrrolic acid without this

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[1] *Monats.*, **1**, 281 (1880).

[2] *Ber.*, **17**, 103 (1884).

[3] *Ibid.*, **19**, 1080 (1886).

[4] *Gazz. chim. ital.*, **19**, 93 (1889).

chance for decomposition. The methyl ester was slowly added to concentrated nitric acid cooled with ice. The dark brown solution was then poured into cold water and the solution made almost neutral with sodium hydroxide, after which it was made slightly alkaline with sodium carbonate and extracted with ether. From the ether extract Anderlini obtained the yellow methyl ester of a mononitro-α-carbopyrrolic acid and again, by the hydrolysis of this ester, he obtained a pale yellow acid crystallizing with one molecule of water of crystallization, as was noted also for the acid melting at 146°. This new acid, when anhydrous, melted at 217°.

In the same year Anderlini[1] was able to isolate the third isomeric nitro-α-carbopyrrolic acid from the mother liquors left upon removal of the ester of the acid melting at 217°. These liquors, already alkaline with sodium carbonate, were acidified and again extracted with ether. From the ether extract a mixture of nitro compounds was obtained, but by fractional crystallization from water a new methyl ester was isolated and, by hydrolysis, was found to give the third nitro-α-carbopyrrolic acid expected. This acid also contained one molecule of water of crystallization but when anhydrous (after standing over sulfuric acid) melted at 161°. The nitration of the methyl ester therefore led to the production of the two previously unknown nitro-α-carbopyrrolic acids. Though all three nitro derivatives may have been present in the nitration product of the ester, Anderlini was unable to isolate the ester of the first known nitro acid of Ciamician (m. p. 146°).

With the three nitro-α-carbopyrrolic acids thus known and obtainable only in minutest quantity, little evidence could be advanced concerning their exact structures. The fact that the ester of the acid melting at 217° could be removed from an alkaline solution by extraction with ether evidenced its lack of any acid properties and led Anderlini to suppose that the nitro group occupied most probably one of the β-positions, a position farthest removed from the imino hydrogen atom.

The study of condensation involving certain dialdehydes—especially that of nitromalonic aldehyde, has led to interesting syntheses of many well-known ring structures. In the use of nitromalonic aldehyde the fixed position of the nitro group upon the middle carbon atom has sufficed for the determination of the constitution of certain hitherto unknown nitro derivatives. Thus the condensation of urea with this aldehyde led to the synthesis of 5-nitropyrimidines.[2] And in the same manner as amino groups, so also methylene groups are found to condense more or less readily with this dialdehyde.[3] It occurred to us, therefore, that a

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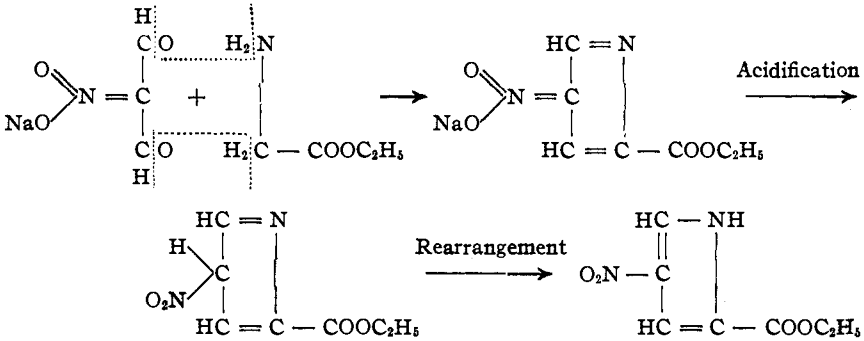
[1] *Gazz. chim. ital.*, **19**, 330 (1889).

[2] THIS JOURNAL, **34**, 82 (1912).

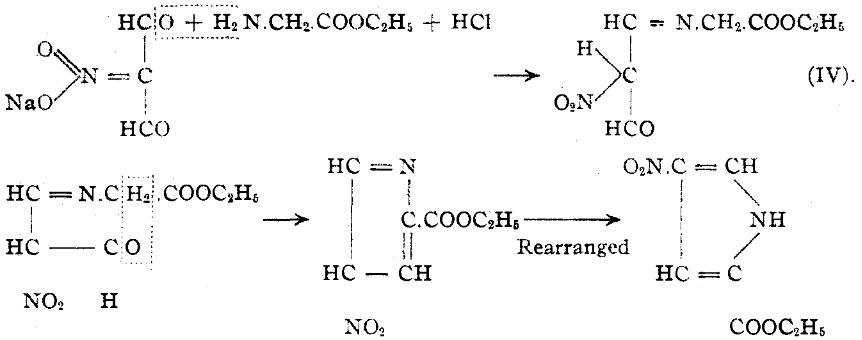
[3] *Ber.*, **45**, 1596 (1912).

simple condensation of nitromalonic aldehyde with amino acetic acid might be expected to yield a pyrrole-carboxylic acid. The presence of an acid is not, however, advantageous for a great majority of such condensations, consequently the ester of amino acetic acid, glycine ester, was selected for the condensation thus to be made in neutral or alkaline solution. The reactions involved may here be shown.



The result of this condensation will be seen at once to give an ethyl ester of a nitro pyrrole-carboxylic acid, namely, the ester of β′-nitro-α-carbopyrrolic acid—one of the three nitro acids under discussion. This possible identification of one of the much-discussed acids with an acid synthesized by simple means, and concerning the constitution of which there can be no room for doubt, offered us the hope that the means before us might lead to establishing the constitution of the other two acids.

When, however, glycine ester hydrochloride and sodium nitromalonic aldehyde were brought together in dilute alcoholic solution, there soon separated from the mixture a slightly soluble yellow compound which was still aldehydic in character and possessed no ring structure (IV). The compound proved to be of an intermediate type, the amino group having first entered into condensation with one aldehyde group, as was evidenced by failure of tests to confirm the presence of either a primary or a secondary amine. The possibility of further condensation between the remaining aldehyde group and the methylene group was not eliminated and reactions to this purpose were found to be easily accomplished in the presence of alkaline condensing agents. In the previous case it was advantageous to add a few drops of sodium hydroxide solution; the alkali facilitated the condensation and yet at the same time was too dilute to form a sodium salt with the almost insoluble acid product precipitated. In order to effect the latter step the reaction mixture was made strongly alkaline with sodium hydroxide and warmed upon the water bath. The intermediate product, β,β-aldehydonitro-ethylidenaminoacetic ester (IV), is easily soluble in an excess of alkali and from the red solution thus formed the colorless insoluble nitropyrrole ester is slowly precipitated. The course of the condensation is shown below:

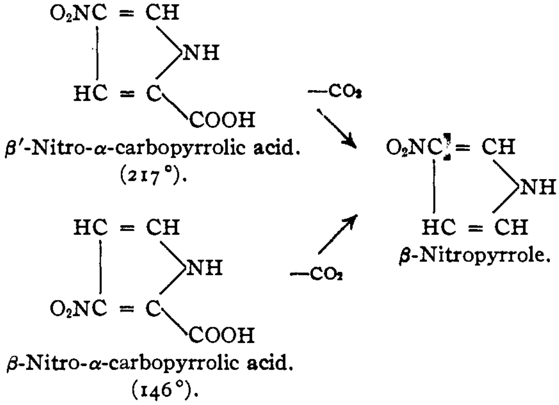


(IV). (V). (VI).

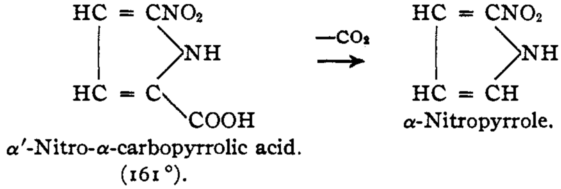
During the first step of the condensation between sodium nitromalonic aldehyde and glycine ester hydrochloride, sodium chloride is removed and the free isonitro group at once transformed into a nitro group and a labile hydrogen atom attached to this same beta carbon atom (IV). The second step proceeding toward ring formation, by an inner condensation as shown in (V), leads to a more or less unstable configuration, but by the final shift of this labile hydrogen atom to the nitrogen atom the more stable structure of the pyrrole ring (VI) is at once introduced. The nitro group thus remains in fixed position upon the same carbon atom, that is, the beta carbon atom of the nitromalonic chain.

The resulting colorless nitropyrrole carboxylic ester was hydrolyzed and found to yield an acid melting at 217°. In appearance and in all properties it was found identical with the acid prepared according to the method of Anderlini, and supposed by him to have a structure in which the nitro group occupied one of the two possible beta positions with reference to the nitrogen atom. In order further to check this result, nitromalonic aldehyde was brought into condensation with glycine methyl ester and the nitropyrrole carboxylic ester which resulted was found in every way identical with the methyl ester prepared by Anderlini and melting at 197°. The ester, as he reported, has no acid properties and naturally is that one of the three possible nitro esters in his nitration mixture which is most likely to be insoluble in alkali; the effect of the strongly negative nitro group in giving an acid character to the imino hydrogen atom is naturally less marked when farthest removed and so also less marked in the β'-position is its effect in conjunction with the carbomethoxyl group. The β'-nitro-α-carbopyrrolic acid as synthesized by us and melting at 217° at once establishes the constitution of the acid obtained by Anderlini and melting at this same point.

In order to fix the constitutions of the two remaining nitropyrrole carboxylic acids we chose to determine which one of these two might be made to yield the same decomposition product as that of the 217° acid upon the loss of carbon dioxide. No further reactions of substitution were planned, and hence by loss of carbon dioxide we should arrive at a simple nitropyrrole. It was known that free carbopyrrolic acids readily evolved carbon dioxide upon heating. Each of the three nitrocarbopyrrolic acids therefore should yield a nitropyrrole but, as will be seen below, the acid with the constitution determined by us must yield the same β-nitropyrrole as one of the other two. In other words, there is no need but to study the decomposition of one of the two remaining nitrocarbopyrrolic acids in order to fix the constitution of all three.



(VII).



(VIII).

The proof of these three structures seemed almost in hand, when it was found that but one nitropyrrole had been prepared and nothing definite was known regarding its constitution. This nitropyrrole in question had been prepared by Angeli and Allessandri[1] by the nitration of pyrrole with ethyl nitrate in the presence of sodium alcoholate. Their method will be described later. Their conclusions seemed to point to the β-position for the nitro group, though their argument was altogether from analogy: α-methyl indole yielded a β-nitroso derivative whereas β-methyl indole gave no similar derivative, hence it is to be supposed that nitration in the pyrrole ring selects the beta position. The nitropyrrole prepared by these investigators was a yellow, crystalline product melting at 63.5°. If Angeli and Allessandri were correct in their deductions

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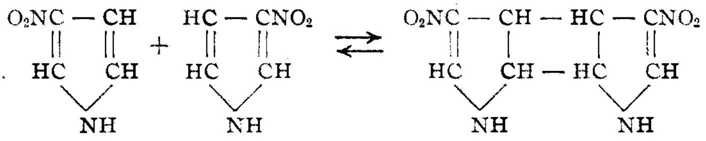
[1] *Atti dei Lincei* [1] 20, 311 (1911).

then we should be able to obtain the same β-nitropyrrole by the action of heat upon our acid of known constitution (m. p. 217°). Numerous attempts to drive off carbon dioxide from this acid met with failure. Upon heating it alone, violent decomposition always ensued. The use of equal quantities of naphthalene, however, sufficed for its successful decomposition, when the two substances were heated together in a sealed tube. From the decomposition products thus finally obtained we have been able to isolate a small amount of a substance melting at 63.5° and in every way identical with the nitropyrrole described by Angeli and Allessandri. The constitution therefore of our acid (m. p. 217°) sufficed in its decomposition for the determination of the structure for nitropyrrole and checked the work of Angeli and Allessandri in selecting the β-position for the nitro group in this final product. There was obtained, however, in this same decomposition mixture as removed from the sealed tube, a new substance melting at 101° and possessing the same empirical formula as nitropyrrole—$C_4H_4O_2N_2$. The molecular weight of the compound, as determined by an elevation of the boiling point of its solution in benzene, corresponded to $C_8H_8O_4N_4$. A further determination of molecular weight by lowering of the freezing point of its aqueous solution indicated a much lower value approaching the value corresponding to a simple nitropyrrole. We may assume, therefore, that β-nitropyrrole polymerizes at higher temperatures and that in aqueous solution we have the conditions favorable for an equilibrium between the two forms. In fact, by repeated crystallization from ice cold water, we have been able to convert the 101° product into the 63.5° product. The structure of the dimolecular nitropyrrole is shown in (IX).

(VII).



(IX).

β,β-Dinitrodipyrrole.

The formation of the dinitrodipyrrole is analogous to the formation of tripyrrole (pyrrole red) but the presence of the nitro group is naturally sufficient to stop the polymerization at the dimolecular stage.

The lower melting nitropyrrole (63.5°) has been found by us to be present only to a small extent. We could not isolate a sufficient product for a molecular-weight determination. The monomolecular product as prepared by us and also as prepared by us in accordance with the method of Angeli and Allessandri, melted accurately at 63.5°, but when heated for several minutes, not to exceed 75–80° in the same melting point tube, the melting point at once arose to the neighborhood of 100°. In fact this change of the lower melting product to the 101° melting product seems entirely to have escaped the notice of Angeli and Allessandri.

The dimolecular form of β-nitropyrrole is thus seen to be more stable than the monomolecular form. These facts do not interfere with our conclusion that β'-nitro-α-carbopyrrolic acid by decomposition loses carbon dioxide and yields β-nitropyrrole (VII).

Naturally the next step must involve a similar decomposition for each of the two remaining nitrocarbopyrrolic acids. The acid melting at 146°, as obtained by Ciamician, was now prepared and mixed with naphthalene and heated in a sealed tube to the point of charring. From the decomposition mixture in the sealed tube we were able to isolate the same nitropyrrole (IX) melting at 101° (as well as a portion of the monomolecular form) that resulted from the decomposition of the acid melting at 217°. We must conclude, therefore, that the acid (of Ciamician) melting at 146° is no other than the β-nitro-α-carbopyrrolic acid (III).

The third acid, melting at 161°, was finally prepared according to the method of Anderlini, and in better yields by a method described in the Experimental Part. When heated with naphthalene in a sealed tube this acid underwent decomposition only slowly. Prolonged action, however, gave eventually a decomposition product which by extraction with water yielded only a very small quantity of a yellow oil. This oil was not stable and could not be obtained sufficiently pure for analysis. There can be no doubt but what this oil is α-nitropyrrole (VIII) which is to be expected from the third possible acid. The proof then of the structure of this acid (I) as an α'-nitro-α-carbopyrrolic acid is established. The instability of α-nitropyrrole is to be expected from its analogy to α-nitrothiophene and α-nitrofurfurane, both of which so far have not been prepared.

Experimental Part.

The preparation of glycine ester was accomplished by the well-known method of Emil Fischer,[1] the hydrolysis of gelatin by the action of hydrochloric acid and the final separation of the ester in the form of its hydrochloride from an absolute alcoholic solution. The preparation of sodium nitromalonic aldehyde was carried out in the usual way, by the action of sodium nitrite upon mucobromic acid.[2]

β,β-Aldehydonitroethylidenaminoacetic Ethyl Ester, $C_7H_{10}O_5N_2$ (IV).—Equimolecular quantities of sodium nitromalonic aldehyde (1.6 grams) and of glycine ethyl ester hydrochloride (1.4 grams) were dissolved in 6–7 cc. of 60–70% alcohol, and the mixture gently warmed for a few minutes upon the water bath to effect complete solution. When this was accomplished the reaction mixture was allowed to stand at room temperature, whereupon, in the course of 15–30 minutes, the yellow product

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[1] *Z. physiol. Chem.*, **33**, 151 (1901); see Fischer's "Untersuchungen über aminosäuren," p. 672 (1906).

[2] *Am. Chem. J.*, **22**, 25 (1899).

crystallized out. Calculated upon the basis of the sodium nitromalonic aldehyde the yield of the crude product came to 80% of the theoretical yield of ethylidenaminoacetic ester. This ester is readily soluble in acetone, chloroform, ethyl acetate or acetic acid; fairly soluble in alcohol, ether, water or benzene, crystallizing well from each; slightly soluble in carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It crystallizes best from alcohol or water in the form of thin, pale yellow prisms melting at 104°. Hofmann's carbylamine test when applied to this ester failed to show the presence of the original primary amine group. The presence of a secondary amine also could not be detected, whereas the action of this ester in the presence of an ammoniacal solution of silver nitrate showed the presence still of an aldehyde group, a point further established by the formation of a crystalline phenylhydrazone by the action of phenylhydrazine. The compound, therefore, may be considered as of the structure previously described. This intermediate product is very stable toward acid solutions, crystallizing well from concentrated hydrochloric acid. Alkalies transform it into the pyrrole derivative, but when in extreme dilution they are comparatively without action upon it. In view of this the first step in the condensation between the glycine ester and nitromalonic aldehyde may often be hastened by the addition of only a few drops of sodium hydroxide solution.

0.1702 g. subst. gave 0.2582 g. CO_2 and 0.0791 g. H_2O; 0.1452 g. subst. gave 18.6 cc. N_2 (24° and 745.4 mm. over H_2O).

Calc. for $C_7H_{10}O_5N_2$: C, 41.57; H, 4.98; N, 13.87. Found: C, 41.37; H, 5.19; N, 14.01.

β'-Nitro-α-carbopyrrolic Ethyl Ester, $C_7H_8O_4N_2$ (VI).—When 1 g. of β,β-aldehydonitroethylidenaminoacetic ethyl ester, dissolved in 8 cc. of 65% alcohol and treated with 40 drops of a 20% sodium hydroxide solution, was warmed on the water bath at a temperature not above 50°, red crystals of β'-nitro-α-carbopyrrolic ester separated from the red reaction mixture in the course of half an hour. Tarry substances were inclined to form when the temperature overstepped 50°. The yield of the product amounted to about 90% of the theoretical nitrocarbopyrrolic ester calculated from the weight of ethylidenaminoacetic ester taken.

The preparation of this intermediate ethylidenaminoacetic ester is in no wise necessary, as the condensation may be carried through in one process. Equimolecular quantities of sodium nitromalonic aldehyde (1.6 g.) and of glycine ethyl ester hydrochloride (1.4 g.) were dissolved in 6–7 cc. of warm 65% alcohol. 40 drops of a 20% sodium hydroxide solution were then added and the red reaction mixture set aside for half an hour at a constant temperature of 50°. At the end of this time the red crystalline mass which had separated was removed, washed with alcohol, and dried. The yield amounted to 75% of the theoretical nitrocarbopyrrolic acid ester when based upon the aldehyde salt employed. The pure product is readily soluble in acetone or acetic acid; fairly soluble in alcohol, ether, benzene, chloroform, or ethyl acetate; slightly soluble in water, carbon tetrachloride, or carbon disulfide, and insoluble in ligroin. It is best purified by crystallization from alcohol, from which it separates in almost colorless, glistening prisms melting at 174°.

0.1736 g. subst. gave 0.2896 g. CO_2 and 0.0702 g. H_2O; 0.1823 g. subst. gave 25.3 cc. N_2 (23.2° and 748.2 mm. over H_2O).

Calc. for $C_7H_8O_4N_2$: C, 45.63%; H, 4.39; N, 15.23. Found: C, 45.50; H, 4.52; N, 15.31.

β'-Nitro-α-carbopyrrolic Methyl Ester, $C_6H_6O_4N_2$.—This product was prepared in an identical manner to that of the preceding ethyl ester, glycine methyl ester replacing the previously employed glycine ethyl ester. The pure substance is readily soluble in acetone; fairly soluble in alcohol, ether, benzene, ethyl acetate, chloroform or acetic acid, crystallizing well from each; slightly soluble in water, carbon disulfide, or carbon tetrachloride, and insoluble in ligroin. It crystallizes best from alcohol in almost colorless prisms melting at 198°. This product was prepared primarily to check that product which had been reported by Anderlini[1] as melting at 197°. The two products were found to be identical in all respects and when mixed melted practically at 198°.

0.1581 g. subst. gave 0.2448 g. CO_2 and 0.0538 g. H_2O.

Calc. for $C_6H_6O_4N_2$: C, 42.35%; H, 3.54%. Found: C, 42.22; H, 3.81.

β'-Nitro-α-carbopyrrolic Acid, $C_5H_4O_2N_2$ (II).—One gram of β'-nitro-α-carbopyrrolic ethyl ester was brought into solution with 15 cc. of a 20% potassium hydroxide solution and the contents of the flask warmed for 5–6 hours under a reflux condenser upon a steam bath. The yellow solution was then cooled by placing the flask in a freezing mixture and concentrated hydrochloric acid added to the point of neutralization, whereupon the yellow color disappeared. Without especial cooling the heat of neutralization would lead to decomposition of the acid sought. The neutral solution was next extracted with ether and a pale yellow product thus removed. The yield amounted to 90% of the theoretical weight of the acid. This free acid is readily soluble in alcohol, ether, ethyl acetate, or acetone; fairly soluble in water or glacial acetic acid; slightly soluble in chloroform, benzene, carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It crystallizes well from hot water in beautiful, colorless needles which melt with decomposition at 217°. It crystallizes unchanged from glacial acetic acid. Anderlini obtained this same acid by the hydrolysis of the nitro-α-carbopyrrolic methyl ester previously described. The acid which he obtained was, of course, the same as is obtained by the hydrolysis of the ethyl ester. Our product melting at 217°,

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[1] *Loc. cit.*

when mixed with his, melted constant at the same point and in all respects the two acids were found to be identical. They each contain one molecule of water of crystallization which is readily lost by standing in a desiccator over sulfuric acid.

0.5033 g. subst. lost 0.0508 g. H_2O over H_2SO_4 in 48 hours.

Calc. for $C_5H_4O_4N_2.H_2O$: H_2O, 10.33%. Found: H_2O, 10.09%.

0.2106 g. anhydrous subst. gave 0.2974 g. CO_2 and 0.0495 g. H_2O; 0.1341 g. anhydrous subst. gave 21.9 cc. N_2 (21° and 745.5 mm. over H_2O).

Calc. for $C_5H_4O_4N_2$: C. 38.47; H, 2.56; N, 17.96. Found: C, 38.52; H, 2.63; N, 18.14.

By the action of potassium carbonate this acid was converted into the corresponding potassium salt, which is extremely soluble in water but crystallizes from its concentrated solution in the form of needles or prisms of a light yellow color.

0.1814 g. K salt gave 0.0827 g. K_2SO_4.

Calc. for $C_5H_3O_4N_2K$: K, 20.17%. Found: K, 20.47.

The salt therefore contains no water of crystallization.

The silver salt of this acid is easily precipitated by the addition of a silver nitrate solution to an aqueous solution of the acid made neutral with ammonium hydroxide. It forms a yellow, flocculent, precipitate.

0.2885 g. subst. gave 0.2064 g. AgBr.

Calc. for $C_5H_3O_4N_2Ag$: Ag, 41.04. Found: Ag, 41.09.

β-Nitro-α-carbopyrrolic Acid, $C_5H_4O_2N_2$ (III).—This acid, the first known of the nitrocarbopyrrolic series, was prepared by Ciamician[1] from pyrocoll by the action of fuming nitric acid. Our method differed but slightly from his and required a definite strength of nitric acid and the maintenance of a constant temperature. Two grams of pyrocoll were added in small portions to about 40 g. of nitric acid (sp. gr. = 1.50) cooled to 4–10°. When all of the pyrocoll had been added, the red solution was warmed upon the steam bath for a few moments and then poured into an excess of ice-water. The dark yellow, noncrystalline precipitate of a dinitropyrocoll was filtered off and treated at once with 20 cc. of a 20% sodium hydroxide solution. The mixture was then heated upon the steam bath until a test portion failed to give a precipitate when acidified with dilute sulfuric acid. When this hydrolysis was thus shown to be complete the solution was cooled by a freezing mixture and finally acidified by dilute sulfuric acid. Extraction with ether removed the yellow, crystalline product melting at 140–6° as obtained by Ciamician. This β-nitro-α-carbopyrrolic acid is readily soluble in acetone, alcohol, ether, ethyl acetate or acetic acid; fairly soluble in chloroform, benzene or water; slightly soluble in carbon disulfide or carbon tetrachloride and insoluble in ligroin. β′-Nitro-α-carbopyrrolic acid is somewhat more

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[1] *Loc. cit.*

soluble in water than this acid, whereas α′-nitro-α-carbopyrrolic acid is somewhat less soluble in water. The acid crystallizes best from water in almost colorless needles containing one molecule of water of crystallization. The anhydrous acid melts at 146°.

β-Nitro-α-carbopyrrolic Methyl Ester, $C_6H_6O_4N_2$.—Although the three nitro-α-carbopyrrolic acids have been known, only two of the corresponding esters are described in the literature. The methyl ester of β′-nitro-α-carbopyrrolic acid, melting at 198°, and the methyl ester of α′-nitro-α-carbopyrrolic acid, melting at 179°. As the third, β-nitro-α-carbopyrrolic acid was readily converted into its methyl ester by an hour's heating of the silver salt with methyl iodide under a reflux condenser. The ether extract of the dry residual mass gave the crude ester. This methyl ester is readily soluble in acetone; fairly soluble in alcohol, ether, benzene, ethyl acetate, chloroform or acetic acid, crystallizing best from alcohol; slightly soluble in water and insoluble in ligroin. The pure ester melted at 162°.

α′-Nitro-α-carbopyrrolic Acid, $C_5H_4O_4N_2$ (I).—This acid can be prepared by the method of Anderlini[1] in which α-carbopyrrolic ester is nitrated directly with nitric acid. The yield is exceedingly small and no appreciable amount can be prepared by this process. We have studied the reaction under a wide range of temperature and concentrations of acid and find it in no way practicable. The α-carbopyrrolic ester here employed may best be prepared by the method of Oddo,[2] which far surpasses the other methods that may be mentioned. But even with a good method for the production of the ester the next step, namely its nitration, failed to give satisfactory results. There is no doubt but what all three nitrocarbopyrrolic acids are to be found in the reaction mixture. For these reasons we have chosen preferably to work with the residues left upon the nitration of pyrocoll according to the method of Ciamician. By certain nitrations of pyrocoll, namely those carried out at lower temperatures, we were able to procure an appreciable quantity of this α′-nitro-α-carbopyrrolic acid sufficient for the purpose of this investigation. In a subsequent communication we shall describe the methods in detail. The pure α′-nitro-α-carbopyrrolic acid as obtained by us from pyrocoll, as well as by the method of Anderlini, is readily soluble in acetic acid, acetone, alcohol, ether or ethyl acetate; fairly soluble in chloroform, benzene, or water, crystallizing from either in small, colorless, needle clusters; slightly soluble in carbon disulfide or carbon tetrachloride, and insoluble in ligroin. It is best purified by crystallization from water from which it separates with one molecule of water of crystallization. The anhydrous acid melts sharply at 161°.

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[1] *Loc. cit.*

[2] *Gazz. chim. ital.*, [1] 39, 649 (1909).

Decomposition of the Nitro-α-carbopyrrolic Acids into the Corresponding Nitropyrroles.—The decomposition of the carbopyrrolic acids by heat alone is well known. Attempts, however, to decompose these three nitrocarbopyrrolic acids met with many failures. Heating the acids alone resulted in explosive decompositions. When the β′-nitro-α-carbopyrrolic acid, m. p. 217°, and of which we possessed a good supply, was heated with pumice, lime, soda-lime, sand, finely divided copper, nickel, and other metals, no satisfactory product could be procured. A distillation of the acid under diminished pressure, however, gave us a very small quantity of a nitropyrrole, but far better results were obtained when equal quantities of this acid and naphthalene were heated in a sealed tube up to, but not beyond, the point of slight charring, when the heating was discontinued. By the action of hot water upon this reaction mixture we were able to extract a fair quantity of a dark yellow crystalline product of no definite melting point. When the product was digested for a few minutes with ice water we obtained a yellow solution which, upon spontaneous evaporation, yielded small prisms of nitropyrrole melting at 63.5°. The part left undissolved by the ice-water was now dissolved in warm water and this solution also allowed to evaporate spontaneously. From this portion we obtained small, yellow prisms melting, when pure, at 101°. It was next observed that the nitropyrrole melting at 63.5° underwent some change when warmed for any length of time at 70–80°. The product resulting was found to have a melting point at 101°. This led us at once to the belief that the higher melting substance was a polymer of the first product. A molecular-weight determination confirmed this view, as will be seen in the discussion of these two nitropyrroles under the next heading.

The preparation of a nitropyrrole by the elimination of carbon dioxide from our β′-nitro-α-carbopyrrolic acid indicates directly the constitution of the nitropyrrole produced, namely that of a β-nitropyrrole. This, as will be seen shortly, is identical with the nitropyrrole obtained by Angeli and Allessandri.[1]

The method just described for the elimination of carbon dioxide from β′-nitro-α-carbopyrrolic acid with consequent production of nitropyrrole, was next applied to the β-nitro-α-carbopyrrolic acid, melting at 146°. Under exactly analogous conditions we were able to reproduce the same results as described with β′-nitro-α-carbopyrrolic acid. The β-nitropyrrole obtained was in every way identical with that previously described. The conclusion is, therefore, evident: these two acids which give the same β-nitropyrrole must have the nitro groups in the β′- and β-positions, respectively.

When the third acid, α′-nitro-α-carbopyrrolic acid, was subjected to

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[1] *Loc. cit.*

this same decomposition reaction with naphthalene in a sealed tube, the product yielded no trace of a β-nitropyrrole but only a yellow, oily substance of no definite stability. We identified it as a nitro product and one which could not be purified. We may, therefore, conclude that it is the α-nitropyrrole which evidently would be formed by the elimination of carbon dioxide from the acid in question.

Monomolecular β-Nitropyrrole, $C_4H_4O_2N_2$.—In order to check conclusively our results with those of Angeli and Allessandri,[1] who first prepared a nitropyrrole, we have reproduced their results as follows: 5 g. of pyrrole were dissolved in 30–40 cc. of dry ether and to this solution 2.4 g. of sodium wire and 9.51 g. of ethyl nitrate were added. The flask with its contents was now warmed under a reflux condenser protected from the air by a U-tube containing strong alkali. The temperature, however, was not permitted to rise over 30°. Into this flask, after about 48 hours, when the sodium had completely dissolved and a dark brown salt had separated out, small pieces of ice were added and the mixture extracted with ether to remove any pyrrole unacted upon. The cold aqueous residue was then treated with bone-black and the clear filtrate treated with a silver nitrate solution, whereupon a dark yellow, non-crystalline precipitate was formed. This latter step must be carried out in the absence of all but a ruby light. Though no mention is made of this fact by the authors, we have found it absolutely essential to the success of the experiment. The precipitate was filtered off and washed repeatedly with cold water until no appreciable amount of silver remained in the washings. While still moist this precipitate was treated with sodium chloride and water. Silver chloride and the excess of sodium chloride were removed by filtration. The clear, yellow solution was now saturated with carbon dioxide and extracted with ether, from which by evaporation a yellow oil was obtained. At this stage we found that it was advantageous to dissolve the oil in a mixture of benzene and high-boiling ligroin and after treating with bone-black to allow the solution to evaporate in the open air. When cooled the residual oil slowly gives small yellow highly refractive crystals of nitropyrrole. These melted at 63.5° as described by the authors. Upon heating for a short time it was observed that this product had slowly changed into that higher melting substance (101°) which we obtained in the decomposition of two of the nitrocarbopyrrolic acids. The yield of β-nitropyrrole from the method just described cannot much exceed 1% of the theoretical quantity, but for our purpose we were able to secure sufficient to confirm the identity of the products from these two sources mentioned. The decomposition of β′-nitro-α-carbopyrrolic acid gave us the best yield in β-nitropyrrole—approximately 50% of the theoretical value.

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[1] *Loc. cit.*

β,β-Dinitrodipyrrole, $C_8H_8O_4N_4$ (IX).—This substance, which we have shown to be readily prepared by heating the monomolecular form for a few minutes at a point slightly above its melting point, 63.5°, is best purified by crystallization from water in pale yellow prisms melting at 101°. It may also be crystallized from benzene in the form of yellow plates. It is readily soluble in alcohol, acetone, ethyl acetate, or acetic acid; fairly soluble in water, benzene, or chloroform, and almost insoluble in ligroin, carbon tetrachloride or carbon disulfide.

0.1437 g. subst. gave 0.2270 g. CO_2 and 0.0493 g. H_2O; 0.1216 g. subst. gave 27.6 cc. N_2 (21.1° and 743.0 mm. over H_2O).

Calc. for $(C_4H_4O_2N_2)_2$: C, 42.85; H, 3.59; N, 25.01. Found: C, 43.08; H, 3.84; N, 25.12.

Subst. 0.1294 g., 0.2694 g., 0.4222 g.; benzene, 15.2 g.; elevation, 0.097, 0.200, 0.401.

Calc. for $(C_4H_4O_2N_2)_2$: 224.06. Found: 222.0.

Subst. 0.0981 g.; water, 32.32 g.; depression, 0.035.

Calc. for $(C_4H_4O_2N_2)_2$: 224.06. Found: 161.3.

Although the product maintains its dimolecular structure at higher temperatures and in anhydrous solvents, the action of cold water alone is seemingly sufficient for a partial dissociation into the monomolecular form as just indicated. The preparation of β-nitropyrrole cannot be successfully accomplished by the method of Angeli and Allessandri. Though the method we have described for its preparation gives fair yields any large quantity must be found difficult to prepare.

Summary.

1. Pyrrole-α-carboxylic acid (α-carbopyrrolic acid) had been known to yield three distinct nitro derivatives. The position of the nitro group, however, in any one of these acids could not be determined.

2. The synthesis of β′-nitro-α-carbopyrrolic acid from nitromalonic aldehyde and glycine ester lead to the identity of one of these three unknown nitro acids.

3. With one acid thus known the decomposition of each was studied. Heating with naphthalene in sealed tubes sufficed for the elimination of carbon dioxide from each and for the consequent production of a nitropyrrole as residue. The β′-nitro-α-carbopyrrolic acid gave β-nitropyrrole as expected. The other nitro acid, therefore, which yielded the same β-nitropyrrole became identified at once as β-nitro-α-carbopyrrolic acid, whereas that acid which yielded the unstable α-nitropyrrole was necessarily accorded the constitution of an α′-nitro-α-carbopyrrolic acid.

4. Although the constitution of nitropyrrole itself had previously been unknown, the work here described establishes it as a β-nitropyrrole, a compound readily transformed into a dimolecular form β,β-dinitrodipyrrol. The unstable α-nitropyrrole was found incapable of isolation.

ANN ARBOR, MICH.