

When the desired vacuum is reached, block *S* is so adjusted that float *M* will just open switch *P*. As the air leaks into the oven, the column of mercury will raise the float *M* and close the switch, thus starting the pump.

The use of the bulb *I* reduces the pressure required to throw the switch to 25 mm. of mercury in place of 80 mm., the height which would be required were the tube without the bulb.

The above apparatus has been in constant use in our laboratory for two months and has given entire satisfaction.

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

THE CONSTITUTION OF THE THREE SYMMETRICAL DINITROPYROCILLS.

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The nitration of pyrocoll, as first reported by Ciamician and Danesi,¹ led to the formation of a dinitropyrocoll of unknown constitution. The hydrolysis of this dinitro derivative yielded a mononitro- α -carbopyrrolic acid in which the position of the nitro group still remained an undetermined factor. In a study of the constitution of each of the three possible mononitro- α -carbopyrrolic acids,² it was found that the method of Ciamician and Danesi was the only practical way of preparing this one acid just mentioned. Eventually, when we were able to establish the position of the nitro group for each of the three acids, this acid became identified as β -nitro- α -carbopyrrolic acid. The constitution therefore of the intermediate product—the unknown dinitropyrocoll—was then open for consideration and in similar manner each of the three possible symmetrical dinitropyrocills may be studied.

The production of this one β -nitro- α -carbopyrrolic acid in the absence of isomers when the unknown dinitropyrocoll is hydrolyzed (a fact noted also by Ciamician), has led us to the conclusion that, during this nitration of pyrocoll, two nitro groups apportion themselves equally and symmetrically upon the two pyrrole nuclei in the pyrocoll molecule. That configuration, therefore, for this dinitropyrocoll, which alone will satisfy this condition and, by hydrolysis, permit of the total conversion into two molecules of β -nitro- α -carbopyrrolic acid, is designated as sym. β, β -dinitropyrocoll.

¹ *Gazz. chim. ital.*, 12, 39 (1882).

² THIS JOURNAL, 37, 2538 (1915).

acid the condensation, in the presence of acetic anhydride, proceeded smoothly and gave an almost quantitative yield of β,β -dinitropyrocoll. The required temperature, that of boiling acetic anhydride, would indicate the initial formation of an acetyl derivative and the subsequent loss of acetic acid between two molecules of this product during the condensation into one molecule of β,β -dinitropyrocoll.

The nitration of pyrocoll, as described by Ciamician and Danesi, led no doubt in most cases to the formation of β,β -dinitropyrocoll. Slight alterations in the concentrations of nitric acid used and in the temperature at which nitration was conducted naturally may be expected to give widely varying results. Ciamician and Danesi employed fuming nitric acid cooled with ice. We, on the other hand, have found that the best conditions for the production of this same β,β -dinitropyrocoll are obtained when fuming nitric acid is reduced to a specific gravity of 1.50 and a constant temperature of $4-10^\circ$ is maintained. Under these conditions the nitration was found to proceed almost exclusively to the formation of β,β -dinitropyrocoll.

When the temperature of the nitric acid was considerably lowered, we were able to isolate from the reaction mixture a new isomer differing entirely from that dinitropyrocoll just described. The best conditions for the production of this second dinitropyrocoll consist in the use of an acid of the specific gravity of 1.6-1.7 and a constant temperature so low as -10° to -4° . The product thus obtained is never pure but more or less contaminated with a third dinitropyrocoll. These two new dinitropyrocills can be separated by gentle warming with acetic acid in which the latter, or third isomer, is scarcely soluble. When thus separated the former, or second named isomer, is best purified by crystallization from acetic acid. It decomposes at $240-5^\circ$. The third isomer is produced in small quantity only, a 10% yield is usually the maximum, whereas the yield of the other two may exceed 60% of the theoretical value.

The second product, obtained as above, was hydrolyzed in the same manner as stated for the β,β -dinitropyrocoll. The acid obtained melted at 161° and proved to be identical in all respects with the acid prepared by Anderlini¹ (m. p. 161°), and lately² shown by us to possess the constitution of an α' -nitro- α -carbopyrrolic acid. By reason of the fact that this acid is the only product resulting from the hydrolysis just mentioned, and further by reason of its ready conversion, through the agency of acetic anhydride, into this same original dinitropyrocoll from which it was prepared, we are led to the conclusion that this second-named isomer of dinitropyrocoll is α',α' -dinitropyrocoll (II).

The third dinitropyrocoll, which, as has been stated, can be procured

¹ *Gazz. chim. ital.*, **19**, 350 (1889).

² *THIS JOURNAL*, **37**, 2545 (1915).

only in very small amounts is that product left undissolved in the glacial acetic acid used to remove the second isomer, or α',α' -dinitropyrocoll. It is best purified by crystallization from nitrobenzene. It is the most stable of the three forms, its decomposition taking place above 315° .

When hydrolyzed by alkali this dinitropyrocoll yielded an acid (m. p. 217°), which was found identical with that synthesized by us from nitromalonic aldehyde and glycine ester, and to which the constitution of a β' -nitro- α -carbopyrrolic acid must be assigned. This acid, prepared by either method, is readily converted by the action of acetic anhydride into the original dinitropyrocoll from which it alone results upon hydrolysis. The structure therefore of this third and last isomer of the symmetrical dinitropyrocolls must accord with that of a β',β' -dinitropyrocoll (III).

The study of the possible unsymmetrical dinitropyrocolls has not been undertaken. The nitration of pyrocoll leads primarily, if not exclusively, to the symmetrical dinitro derivatives. Though we may well have undertaken to synthesize the unsymmetrical derivatives by condensation between mixed acids, our interest lay primarily in the nitration of pyrocoll itself.

Experimental Part.

Preparation of Pyrocoll.—In a general way our method of preparation was the same as that described by Weidel and Ciamician.¹ 100 g. of commercial gelatin (preferably of low grade), were tightly compressed into a copper retort of about 750 cc. capacity. The retort cover was then clamped tightly upon the vessel. A slightly bent glass tube 1 meter long and 16 mm. diameter, to serve as a condenser, was now fitted into the 20 mm. opening in the retort cover and the joint tightly packed with shredded asbestos. It was found best to tilt the retort slightly toward the exit tube and to apply the full flame of a large Méker burner just behind the cover or exit. The tendency for the gelatin to foam out through the exit tube is thus avoided as all of the material in passing over the heated portion of the retort undergoes instant decomposition. After 15–20 minutes' heating oily drops begin to collect in the upper end of the condenser and at the same time pyrocoll distills over, condensing as a yellow crystalline product on the walls of the tube. The heating must be sufficiently rapid to insure complete decomposition and also to avoid the slow formation of ammonium salts, which are likely to be seen as a white crystalline deposit at the farther end of the condenser. On the other hand, a too rapid heating may easily lead to a choking of the delivery tube. When the decomposition of this amount of gelatin was complete, usually one hour's time, the contents of the tube were washed out with alcohol and the insoluble pyrocoll collected upon a filter. The yield amounted to

¹ *Monats.*, 1, 280 (1880).

0.5–0.6 g. for 100 g. of gelatin. The pyrocoll (m. p. 268°), was purified by crystallization from boiling glacial acetic acid.

β,β -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$ (I).—This product is that which was obtained by Ciamician and Danesi,¹ in nitrating pyrocoll with fuming nitric acid. By hydrolysis with alkali he obtained from it the nitro- α -carbopyrrolic acid melting at 146°. The constitution of this acid, now known, establishes the constitution of this dinitropyrocoll as already discussed. The method employed by Ciamician and Danesi does not give uniform results, but leads to mixtures of all three of the possible dinitropyrocills. The following method, however, will give the best yield of this particular β,β -dinitropyrocoll with the smallest portions of the other two isomers.

Two grams of pyrocoll were added in about 0.1 g. portions to approximately 40 g. of nitric acid of 1.50 sp. gr. A temperature of 4 to 10° must be maintained throughout these additions. The pyrocoll dissolved readily with the attendant evolution of nitrogen tetroxide. When all of the pyrocoll was thus dissolved the dark brown liquid was gently warmed on the steam bath for a few moments, or until the evolution of the excess of nitric oxides had ceased. The red liquid was then poured into an excess of ice and water (150 cc.), whereupon a yellow noncrystalline product was precipitated. This product removed and dried upon a porous plate was treated with cold ethyl acetate which leaves undissolved the other dinitropyrocills possibly present. That product left upon the evaporation of the ethyl acetate was dissolved in hot glacial acetic acid, from which it crystallizes in fine yellow prisms. The yield amounts to about 60% of the theoretical quantity. This β,β -dinitropyrocoll is fairly soluble in acetic acid, nitrobenzene, acetone or ethyl acetate; slightly soluble in alcohol or benzene; and practically insoluble in ether, ligroin, chloroform or water. It dissolves to a considerable extent in cold ethyl acetate. Crystallization is best accomplished from a solution in nitrobenzene or glacial acetic acid. β,β -Dinitropyrocoll has no melting point but decomposes at 220–5°. When warmed with a 20% potassium hydroxide solution until a test portion fails to give a precipitate upon acidification with dilute sulfuric acid the hydrolysis of this dinitropyrocoll is complete, and from the original alkaline solution, when thoroughly cooled and acidified, extraction with ether will give the β -nitro- α -carbopyrrolic acid as previously described.

0.1191 g. subst. gave 22.3 cc. N_2 (24.7° and 748.4 mm. over H_2O).

Calc. for $C_{10}H_4O_2N_4$: N, 20.30. Found: N, 20.49.

If now this β -nitro- α -carbopyrrolic acid is dissolved in acetic anhydride and heated to boiling under a reflux condenser for one hour the resulting dark yellow solution, upon evaporation, is found to give the original β,β -dinitropyrocoll as anticipated.

¹ *Loc. cit.*

α',α' -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$ (II).—No mention is made by Ciamician and Danesi¹ of having obtained even a trace of this isomer along with the dinitropyrocoll which they prepared. The following method for the nitration of pyrocoll was found to yield chiefly the α',α' -dinitropyrocoll. Two grams of pyrocoll were added in about 0.1 g. portions to about 40 g. of strong nitric acid of 1.6 to 1.7 sp. gr. A temperature of -10° to -4° must be maintained throughout this nitration. If the temperature should rise we naturally may expect a certain quantity of the β,β -dinitropyrocoll will be formed as in the preceding preparation. If the temperature falls too low the pyrocoll dissolves without attendant nitration and the subsequent dilution of the nitration mixture yields a tarry product of unknown composition. When the nitration was complete, according to the method just described, the red solution was warmed upon the water bath for a few minutes and then poured into about 150 cc. of ice water. The precipitate thus formed has a somewhat more voluminous appearance than the corresponding precipitate in the case of the β,β -dinitropyrocoll. After filtration the precipitate is dried upon a porous plate and treated with cold ethyl acetate to remove any traces of the β,β -dinitropyrocoll. It is next treated with glacial acetic acid, under gentle warming, and the solution concentrated, whereupon the α',α' -dinitropyrocoll crystallizes out in fine, yellow prisms. The yield is about 60% of the theoretical quantity. This α',α' -dinitropyrocoll is fairly soluble in acetic acid, nitrobenzene, or acetone; slightly soluble in alcohol, benzene, or ethyl acetate, and practically insoluble in ether, ligroin, chloroform, or water. It crystallizes best from acetic acid or nitrobenzene. It has no sharp melting point, but decomposes at $240-5^\circ$.

0.1406 g. subst. gave 26.2 cc. N_2 (24.3° and 746.6 mm. over H_2O).

Calc. for $C_{10}H_4O_2N_4$: N, 20.30. Found: N, 20.39.

When warmed with alkali α',α' -dinitropyrocoll is hydrolyzed in exactly the same manner as β,β -dinitropyrocoll but with the production in this case of α' -nitro- α -carbopyrrolic acid melting at 161° . This acid in turn when treated with boiling acetic anhydride is reconverted into the corresponding α',α' -dinitropyrocoll.

β',β' -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$, (III).—In the nitration of pyrocoll, as described for the preparation of α',α' -dinitropyrocoll there is always found a variable amount of this third isomeric dinitropyrocoll. Scarcely any β',β' -dinitropyrocoll is produced in that nitration carried out primarily for the preparation of β,β -dinitropyrocoll. Consequently in the preceding preparation the product left after treatment with ethyl acetate, which removes any traces of β,β -dinitropyrocoll, is next treated with warm glacial acetic acid, in which α',α' -dinitropyrocoll is quite soluble. The residue left after this second process of extraction is practically pure

¹ *Loc cit.*

β',β' -dinitropyrocoll. This latter is only sparingly soluble in hot glacial acetic acid and when so dissolved may be crystallized out in fine, yellow prisms. It is best however to crystallize it from nitrobenzene, in which it is more soluble. β',β' -Dinitropyrocoll is fairly soluble in nitrobenzene or acetone; slightly soluble in acetic acid, alcohol, benzene, or ethyl acetate, and practically insoluble in ether, ligroin, chloroform or water. It decomposes without melting at $315-20^\circ$. Upon hydrolysis with strong alkali, in the same manner as directed for the preceding dinitropyrocolls, this product yielded β' -nitro- α -carbopyrrolic acid, melting at 217° . And again by the action of acetic anhydride this latter is most readily converted into the original β',β' -dinitropyrocoll.

0.1392 g. subst. gave 0.2211 g. CO_2 and 0.0225 g. H_2O ; 0.1734 g. subst. gave 32.8 cc. N_2 (25.5° and 741.3 mm. over H_2O).

Calc. for $\text{C}_{10}\text{H}_4\text{O}_6\text{N}_4$: C, 43.46; H, 1.46; N, 20.30. Found: C, 43.33; H, 1.81; N, 20.42.

Since β' -nitro- α -carbopyrrolic acid is that particular acid which is easily synthesized from glycine ester and nitromalonic aldehyde,¹ its preparation by the nitration of pyrocoll is not to be advised. Furthermore, the nitration of pyrocoll with this acid in view has never yielded more than 10% of the theoretical quantity. It should be stated further that a small amount of this β',β' -dinitropyrocoll is also usually found in the product obtained from the nitration of pyrocoll according to the method of Ciamician and Danesi. In this connection we wish to express our indebtedness to Mr. E. M. Honan, of this laboratory, for the care he has taken in checking our results.

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THE REACTION BETWEEN ALCOHOLS AND AQUEOUS SOLUTIONS OF HYDROCHLORIC AND HYDROBROMIC ACIDS.

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In a previous paper² it was shown that a large number of aliphatic and aromatic alcohols react with aqueous solutions of hydrobromic acid and hydriodic acid and form the corresponding organic bromides and iodides, and that, in certain cases, analogous reactions take place with hydrochloric acid. When the alcohols and the constant-boiling mixtures of the acids and water were distilled, good yields of the halides were obtained. The substances formed in this way were free from the impurities which are present when phosphorous compounds are used to prepare them. The method has been used when especially pure halides

¹ *Loc. cit.*

² *Am. Chem. J.*, 38, 627 (1907).