

dilute sulfuric acid was added and then, after half an hour, or longer, the solution was diluted with water and the acids extracted with petroleum ether. After distilling the latter, the acids were dissolved in a 10% solution of sodium carbonate, the solution cooled with ice water and a 4% solution of potassium permanganate added in portions to destroy the unreduced campholytic acid. Sulfuric acid and acid sodium sulfite were added till the oxides of manganese passed into solution and the acids were extracted with ether and distilled with steam. The treatment with potassium permanganate was repeated to make sure of the removal of all unchanged campholytic acid and the purified acid was also dissolved in a solution of sodium carbonate and the solution extracted with ether to remove some campholytolactone which was likely to be present. The specific rotation of the acid and the melting point and rotation of its amide are given above. The acid is an oily liquid which has a specific gravity of 0.9915 at 20°.

Calculated for $C_8H_{15}CO_2H$: C, 69.11; H, 10.33.

Found: C, 69.21; H, 10.15.

0.0517 gram took 3.32 cc. 0.1 N NaOH; calculated 3.33 cc.

The *amide*, $C_8H_{15}CONH_2$, crystallizes from petroleum ether in plates, which melt at 86.5°.

Calculated for $C_9H_{17}ON$: N, 9.05%; found: 9.10%.

Attempt to Prepare Active Δ^5 -Campholytic Acid.—The *dl*- Δ^5 -campholytic

acid, $\begin{array}{c} CH_2 - CHCH_3 \\ | \quad | \\ C(CH_3)_2 \\ | \\ CH = C - CO_2H \end{array}$, was prepared some time ago.¹ It was hoped

that by preparing the acid from *d*-dihydrocampholytic acid an optically active form could be obtained. The preparation was carried out essentially as with the racemic compound. The acid obtained melted at 91° and when mixed with some of the acid previously prepared the melting point was not changed. No rotation could be established for the acid with a 7% solution in alcohol. The preparation of the α -bromo derivative had evidently changed the original acid to a racemic form.

The solubility of Δ^5 -campholytic acid is approximately one part in 5000 parts of water at 25°.

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THE PHTHALYL CYANIDES.

By GIBBS BLACKSTOCK.

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Some time ago Mr. C. H. Robinson, in this laboratory, prepared phthalyl cyanide in the hope of obtaining from it, by hydrolysis, the corresponding dibasic acid, but his work was interrupted before completion. The

¹ *Am. Chem. J.*, 26, 289 (1901).

author has repeated and extended Mr. Robinson's work and also prepared and studied isophthalyl cyanide and terephthalyl cyanide.

Three methods were used for the preparation of the cyanides.

I. The method used by Claisen¹ for the preparation of benzoyl cyanide. The acid chloride was dissolved in about three times its weight of anhydrous ether and to this was added about twice the calculated amount of anhydrous hydrogen cyanide and a slightly larger excess of pyridine was then added gradually to the ethereal solution. In each case a white precipitate was immediately thrown down, which gradually disappeared and at the end of one to two days the crude cyanides had completely separated out as dark viscous oils. This white precipitate appears to be a product of the acid chloride and pyridine and will be further investigated.

II. The acid chloride and mercuric cyanide in acetone solution were boiled for several hours with reflux condenser. This method did not give satisfactory yields and was abandoned.

III. The acid chloride was heated in a sealed tube with excess of mercuric cyanide for 5-7 hours at 140-160°. Mercuric cyanide gave much better results in this method than potassium cyanide.

The three isomeric cyanides are very similar in properties. They are all brown powders, soluble in acetone, alcohol, pyridine, ammonia and potassium hydroxide solution and insoluble in water, ether, benzene, ligroin and dilute acids. They become viscous at temperatures in the neighborhood of 300°, with apparent decomposition. When heated in a sealed tube with conc. hydrochloric acid they were not hydrolyzed, but with 15-20% potassium hydroxide solution either in sealed tubes or with reflux condenser they gave a slight odor of ammonia which probably indicated slight hydrolysis of the nitrile.

Phthalyl Cyanide.—16 grams pyridine were added, gradually, to a solution of 10 grams phthalyl chloride and 5 grams hydrogen cyanide in 25 cc. ether. After 2 days the viscous mass was dissolved in ammonia, precipitated by acidification and washed with hot water. Yield, 3.5 grams (40%). The phthalyl cyanide prepared by this method was always found to be too high in nitrogen unless very carefully purified.

Ten grams phthalyl chloride and 16 grams mercuric cyanide were heated in a sealed tube for 6 hours at 140-160°. The product was dissolved in acetone and precipitated with ether, then dissolved in ammonia and purified as above. Yield, 4.4 grams (50%).

Calculated for $C_6H_4(COON)_2N$, 15.2. Found: N, 15.3.

Isophthalyl Cyanide.—Ten grams isophthalyl chloride were dissolved in 30 cc. ether, 3 grams hydrogen cyanide added and then, gradually, 16 grams pyridine. The crude cyanide was dissolved in ammonia, pre-

¹ Ber., 31, 1023.

cipitated by hydrochloric acid, washed with water, again dissolved in ammonia and reprecipitated by boiling off the ammonia. Yield, 3.5 grams (40%).

Five grams isophthalyl chloride was heated in a sealed tube with 8 grams of mercuric cyanide for 6 hours at 200°. Yield, 1.7 grams (30%).

Calculated for $C_6H_4(COON)_2$: N, 15.2. Found: N, 15.0.

Terephthalyl Cyanide.—Ten grams terephthalyl chloride were dissolved in 25 cc. ether, 4 grams hydrogen cyanide added and 16 grams pyridine. The cyanide was purified in the same manner as the isophthalyl cyanide. Yield, 4 grams (45%).

In the sealed tube, 4 grams terephthalyl chloride and 7 grams mercuric cyanide gave 1.2 grams (30%).

Calculated for $C_6H_4(COON)_2$: N, 15.2. Found: N, 15.2.

The first method of preparation is not recommended for phthalyl cyanide, as there is a product rich in nitrogen from which it is hard to purify it, but in the other cases it gives better yields than the preparation from mercuric cyanide.

These experiments were carried out under the direction of Professor F. B. Allan.

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ACTION OF ALCOHOLIC AMMONIA ON α,β -DIBROMOPROPIONIC ACID.

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By heating α,β -dibromopropionic acid with concentrated aqueous ammonia in a sealed tube, Klebs¹ obtained α,β -diaminopropionic acid, the yield of which never exceeded 58%, and in most cases was considerably less. Klebs suspected the presence of other products but succeeded in isolating only the product mentioned. Subsequently, Neuberg and Ascher,² while using the method proposed by Neuberg and Silbermann,³ which increased the yield of α,β -diaminopropionic acid to 65%, isolated α -oxy- β -aminopropionic acid (isoserine) to the amount of 10%.

Some experiments, originally undertaken for the purpose of still further increasing the yield of α,β -diaminopropionic acid and in which α,β -dibromopropionic acid was acted upon by a cold saturated solution of ammonia in absolute alcohol, have shown that ammonia will form still another compound. Under these conditions, α,β -diaminopropionic acid is not formed but the sole product seems to be ammonium α -bromoacrylate. Since the yield of this salt is very good, it would seem to present an easy

¹ *Z. physiol. Chem.*, **19**, 301-338 (1894).

² *Biochem. Z.*, **6**, 559-62 (1907).

³ *Ber.*, **37**, 341-345 (1904).