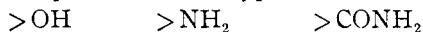


scores of other organic groups, it is concluded that hypobromite is an invaluable reagent for detecting and distinguishing phenolic and aromatic amino compounds. None of the aliphatic or terpene compounds tested gave color effects; only compounds of the types:



With *p*-phenylenediamine, it yields nearly quantitatively a white crystalline solid melting with decomposition at 105°. This and other products of the hypobromite reaction are being investigated.

SEATTLE, WASH., July 4, 1908.

## THE OXIDATION AND THE REDUCTION OF $\beta,\gamma$ -DIPHENYL- $\gamma$ -CYANBUTYRIC ACID.

BY S. AVERY AND G. R. MCDOLE.

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*Oxidation.*—As additional evidence of the correctness of the constitution of the acid under consideration, the formation of which by the action of sodium hydroxide on cinnamic ester mixed with benzyl cyanide has been described by us<sup>1</sup> in a previous communication, we will briefly give the results obtained by oxidation.

The alkali salt of the acid was found to be attacked very readily by alkaline permanganate. Difficulty, however, was experienced in stopping the action till the greater part of the substance had been oxidized to benzoic acid. The oxidation of the acid with neutral permanganate is more easily controlled. The following procedure was found to give the most satisfactory results:

One and one-half grams of potassium permanganate were dissolved in about 100 cc. of water and 1 gram of the cyan acid stirred into the solution. After mixing as thoroughly as possible, the whole was heated on the water bath. The acid gradually went into solution and the odor of hydrocyanic acid became evident. Towards the end of the reaction an odor resembling acetophenone was noticed. As soon as the permanganate was completely reduced, the acid in the meantime having gone into solution, the product of the reaction was filtered from the manganese dioxide formed and precipitated by means of hydrochloric acid. Yield, 0.6 gram. By repeated recrystallization from alcohol, 0.3 gram of pure benzoyl hydrocinnamic acid was obtained. This substance was identified by the melting point 162°,<sup>2</sup> crystalline form (octahedrons),<sup>3</sup> and analysis of a silver salt which gave 30.1 per cent. Ag. Calculated, 29.9. The formation of benzoyl hydrocinnamic acid by oxidation of the cyan acid can be explained only on the supposition that the latter

<sup>1</sup> THIS JOURNAL, 30, 596.

<sup>2</sup> Ber., 21, 1350.

<sup>3</sup> Ibid., 29, 2586.

possesses the constitution assigned it, namely,  $\beta,\gamma$ -diphenyl- $\gamma$ -cyanbutyric acid.

*Reduction.*— $\beta,\gamma$ -Diphenyl- $\gamma$ -cyanbutyric acid dissolved in acetic acid is not reduced by zinc dust. Dissolved in moist ether it is indifferent to aluminum amalgam. In alcoholic solution it is very slightly attacked by sodium amalgam even with long-continued treatment. Hydriodic acid hydrolyzes it to diphenylglutaric acid but seems to have no reducing action. Metallic sodium added to a cold solution in absolute alcohol, provided the solution be kept cold by surrounding with ice, has only a slight effect. Reduction was finally effected by this agent when the temperature was carefully regulated. Five grams of the cyan acid were dissolved in 100 cc. absolute alcohol. The solution was heated to boiling, sodium gradually added in small quantities at a time through a return flow condenser, and sufficient absolute alcohol added from time to time to hold the greater part of the sodium ethylate in solution. In all 25 grams of sodium were used. The heating was continued through the entire operation, during which the maximum temperature was not allowed to exceed  $105^{\circ}$ . After cooling, the mixture was acidified strongly with hydrochloric acid on the addition of which hydrocyanic acid was evolved, while salt and a milky organic substance were precipitated. Water was now added in sufficient quantity to dissolve the salt formed. The mixture was heated on the water bath and as the excess of alcohol was removed by evaporation, the milky substance collected as an oil on the surface and on cooling solidified to a semicrystalline mass. This was found to be  $\beta,\gamma$ -diphenylbutyric acid mixed with a little of the hydrochloride of  $\beta,\gamma$ -diphenyl- $\delta$ -amino-valeric acid. The semicrystalline mass was removed and the clear solution allowed to stand for several days, during which time crystals gradually formed. These proved to be the nearly pure hydrochloride just mentioned. The two reduction products under consideration can be separated almost quantitatively by boiling in benzene. The relative amounts of the butyric and valeric derivatives appear to be about 4 to 1, but in each case much of the material was lost in the recrystallization necessary to obtain the acids in pure condition.

The portion soluble in benzene was recrystallized from dilute acetic acid. After recrystallization a number of times it melted fairly sharply at  $96^{\circ}$ .<sup>1</sup>

Calculated for  $C_{16}H_{16}O_2$ : C, 80.0; H, 6.7.  
Found: C, 79.8; H, 6.9.

Titration 0.2077 gram required 12.0 cc. 0.1 N NaOH. Calculated for 1 acid H in  $C_{16}H_{16}O_2$  12.8 cc. NaOH.

The substance is therefore  $\beta,\gamma$ -diphenylbutyric acid.

<sup>1</sup> *J. Chem. Soc.*, **71**, 156.

The portion not soluble in benzene was dissolved in dilute acetic acid and precipitated with concentrated hydrochloric acid. The process was repeated till clean, white, blunt needles were obtained, which melted sharply at 256°. These were dried over sulphuric acid in an atmosphere containing a little hydrochloric acid gas, and then in vacuum.

Calculated for  $C_{17}H_{20}O_2NCl$ : C, 66.9; H, 6.6; N, 4.6; Cl, 11.6.

Found: C, 66.4; H, 6.8; N, 4.8; Cl, 11.6.

This substance is then the hydrochloride of  $\beta$ , $\gamma$ -diphenyl- $\delta$ -amino-valeric acid. Up to the present time a sufficient yield has not been secured to enable a careful study of derivatives of the substance to be made.

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## THE NITRATION OF $\beta$ -*p*-TOLYLGLUTARIC ACID.

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Early in the spring of 1902 the senior author collected all of the unpublished work done under his direction on the aromatic glutaric acids. After the usual delay in the hands of the editor, this work appeared in the July number of the *American Chemical Journal*<sup>1</sup> with no mention of the date when it was received. A part of the article related to the nitration of  $\beta$ -phenylglutaric acid.<sup>2</sup> In the meantime there appeared an article on the same subject by Schroeter and Meerwein,<sup>3</sup> received by the editor of the *Berichte*, May 27th, and published with the usual promptness. The two articles appeared simultaneously in America, though, of course, Schroeter and Meerwein's work was seen first by European readers. The results obtained were essentially the same in both cases. The nitration product obtained in the greater quantity proved to be  $\beta$ -*p*-nitrophenylglutaric acid, m. p. 237°. The product obtained in smaller quantity was described as follows:<sup>4</sup> "This product has not as yet been investigated, but is probably  $\beta$ -*orthonitro*phenylglutaric acid. Under the conditions of nitration given, the amount of this compound formed does not exceed ten per cent. of the phenylglutaric acid used." It may be added that Meerwein and Schroeter<sup>5</sup> have since shown this product to consist of a mixture of the *orthonitro* and *metanitro* acids. The *ortho*-nitro acid is of especial interest because of the possibility of converting it into quinoline derivatives, but on account of their technical priority,

<sup>1</sup> *Amer. Chem. J.*, **28**, 48.

<sup>2</sup> Avery and Beans, *Amer. Chem. J.*, **28**, 55.

<sup>3</sup> *Ber.*, **35** 2073 (compare also statement of Meerwein & Schroeter, *Ber.*, **36**, 2670).

<sup>4</sup> *Amer. Chem. J.*, **28**, 55.

<sup>5</sup> *Ber.*, **40**, 1586.