

## NOTES

N-Derivatives of *p*-Arsanilic Acid

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In a previous study<sup>1</sup> attempts were made to synthesize N-triazinylaminobenzeneearsonic acids by reaction of *p*-arsanilic acid with various compounds known to produce melamine. None of the reaction products proved to be the desired compound but several new and interesting arsenicals were isolated and identified.

When cyanogen bromide was treated with *p*-arsanilic acid under neutral conditions, hydrobromic acid was produced and a reaction product of the composition  $\text{NCNHC}_6\text{H}_4\text{AsO}_3\text{H}_2$  was isolated. On hydrolysis in dilute alkali, it gave *p*-carbamidobenzeneearsonic acid, identical with the reaction product obtained from potassium cyanate and *p*-arsanilic acid.<sup>2</sup> Sticklings has reported<sup>3</sup> the isolation of *p*-carbamidobenzeneearsonic acid from the interaction of cyanogen bromide and *p*-arsanilic acid but apparently did not isolate the intermediate cyanamido compound. *p*-Cyanamidobenzeneearsonic acid also reacted with alcoholic hydrogen chloride to give a substance with the properties of an imino ether. Ammonolysis with alcoholic ammonia converted the imino ether to a substance having the properties of a guanidine but which failed to crystallize. A solution of this gummy product could also be hydrolyzed to the carbamido derivative.

Dicyandiamide also condensed with *p*-arsanilic acid in neutral solution to give 4-biguanidobenzeneearsonic acid. After the biguanido compound had been heated with 4 *N* hydrochloric acid, 4-guanylcarbanido- or 4-carbamylguanidobenzeneearsonic acid hydrochloride crystallized upon cooling the solution. Further hydrolysis resulted in complete decomposition to arsanilic acid.

**4-Cyanamidobenzeneearsonic Acid.**—*p*-Arsanilic acid (108 g.) and sodium hydroxide (20 g.) were dissolved in water (500 ml.). A solution of potassium cyanide (65 g.) in water (500 ml.) was treated with bromine (*ca.* 160 g.) until a faint bromine color was evident. The solution of cyanogen bromide was added to the solution of arsanilic acid with cooling and the resulting mixture allowed to stand forty-eight hours at room temperature. The product crystallized as a yellow granular mass and was dissolved in hot water, charcoaled, filtered and the filtrate cooled to yield 85 g. (70%) of the colorless, crystalline material. The compound was insoluble in cold water but soluble in hot water and in acids and alkalis with decomposition.

*Anal.* Calcd. for  $\text{C}_7\text{H}_7\text{AsN}_2\text{O}_3$ : As, 30.95; N, 11.58. Found: As, 30.98; N, 11.62.

Five grams of 4-cyanamidobenzeneearsonic acid was dissolved in sodium hydroxide, filtered and the resulting solution made acid to congo red paper. The resulting crystal-

line solid was identical in properties and analysis with 4-carbamidobenzeneearsonic acid.

*Anal.* Calcd. for  $\text{C}_7\text{H}_9\text{AsN}_2\text{O}_4$ : As, 28.70. Found: As, 28.82.

**4-Biguanidobenzeneearsonic Acid.**—*p*-Arsanilic acid (217 g.) was dissolved in hot water (1000 ml.) with sufficient sodium hydroxide to give a solution of pH 4.8. Dicyandiamide (200 g.) was added and the solution refluxed for two hours and then cooled. The product crystallized in small granules (150 g.) which were recrystallized from hot water. The compound was soluble in dilute acids and alkalis and could be recovered unchanged from such solutions.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{As}_2\text{O}_3$ : As, 24.87; N, 23.26. Found: As, 24.79; N, 23.02.

**4-Guanylcarbamido Acid or Carbamylguanidobenzeneearsonic Acid Hydrochloride.**—4-Biguanidobenzeneearsonic acid (50 g.) was refluxed for thirty minutes in 4 *N* hydrochloric acid (375 ml.). The hydrochloride, which crystallized from the cold solution, was recrystallized from dilute hydrochloric acid, yield 25 g.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{AsClN}_4\text{O}_4$ : As, 22.20; N, 16.58. Found: As, 22.22; N, 16.30.

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The Preparation of  $\alpha$ -Phenyl- $\beta$ -benzoylpropionic and  $\alpha,\gamma$ -Diphenylbutyric Acids

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In connection with another problem it was desirable to synthesize a large quantity of  $\alpha,\gamma$ -diphenylbutyric acid. Alkaline hydrolysis of the easily available  $\alpha$ -phenyl- $\beta$ -benzoylpropionitrile<sup>1</sup> was found to be more reliable than acid hydrolysis<sup>2</sup> and the catalytic reduction of the resulting  $\alpha$ -phenyl- $\beta$ -benzoylpropionic acid was superior to the Clemmensen method of producing the  $\alpha,\gamma$ -diphenylbutyric acid.<sup>3</sup>

**$\alpha$ -Phenyl- $\beta$ -benzoylpropionic Acid.**—To a paste of 70 g. (0.3 mole) of  $\alpha$ -phenyl- $\beta$ -benzoylpropionitrile and 15 ml. of ethanol was added 350 ml. of 10% aqueous sodium hydroxide solution. The mixture was refluxed for six hours, then the almost clear solution was diluted with 2.5 liters of water and clarified by filtration with Norit. Acidification of the filtrate with glacial acetic acid to incipient crystallization followed by complete precipitation with hydrochloric acid gave 58 g. (76.7%) of crude acid, m. p. 148–149°.

The crude acid, 66 g. from this and another run, was crystallized from 400 ml. of hot chloroform by adding 500 ml. of petroleum ether (b. p. 60–70°) and allowing the solution to stand at 40° overnight. The yield of white crystals was 65 g., m. p. 150–151° (reported<sup>2</sup> 152–153°).

A similar run with 65 g. of the nitrile gave 64 g. (90%) of the crystallized acid, m. p. 150–151°.

**$\alpha,\gamma$ -Diphenylbutyric Acid.**—To a warm solution of 25.4 g. (0.10 mole) of  $\alpha$ -phenyl- $\beta$ -benzoylpropionic acid in 100 ml. of glacial acetic acid was added 2 ml. of 60%

(1) Banks, Grmizit, Tillitson and Controulis, *THIS JOURNAL*, **66**, 1771 (1944).

(2) German Patent 213,155.

(3) Sticklings, *J. Chem. Soc.*, 3131 (1928).

(1) "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 498.

(2) Lapworth and Wechsler, *J. Chem. Soc.*, **97**, 38 (1910); Hahn and Lapworth, *ibid.*, **85**, 1355 (1904).

(3) Kohler and Kimball, *THIS JOURNAL*, **55**, 4632 (1933).