

anilide and the chloroacetanilide-Cl<sup>36</sup> recrystallized from water; yield 23.8 mg. (28.6%).

**$\delta$ -(*p*-Chlorophenyl)-hydantoic Acid-Cl<sup>36</sup>.**—Chloroacetanilide-Cl<sup>36</sup> was hydrolyzed by heating under reflux with 0.5 ml. of concd. HCl and *p*-chlorophenyl isocyanate Cl<sup>36</sup> was formed by the reaction of *p*-chloroaniline-Cl<sup>36</sup> hydrochloride with phosgene in dioxane. Excess phosgene was removed by evacuation at 0° and the isocyanate reacted with glycine (30 mg.) in alkaline solution. Acidification precipitated  $\delta$ -(*p*-chlorophenyl)-hydantoic acid-Cl<sup>36</sup>; yield 17.6 mg. (15.6%). Non-radioactive hydantoic acid, prepared by this method, melted at 189–191° with decomposition.

CONTRIBUTION FROM THE  
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### Synthesis of $\alpha$ -Aminocyclopropylacetic Acid

BY PETER H. LOWY

In a study of the biological effect of analogs of the naturally occurring amino acids, D,L- $\alpha$ -aminocyclopropylacetic acid was synthesized. It was prepared by a Strecker synthesis from cyclopropanecarboxaldehyde. The intermediate hydroxynitrile was aminated in methanolic ammonia.<sup>1</sup> Because of the instability of cyclopropane compounds toward acids the hydrolysis was carried out with barium hydroxide.<sup>2</sup> Like many other D,L-amino acids cyclopropylaminoacetic acid tastes slightly sweet. The structure was confirmed by oxidation with ninhydrin to cyclopropanecarboxaldehyde.

The amino acid did not affect the growth of wild type *Neurospora crassa* 25a on minimal medium<sup>3</sup> in concentrations of 10 and 40  $\gamma$  per 3 ml.<sup>4</sup>

#### Experimental

**Cyclopropylcyanide** was prepared from  $\gamma$ -chlorobutyronitrile<sup>5</sup> by the method of Schlatter.<sup>6</sup>

**Cyclopropane carboxaldehyde** was prepared by reduction of cyclopropyl cyanide with one-quarter mole of lithium aluminum hydride according to Smith and Rogier.<sup>7</sup>

**$\alpha$ -Aminocyclopropylacetic Acid.**—A solution of 12.7 g. of ammonium chloride in 32 ml. of water was kept at 0–5° and stirred mechanically while 14 g. of cyclopropane carboxaldehyde, followed by a solution of 14.3 g. of potassium cyanide in 22 ml. of water, was added dropwise. The mixture was stirred for 2 hours at room temperature and allowed to stand overnight. It was extracted with six 30-ml. portions of ether. After removal of the ether by distillation, the residue of the combined ether extracts was dissolved in 80 ml. of methanol. The solution was saturated with dry ammonia at 0–5°, and allowed to stand for 4 days. Excess ammonia was driven off with an air stream and the solvent removed *in vacuo*. The residual crude cyclopropylaminoacetonitrile weighed 9.9 g.

18.5 g. of barium hydroxide octahydrate was dissolved in its crystal water (steam-bath). It was stirred mechanically at ca. 95° while the nitrile (thinned with 5 ml. of methanol) was added dropwise over 40 minutes. After heating and stirring for another 40 minutes, 100 ml. of hot water was added. The hot solution was saturated with carbon dioxide and filtered by suction with the aid of Super-Cel. The precipitate was extracted twice with 50 ml. of hot water while bubbling with carbon dioxide. The combined clear filtrates were concentrated *in vacuo* to 10–20 ml. 2.21 g. (9.3% based on the aldehyde) of the crude amino acid was obtained in several crops (directly from the aqueous concentrate and by precipitation with methanol or ethanol).

(1) H. T. Clark and H. J. Bean, "Organic Syntheses," Coll. Vol. II, 2nd Printing, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 29.

(2) J. Ford, THIS JOURNAL, **67**, 876 (1945); *Org. Synth.*, **27**, 1 (1947).

(3) G. W. Beadle and E. L. Tatum, *Am. J. Bot.*, **32**, 678 (1945).

(4) Kindly tested by Phyllis B. Ellman.

(5) C. F. H. Allen, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 156.

(6) M. J. Schlatter, *Org. Syntheses*, **23**, 20 (1943).

(7) L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 4047 (1951).

*Anal.* Calcd. for C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>N: C, 52.15; H, 7.88; N, 12.17. Found: C, 51.99; H, 7.66; N, 12.33.<sup>8</sup>

**Degradation with Ninhydrin.**—To 115 mg. of the amino acid dissolved in 5 ml. of hot water a solution of 700 mg. of ninhydrin in 20 ml. of 0.2 molar citrate buffer (pH 5) was added.<sup>9</sup> The mixture turned dark purple and was heated in a steam-bath for 20 minutes, while with a slow stream of nitrogen the volatile aldehyde was driven into a trap containing a solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The 2,4-dinitrophenylhydrazone alone as well as mixed with that prepared from authentic cyclopropanecarboxaldehyde melted at 186°.

(8) Microanalysis by G. A. Swinehart.

(9) S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

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### Ion Aggregation in Gallium(III) Chloride Solutions Containing Added Alkali

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In an earlier communication,<sup>1</sup> it was reported that solutions of gallium(III) chloride, bromide, or nitrate may be treated with up to approximately 3 moles of hydroxyl ion per mole of gallium ion initially present without effecting precipitation of the hydrous oxide. Such solutions remain perfectly clear but flocculate sharply and completely upon addition of more alkali. Although appreciable delays in hydrous oxide or hydroxide precipitation are not particularly uncommon, lack of precipitation in the presence of essentially stoichiometric quantities of hydroxyl ion is unusual. Either excessive ion aggregation in solution due to added hydroxyl ion or peptization of the hydrous oxide by excess gallium ion may be regarded as a possible explanation.

Electrometric titration data<sup>1</sup> indicate that in the range prior to flocculation added hydroxyl ion is consumed without appreciable increase in pH, but they do not permit decision between an ion aggregation process and a peptization process. If, however, the diffusion current in a gallium(III) salt solution is proportional to gallium ion concentration and remains reasonably constant, polarographic data might permit such a decision. It seems reasonable that any ion aggregation resulting from binding of gallium ions by hydroxyl ions would manifest itself in a corresponding reduction in the magnitude of the diffusion current, whereas if the nature of the gallium species remained the same (as in peptization), no alterations in diffusion current would result when hydroxyl ion is added.

Zeltzer<sup>2</sup> reported that gallium(III) is reduced irreversibly at the dropping mercury electrode at a potential of  $-1.08$  v. (*vs.* normal calomel electrode) from dilute solutions of its salts in 0.001 *N* hydrochloric acid. For solution of the present problem, irreversibility is of no consequence if level diffusion regions can be obtained. Experiment showed this to be possible in chloride solutions containing 0.05 *M* potassium chloride as supporting electrolyte. Corrected diffusion current values obtained by subtracting residual current values were found to be

(1) T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).

(2) S. Zeltzer, *Collection Czechoslov. Chem. Commun.*, **4**, 319 (1932).