

solution, was treated with one mole of a dilute hypobromous acid solution. Its method of preparation is identical with that described above for the dichlorohydrin. The pure crystalline dibromohydrin melts at 148–149°. It has approximately the same solubilities as the monobromohydrin.

*Anal.* Calcd. for  $C_5H_8O_4Br_2$ : Br, 54.76. Found: Br, 54.84.

### Summary

1. Vinylacrylic acid absorbs hypochlorous and hypobromous acid in the 3,4-positions to form 3-chloro-4-hydroxyvinylacrylic acid and 3-bromo-4-hydroxyvinylacrylic acid, respectively.

2. Vinylacrylic acid chlorohydrin absorbs a molecule of hypochlorous acid to give a dichlorohydrin. In the same way vinylacrylic acid bromohydrin absorbs a molecule of hypobromous acid to give a dibromohydrin.

3. These addition reactions of vinylacrylic acid are found to be in perfect agreement with the general theory on the addition reactions of conjugated systems as previously developed.

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### NOTES

#### A Simplified Method of Preparation of Alpha Amino Acid Amides.<sup>1</sup>—

It has been generally recognized by investigators of the chemistry of alpha amino acids that good yields of the amides of these acids are difficult to obtain. Fischer,<sup>2</sup> Koenigs<sup>3</sup> and Bergell<sup>4</sup> were leaders in this field of work. The Fischer method and that of Koenigs for obtaining the amides consists in treatment of the alpha amino acid esters with liquid ammonia in sealed tubes at room temperature for from ten days to three months. Bergell, Heintz,<sup>5</sup> and others obtained the amides by treatment of the alpha halogen fatty acid esters or amides with alcoholic ammonia at fairly high temperatures. The yields of amides obtained by the use of these methods were not particularly satisfactory.

The authors undertook the preparation of certain alpha amino acid amides as a preliminary to the study of the chemistry of their biuret reactions.<sup>6</sup> A simplification of the older methods for obtaining the amides was accomplished. The esters of glycine, *d*-alanine and *dl*-leucine were treated separately in a shaking device with methyl alcohol which had been saturated previously with ammonia at 0°. The reactions were allowed

<sup>1</sup> The contents of this paper were reported at the National Meeting of the American Chemical Society held at Cincinnati, September, 1930.

<sup>2</sup> E. Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine," Julius Springer, Berlin, 1906.

<sup>3</sup> E. Koenigs and B. Mylo, *Ber.*, **41**, 4427 (1908).

<sup>4</sup> P. Bergell and T. Brugsch, *Z. physiol. Chem.*, **67**, 97 (1910).

<sup>5</sup> W. Heintz, *ibid.*, **64**, 348 (1910).

<sup>6</sup> Mary M. Rising and C. A. Johnson, *J. Biol. Chem.*, **80**, 709 (1928); Mary M. Rising, J. S. Hicks and G. A. Moerke, *ibid.*, **89**, 1 (1930).

to proceed at room temperature for a number of hours, and the excess of alcohol and ammonia was then removed under reduced pressure, the amides remaining in the form of white crystals, or as oils which solidified when placed in the refrigerator. This treatment of the esters named produced the amides in good yield. Table I shows at a glance the conditions used by us and the advantages of this plan as compared with the methods and results of previous workers. Glycine amide<sup>7</sup> and *d*-alanine amide were purified by solution in chloroform and reprecipitation from this solution by means of dry ether. *dl*-Leucine amide was purified by recrystallization from benzene. The glycine amide, *d*-alanine amide and *dl*-leucine amides obtained by us melted at 67–68° (uncorr.), 71–72° (uncorr.) and 105–106° (uncorr.), respectively.

TABLE I  
THE PREPARATION OF ALPHA AMINO ACID AMIDES

Amide	Present method		Previous methods	
	Conditions	Yield	Conditions <sup>a</sup>	Yield, %
Glycine amide	Glycine ester (20 g.), CH <sub>3</sub> OH satd. with ammonia (300 cc.), shaking 20 hrs.	(8 g.) 55.7%	Liquid ammonia, bomb, 10 days	33
<i>d</i> -Alanine amide	Alanine ester (3.5 g.), CH <sub>3</sub> OH satd. with ammonia (60 cc.), shaking 50 hrs.	(2.6 g.) 83.7%	Liquid ammonia, bomb, 1 mo.	53
<i>dl</i> -Leucine amide	Leucine ester (4.9 g.), CH <sub>3</sub> OH satd. with ammonia (75 cc.), shaking 80 hrs.	(3.6 g.) 88.5%	Liquid ammonia, bomb, 3 mo.	80–85

CONTRIBUTION FROM THE  
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RECEIVED MAY 15, 1931  
PUBLISHED AUGUST 5, 1931

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**The Reaction of Acetophenone Derivatives with Sodium Hypochlorite.**—It has long been known that acetophenone, when treated with sodium hypochlorite, is changed into benzoic acid. Likewise benzalacetone is decomposed into cinnamic acid.<sup>1</sup> The literature, however, gives very little information regarding the general scope of this procedure for the synthesis of aromatic acids.

The lowered cost of aluminum chloride provides an inexpensive method for the synthesis of certain acetophenone derivatives by means of the Friedel-Crafts reaction. The oxidation of these derivatives with sodium hypochlorite is, however, restricted to compounds which do not contain

<sup>7</sup> During the preparation of glycine amide some glycine anhydride separated and was removed from the reaction mixture at the conclusion of the reaction by filtration.

<sup>1</sup> Noyes, "Organic Chemistry for Laboratory," Chemical Publishing Co., Easton, Pa., 1920, p. 99.