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.[1]— 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,[2] Koenigs[3] and Bergell[4] 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,[5] 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.[6] 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

[1] The contents of this paper were reported at the National Meeting of the American Chemical Society held at Cincinnati, September, 1930.

[2] E. Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine," Julius Springer, Berlin, 1906.

[3] E. Koenigs and B. Mylo, *Ber.*, **41**, 4427 (1908).

[4] P. Bergell and T. Brugsch, *Z. physiol. Chem.*, **67**, 97 (1910).

[5] W. Heintz, *ibid.*, **64**, 348 (1910).

[6] 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[7] 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 Conditions	Yield	Previous methods Conditions[3]	Yield, %
Glycine amide	Glycine ester (20 g.), CH_3OH satd. with ammonia (300 cc.), shaking 20 hrs.	(8 g.) 55.7%	Liquid ammonia, bomb, 10 days	33
d-Alanine amide	Alanine ester (3.5 g.), CH_3OH satd. with ammonia (60 cc.), shaking 50 hrs.	(2.6 g.) 83.7%	Liquid ammonia, bomb, 1 mo.	53
dl-Leucine amide	Leucine ester (4.9 g.), CH_3OH satd. with ammonia (75 cc.), shaking 80 hrs.	(3.6 g.) 88.5%	Liquid ammonia, bomb, 3 mo.	80–85

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PETER S. YANG
MARY M. RISING

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.[1] 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

[7] 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.

[1] Noyes, "Organic Chemistry for Laboratory," Chemical Publishing Co., Easton, Pa., 1920, p. 99.

reactive groups such as nitro or free hydroxyl groups. The results with various derivatives are shown in the following table.

Compound	Observed m. p., acid, °C.	Given[a] m. p., acid, °C.	Yield of acid, %
Acetophenone	121	121	85
4-Methoxyacetophenone	180–183	184	90
4-Chloroacetophenone	234–236	236	93
4-Bromoacetophenone	250–251	250–251	91
4-Methylacetophenone	171–175	176–177	96
3-Nitroacetophenone	.....	140	0
3,4-Dimethylacetophenone	160–162	163	92
3-Methyl-4-methoxyacetophenone	190–192	192–193	92
2-Methyl-4-methoxyacetophenone	175	175	90
Resacetophenone	.....	199	0
Nitroresacetophenone	.....	215	0
p-Hydroxyacetophenone	.....	158	0

Five to 10 gram samples were used in each case.

[a] From Richter "Lexikon" and Beilstein.

Compounds which are not easily halogenated may be treated by passing chlorine slowly into a suspension of the compound in sodium hydroxide solution. Those which easily react with halogens, such as *p*-methoxyacetophenone, may be treated by adding a cold alkaline hypochlorite solution to a methyl alcohol solution of the compound. The latter solvent may frequently be used to increase the solubility of the acetophenone derivative and thereby increase the speed of the reaction. A considerable excess of hypochlorite must be used to ensure complete reaction. At the end of the reaction acetone or sulfur dioxide was added to destroy the excess halogen before the solution was acidified. The free chlorine is easily detected by adding a few drops of the solution to a solution of potassium iodide. Hypochlorite proved much more efficient and convenient than the hypobromite or iodite. With the latter reagents the reaction was much slower and less complete. Furthermore, the separation of bromoform or iodoform from the reaction was often difficult. The general procedure used may be illustrated as follows.

***p*-Chlorobenzoic Acid.**—Five grams of *p*-chloroacetophenone was dissolved in 25 cc. of methyl alcohol and 50 cc. of 20% sodium hydroxide was then added to the solution. Chlorine was passed into the solution while stirring rapidly. The cloudy solution soon began to clear as the temperature rose to about 80°. More alkali was added from time to time until a total volume of 100 cc. had been used. When the solution was practically clear, the chlorine addition was stopped and the solution stirred for about fifteen minutes longer. A small amount of acetone was added to react with the excess chlorine. The solution was treated with a small quantity of Norite and filtered. Upon acidifying with hydrochloric acid

the organic acid was precipitated. The product was practically pure, but was further purified by reprecipitating it from dilute sodium hydroxide. The yield was 93%, m. p. 234–236°.

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Correction. Para-Nitrophenyl Carbamyl Chloride and Para-Nitrophenyl Isocyanate.—In a recent paper it was stated that the product of the action of phosgene on *p*-nitraniline was *p*-nitrophenyl carbamyl chloride.[1] While this is the primary product of the reaction mixture, it has been found that after recrystallization from hot carbon tetrachloride as recommended in the procedure, the final purified product is then free from halogen and is *p*-nitrophenyl isocyanate, m. p. 57.° The analysis given is incorrect. Determination of the nitrogen by the micro Dumas method gave the following results.

Anal. Subs., 3.322 mg.: N_2 gas, 0.577 cc. at 31° and 744 mm. Calcd. for $C_7H_4O_3N_2$: N, 17.07. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 17.09.

The purified product with m. p. 57° is therefore *p*-nitrophenyl isocyanate[2] and is the reagent from which the urethans were prepared. It is evident that the *p*-nitrophenyl carbamyl chloride lost hydrogen chloride during the recrystallization from boiling carbon tetrachloride.

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COMMUNICATIONS TO THE EDITOR

INTERATOMIC FORCES IN BINARY ALLOYS

Sir:

Under this title, N. W. Taylor has recently published [THIS JOURNAL, **53**, 2423 (1931)] a test of Langmuir's theory of non-electrolyte solutions which seems to me unfortunate in three respects. Following Hildebrand and Sharma [*ibid.*, **51**, 467 (1929)], he has confused Hildebrand's definition [*ibid.*, **51**, 66 (1929)] of a "regular solution," for which at constant composition $T \log a_1/N_1$ is independent of the temperature, with that of a "symmetrical system," for which at constant temperature $\log (a_1/N_1)/N_2^2$

[1] Shriner and Cox, THIS JOURNAL, **53**, 1601 (1931).

[2] This has also been noted by van Hoogstraten, Doctor's Dissertation Rijks University, Leiden, June 30, 1931.