

By the use of the pyridine and alcohol method glycine was obtained from the glycine hydrochloride in a 65-73% yield.

This method of synthesis is being extended to the preparation of numerous other amino acids.

We wish to thank Eli Lilly and Company for assistance in this work.

Experimental

β -Hydroxyethylphthalimide.—In a 1-liter Erlenmeyer flask fitted with a variable take-off condenser was placed 148 g. of phthalic anhydride. To this was added 61 g. of pure ethanolamine at such a rate that the reaction did not become too vigorous. The reaction mixture was then heated to 175° and kept at that temperature for two hours at the end of which time 18 cc. of water had been removed at the take-off. The melt was cooled and recrystallized out of 500 cc. of water. A yield of 181 g. melting at 126-127° was obtained. An additional 8 g. of pure material was obtained by evaporating the filtrate to 50 cc. The total yield was 189 g. or 99%.

Phthalylglycine.—In a 2-liter three-neck flask fitted with a dropping funnel and a stirrer, was placed 25 g. of β -hydroxyethylphthalylimide, 800 cc. of water containing 30.1 g. of potassium dichromate and 10 cc. of glacial acetic acid. A solution of 25.5 g. of sulfuric acid and 250 cc. of water was added to the above mixture over a period of fifteen minutes during which time the solution was being heated to boiling. After the solution had boiled for one-half hour the flame was removed and the mixture was allowed to cool overnight. The next day the phthalylglycine was filtered off, washed with cold water to remove the chromium salts, and the combined filtrates placed in a two-liter flask. The solution was concentrated under reduced pressure to about 450 cc., cooled to 5°, filtered and washed. The total weight of phthalylglycine separated at this point was about 20 g. Upon further concentration to about 200 cc. a precipitate was obtained which was contaminated with a considerable amount of chromium salts. This mixture along with the material

obtained by further evaporation to 50 cc. was dried and extracted with acetone. The acetone solution was evaporated to dryness and yielded an additional 4 to 5 g. of phthalylglycine free from chromium compounds. This made a total of 24.0-24.8 g. of crude product; yield 89-93%. Attempts at this point to purify the phthalylglycine took considerable time and caused some loss of the phthalyl compound. Since the only impurity at this point is phthalic acid which is removed in the next step it is advisable to use the crude material for the following hydrolysis.

Glycine Hydrochloride.—To 24.8 g. of the impure phthalylglycine in a 500-cc. ground-glass jointed flask, fitted with a reflux condenser, was added 250 cc. of 18% hydrochloric acid and the mixture refluxed vigorously for ten hours. The solution was then cooled to 5° and filtered to remove the phthalic acid. The filtrate was then evaporated to dryness under reduced pressure. Two 20-cc. portions of water were added to the flask and the mixture evaporated to dryness, under reduced pressure, after each addition. The process was then repeated three more times using 15 cc. of absolute alcohol in place of the water; yield 11.6-12.6 g. or 79-85% based on ethanolamine. Purified phthalylglycine gives a 98% yield.

Glycine.—To 10 g. of glycine hydrochloride was added 10 cc. of water and the mixture was warmed until the glycine hydrochloride dissolved. At this point 10 cc. of pyridine was added and the glycine was precipitated by the addition of 50 cc. of methyl alcohol. The mixture was allowed to cool for four hours in the refrigerator. The glycine was then filtered off and washed with three or four 20-cc. portions of methyl alcohol to free it of pyridine. Glycine obtained by this method was free of halogen and weighed 4.4-4.9 g.; yield 65-73%.

Summary

1. Glycine hydrochloride has been prepared in a 79-85% yield by a new method.
2. Glycine has been obtained from glycine hydrochloride in a 65-73% yield.

BLOOMINGTON, INDIANA RECEIVED FEBRUARY 15, 1943

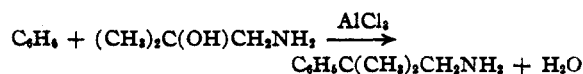
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Condensation of Amino Alcohols with Benzene

BY C. M. SUTER AND A. WAYNE RUDDY¹

The condensation of simple alcohols with benzene in the presence of aluminum chloride has been described in the literature² but no report has been found of such a condensation when the alcohol molecule also contains an amino group. In the present study of the behavior of a variety of amino alcohols with benzene it has been shown that in the presence of a considerable excess of

anhydrous aluminum chloride a tertiary amino alcohol such as 1-amino-2-methyl-2-propanol gives a high yield of the β,β -dialkylphenethylamine.



On the other hand 1-amino-2-propanol reacts to only a slight extent and no reaction occurs with ethanolamine. The condensation takes place with the amino alcohols containing a

(1) Sharp and Dohme post-doctorate Fellow, 1940-1941.
 (2) Huston and Kaye, *THIS JOURNAL*, **64**, 1576 (1942). This reference reviews much earlier work.

tertiary hydroxyl regardless of whether the amino group is primary, secondary, or tertiary. The results obtained in these condensations are summarized in Table I; the last two phenethylamine derivatives are new compounds. These were converted into their hydrochlorides which were analyzed. The other hydrochlorides correspond in properties to those obtained from the phenethylamines prepared by condensing benzene and an unsaturated amine^{3a} or from the action of formamide on an alkylated phenylacetone.^{3b}

TABLE I
CONDENSATION OF BENZENE AND AMINO ALCOHOLS

Amino alcohol	Phenethylamine derivative			
	Yield, %	B. p., °C.	(Mm.)	M. p., HCl salt, °C.
(CH ₃) ₂ C(OH)CH ₂ NH ₂	87	87-89	10
(CH ₃) ₂ C(OH)CH ₂ NHCH ₃	78	92-92.5	11
(CH ₃) ₂ C(OH)CH ₂ NHC ₂ H ₅	86	96-98	11	191.5-192.5
(CH ₃) ₂ C(OH)CH(NH ₂)CH ₃	63	100-102	10	214-215
(CH ₃) ₂ C(OH)CH(NHC ₂ H ₅)CH ₃	63	99-100.5	9	230-231 ^a
(CH ₃) ₂ C(OH)C(NH ₂)(CH ₃) ₂	73	123-126	14	207-210 ^b

^a Anal. Calcd. for C₁₂H₂₀NCl: Cl, 16.59. Found: Cl, 16.63. ^b Anal. Calcd. for C₁₂H₂₀NCl: Cl, 16.59. Found: Cl, 16.39.

Experimental

Amino Alcohols.—The amino alcohols were prepared by the action of ammonia or an amine upon the proper ethylene oxides. A sample of 1-amino-2-methyl-2-propanol was also obtained from the Shell Development

(3) (a) Weston, Ruddy and Suter, *THIS JOURNAL*, **68**, 674 (1943); (b) Suter and Weston, *ibid.*, **64**, 533 (1942).

Company.⁴ 3-Methylamino-2-methyl-2-butanol is apparently a new compound. It was obtained in 85% yield by heating 160 g. (1.6 moles) of 33% methylamine and 34.5 g. (0.4 mole) of trimethylethylene oxide in a pressure bottle at 100° for three hours. It distilled at 152-155° (750 mm.), n_D^{20} 1.4394, d_4^{20} 0.9018.

Anal. Calcd. for C₈H₁₅ON: N, 11.91. Found: N, 11.97.

Condensation Reactions.—A typical reaction is described. To a cooled well-stirred mixture of 80 g. (0.6 mole) of anhydrous aluminum chloride and 78 g. (1 mole) of benzene was added 17.8 g. (0.2 mole) of 1-amino-2-methyl-2-propanol. Much heat was evolved. The mixture was then stirred and refluxed for three hours, allowed to stand overnight, and poured on ice. The benzene layer was extracted with dilute hydrochloric acid and this extract combined with the aqueous layer which was then made strongly alkaline. The amine which separated was taken up in ether and the ether solution was dried and distilled. The fraction distilling at 87-90° (10 mm.) weighed 26 g. corresponding to 87% of the theoretical amount of β,β -dimethylphenethylamine. The phenylthiourea of the amine melted at 106-106.5°.

An attempt to condense 1-amino-2-propanol with benzene under the conditions just described gave about 1% of β -methylphenethylamine.

Summary

Amino alcohols containing a tertiary hydroxyl group condense with benzene in the presence of excess aluminum chloride to give β,β -dialkylphenethylamine derivatives.

(4) We wish to express our thanks for the gift of this material.
EVANSTON, ILLINOIS RECEIVED FEBRUARY 10, 1943

[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Pyrolysis of Lactic Acid Derivatives. Preparation of Allyl and Methallyl Acrylates¹

BY C. H. FISHER, CHESSIE E. REHBERG AND LEE T. SMITH

In recent years considerable attention²⁻⁶ has been devoted to the pyrogenic conversion of various lactic acid derivatives into acrylic esters, which have become well known as intermediates used in the production of certain acrylic resins⁷

(1) Presented before the Division of Organic Chemistry at the 104th meeting of the American Chemical Society at Buffalo, New York, September 7-11, 1942. Not copyrighted.

(2) Burns, Jones and Ritchie, *J. Chem. Soc.*, 400, 714, 1054 (1935); U. S. Patent 2,265,814, Dec. 9, 1941.

(3) Smith and Claborn, *Ind. Eng. Chem., News Ed.*, **17**, 370, 641 (1939).

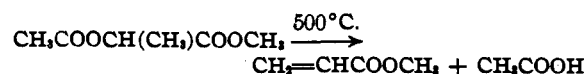
(4) Stearn, Makower and Groggins, *Ind. Eng. Chem.*, **32**, 1335 (1940).

(5) Claborn, U. S. Patent 2,229,097, Jan. 28, 1941.

(6) Smith, Fisher, Ratchford and Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

(7) Neher, *ibid.*, **32**, 267 (1936).

and synthetic rubber.⁸ Several of these investigations^{2,3,6} were concerned with methyl α -acetoxypropionate, a lactic acid derivative which decomposes smoothly and readily when pyrolyzed, yielding methyl acrylate and acetic acid



In view of the fact that high yields of methyl acrylate are obtained when methyl acetoxypropio-

(8) Ziegler, *Chem.-Zig.*, **62**, [14] 125 (1938); *Rubber Chem. and Technology*, **11**, 501 (1938); I. G. Farbenindustrie A.-G., British Patent 360,822, Oct. 30, 1931; Anderson, Hill and Morgan, British Patent 514,912, Nov. 21, 1939; Starkweather and Collins, U. S. Patent 2,218,362, Oct. 15, 1940; Clifford, U. S. Patent 2,279,292, Apr. 14, 1942.