

of the racemization by strong acids warrants further investigation.

The assistance of Miss J. E. Tietzman is gratefully acknowledged by the authors.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED DECEMBER 22, 1941

An Improved Procedure for the Preparation of Glycine

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By modifying the Orten and Hill synthesis of glycine,¹ it is possible to improve their yield of 60–64% of pure glycine to 75–77%.

Method.—Pour a solution of 0.5 mole (47.2 g.) of good-quality monochloroacetic acid in 100 cc. of water into a rapidly swirling four-pound bottle of ammonium hydroxide of sp. gr. 0.9 (1.8 kg. or 30 moles). After twenty-four hours (longer standing is not necessary), evaporate the solution to dryness on a water-bath, preferably under reduced pressure. Dissolve the crust in a minimum amount of warm water, and filter out traces of insoluble material. With the aid of vacuum, dry the material as thoroughly as possible in a 2-liter round-bottom flask on a water-bath. Dissolve out the ammonium chloride by refluxing with 1 liter of methanol on a water-bath for about four hours. After cooling to room temperature, filter with suction on a 7-cm. Büchner. Place the glycine (about 36 g. dry weight) in a 500-cc. flask fitted with a condenser, and add just enough water (about 50 cc.) to dissolve the solid completely upon boiling. Discontinue heating and place the flask and condenser under a hood. Slowly add four volumes of methanol (about 200 cc.), keeping the flask swirling. Cool to 30° or less, then suction-filter the material as dry as possible. Repeat the precipitation with the same amounts of water and methanol. Wash the cake with two 50-cc. portions of methanol, allowing it to soak in well before being suctioned off.

When dry, the glycine weighs 28–29 g., 75–77% yield. It contains no chloride and not more than a faint trace of ammonia. Analysis gave 18.54% N (Kjeldahl method), calcd. 18.67%; m. p. 233–236° with decomposition.

Discussion.—Methanol of 99% or more by weight is satisfactory. The yield would probably be slightly reduced if 95% methanol were

used. The preliminary removal of ammonium chloride can be done by seven hours of Soxhlet extraction with 500 cc. of methanol on a water-bath at 85°, but 99.5–100% methanol must be used, since even a little water greatly increases the solubility of glycine in warm methanol. The yields are a little lower, about 27–28 g.

However, Soxhlet extraction with 99.5–100% methanol gives excellent results in purifying certain amino acids prepared from the corresponding bromo acids. This is probably due to the fact that ammonium bromide is more soluble in methanol than is ammonium chloride. By treating α -bromo-*n*-butyric acid for twenty-four hours with aqueous ammonia in a 1 to 50 ratio, we obtained a 65% yield of very pure α -amino-*n*-butyric acid by Soxhlet extraction alone, without the necessity of subsequent precipitation from aqueous solution with methanol. An additional 15% of pure amino acid was isolated from the methanol extract through the copper salt.

AMERICAN CYANAMID CO. RECEIVED DECEMBER 19, 1941
STAMFORD, CONNECTICUT

NEW COMPOUNDS

2-Methyl-1,4-naphthoquinone Derivatives

With a view to obtaining derivatives of 2-methyl-1,4-naphthohydroquinone and 2-methyl-1,4-naphthoquinone sufficiently soluble for therapeutic use, the following four compounds were made. The first was not tested for coagulation time, the solution being insufficiently stable. The other three compounds were ineffective at the 12 microgram level in the usual chick assay.

2-Methyl-1,4-naphthohydroquinone Acetate Acid Succinate.—0.5 g. of 2-methyl-1,4-naphthohydroquinone hydrogen succinate¹ was heated on the steam-bath with 3.0 cc. of acetic anhydride for two hours. The mixture was poured into water and left overnight and the product recrystallized twice from ether-pentane mixture. The compound forms white aggregates of tiny needles, melting at 129° and dissolving in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{17}H_{16}O_6$: C, 64.54; H, 5.10. Found: C, 64.55; H, 5.32.

2-Methyl-1,4-naphthoquinone-*p*-carboxyphenylhydrazine.—A solution of 1.5 g. of 2-methyl-1,4-naphthoquinone, 100 cc. of 95% alcohol, 3.5 cc. of acetic acid and 1.6 g. of *p*-hydrazinobenzoic acid² was refluxed for two hours, allowing most of the alcohol to evaporate. The solid which separated was taken up in potassium carbonate solution, the solution extracted with ether and the aqueous layer

(1) Orten and Hill, *THIS JOURNAL*, **53**, 2797 (1931).

(1) Baltzly and Buck, *THIS JOURNAL*, **63**, 882 (1941).

(2) Anchel and Schoenheimer, *J. Biol. Chem.*, **114**, 539 (1936).