etc. No sufficient knowledge of these factors is available to warrant any speculation about the causes of the changes observed.

Summary

In reaction mixtures approximating the composition of dried apples and containing invertase this enzyme has been found active in the presence of 4.75–5% moisture at 25°. No definite enzyme action could be found at lower water concentrations. Raising the water content above 5% resulted in quicker and more regular hydrolyses.

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[CONTRIBUTION FROM THE NICHOLS LABORATORY, NEW YORK UNIVERSITY]

The Preparation of Some β-Amino Acids

BY JOHN V. SCUDI

In analogy with the addition of piperidine to benzalmalonic ester[1] $C_6H_5CH{=}C(COOC_2H_5)_2 + HNC_5H_{10} \longrightarrow C_6H_5CH(NC_5H_{10})CH(COOC_2H_5)_2$ it has been found that ammonia reacts similarly, the amino group entering the β-position, with a 47% yield as compared with a yield of 19% obtained by the preparation of this substance by the interaction of benzaldehyde, ammonia and malonic ester.[2] Hydrolysis and decarboxylation produce β-amino-β-phenylalanine. Benzalmalonic acid reacts with ammonia, yielding β-amino-β-phenylalanine directly. Piperidine reacts with benzalmalonic acid to give the salt and not the β-piperidyl-β-phenyl α,α-dicarboxylic ethane structure previously assigned[3] to the same product obtained by the condensation of benzaldehyde, piperidine and malonic acid. Goldstein[1] has shown the β-amine to be unstable.

Experimental Part

β-Phenyl-β-amino-α,α-dicarbethoxyethane (I).—Benzalmalonic ester[4] (15 g.) in 20 cc. of 10% alcoholic ammonia (1.5 moles) was evaporated over a period of one hour on a steam-bath and from the ether extract of the residue 8.5 g. (47% yield) of the hydrochloride separated on saturation of the solution with hydrogen chloride. After recrystallization from an equal part mixture of alcohol–ether, the hydrochloride was identified through comparison with an authentic sample (m. p. 159–160°). From the ethereal filtrate 3.4 g. of benzalmalonic ester, 1.2 g. of benzaldehyde and 2.1 g. of diethyl malonate were recovered. Doubling the time of heating and the amount of alcoholic ammonia gave a 45% yield of I.

β-Phenyl-β-aminopropionic Acid.—One gram of the above amino ester (I) was boiled for one hour in 10 cc. of concentrated hydrochloric acid and 20 cc. of water, and evaporated to dryness on a steam-bath. The residue recrystallized from alcohol–ether solution melted at 220–222° and showed no depression when mixed with an authentic sample; yield, 0.43 g. (70%).

Addition of Ammonia to Benzalmalonic Acid.—Benzalmalonic acid (8.5 g.) in 35 cc. of 10% aqueous ammonia when evaporated to dryness on a steam-bath gave 5.6 g. of residue from which 2.7 g. of β-phenyl-β-alanine was extracted with dilute hydrochloric acid, leaving 1.9 g. of cinnamic acid undissolved.

Piperidinium Acid Benzalmalonate.—Adding 0.5 g. of piperidine to 1.0 g. of benzalmalonic acid in 5 cc. of alcohol immediately gave 1.5 g. of the product (m. p. 163–164°) obtained by the condensation process.[3] Treatment with dilute acids precipitated benzalmalonic acid quantitatively from aqueous solutions of the salt.

Summary

Ammonia has been added to the double bond of benzylidene–malonic acid and its ester, producing beta amino derivatives under conditions approximating those used to produce these amines by the Knoevenagel method.

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(1) J. Goldstein, *Ber.*, **29**, 814 (1896).

(2) W. M. Rodionow and A. M. Fedorova, *ibid.*, **60**, 805 (1927).

(3) W. M. Rodionow and Holmogorzeva, THIS JOURNAL, **51**, 851 (1929).

(4) E. Knoevenagel, *Ber.*, **31**, 2591 (1898).