

average reader. Methods of construction of nomograms are discussed in L. J. Henderson's book on blood<sup>6</sup> and in an admirable little book in French by Frechet and Rouillet<sup>7</sup> and in other books, such as those by Swett,<sup>8</sup> Davis<sup>9</sup> and Allcock and Jones.<sup>10</sup>

(6) L. J. Henderson, "Blood, a study in general physiology," Yale University Press, New Haven, Conn., 1928.

(7) M. Frechet, and H. Rouillet. "Nomographie," Armand Colin, Paris, 1928.

(8) G. W. Swett, "Construction of Alignment Charts," John Wiley and Sons, Inc., New York, N. Y., 1928.

(9) D. S. Davis, "Empirical Equations and Nomography," McGraw-Hill Book Company, Inc., New York, N. Y., 1943.

(10) H. J. Allcock, and J. R. Jones, "The Nomogram," 2nd ed., Pitman, N. Y., 1932.

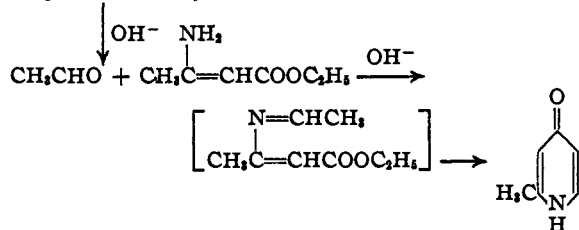
DEPARTMENT OF PHYSICAL CHEMISTRY  
HARVARD MEDICAL SCHOOL  
BOSTON, MASS.

RECEIVED APRIL 3, 1945

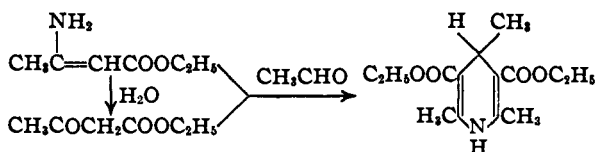
### Condensation of Vinyl Acetate with Ethyl $\beta$ -Aminocrotonate

BY JOHN A. KING

Although the instability of aliphatic aldimines is well known,<sup>1</sup> it was hoped that by slow generation of the aldehyde *in situ*, under mild condensing conditions, it might be possible to prepare ethyl  $\beta$ -ethylideneaminocrotonate which then, in the reaction mixture or subsequently, could be cyclized to 2-methyl-4-pyridone. The slow generation of acetaldehyde under condensing conditions was accomplished by the use of vinyl acetate in an aqueous alkaline medium but neither the intermediate ethylideneaminocrotonate nor the pyridone was obtained. Instead there was formed dihydrocollidine dicarboxylic ester, probably via a Hantzsch synthesis<sup>2</sup> from the aldehyde, the amino ester and acetoacetic ester produced by hydrolysis of some of the amino ester.



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(1) After this work was done the elegant synthesis of aldimines by Campbell, Sommers and Campbell, *THIS JOURNAL*, **66**, 82 (1944), was published.

(2) Hantzsch, *Ann.*, **215**, 8 (1882).

(3) Collie, *ibid.*, **226**, 314 (1884).

warm sulfuric acid as the condensing agent and noted that the reactants did not condense if the acid catalyst were omitted.

#### Experimental

A mixture of ethyl  $\beta$ -aminocrotonate (12.9 g., 0.10 mole), vinyl acetate (17.2 g., 0.20 mole), potassium carbonate (27.6 g., 0.20 mole) and water (100 cc.) was allowed to stand for three weeks at room temperature in a stoppered flask, by which time all the water-insoluble reactants had disappeared and a semi-solid precipitate had formed. This semi-solid material (12.3 g., 92% yield, crude) was recrystallized four times from aqueous ethanol to give a nicely crystalline solid, m. p. 130°. When this was mixed with a sample of dihydrocollidine dicarboxylic ester, m. p. 129–130°, prepared from acetaldehyde ammonia and ethyl acetoacetate by the procedure of Hantzsch,<sup>2</sup> the mixture melted at 129–130°.

RESEARCH LABORATORIES

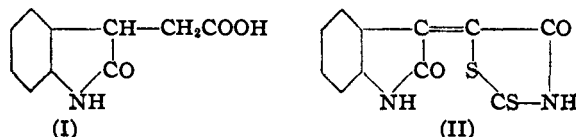
WINTHROP CHEMICAL COMPANY, INC.

RENSSELAER, NEW YORK RECEIVED MARCH 26, 1945

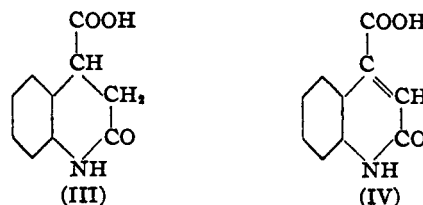
### The Reduction of Ethyl Oxindole-3-glyoxalate under Clemmensen Conditions

BY WARD C. SUMPTER, MARION MILLER AND  
LAURA NELL HENDRICK

In 1923 Gränacher and Mahal<sup>1</sup> prepared a compound which they designated as oxindoleacetic acid (I) from  $\beta$ -rhodanal oxindole (II) by reduction and subsequent hydrolysis of the reduction product.



Subsequently Aeschlimann<sup>2</sup> found that Gränacher's "oxindole-acetic acid" was in reality 2-keto-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (III) a fact later recognized by Gränacher and Kouniniotis<sup>3</sup> and confirmed by Hill, Schultz and Lindwall.<sup>4</sup> Aeschlimann found that compound III could be prepared quite readily by the reduc-



tion of 2-quinolone-4-carboxylic acid (IV) which in turn was prepared by condensing isatin with malonic acid<sup>2,5</sup> or by the action of alkali on acetyl-isatin.<sup>2,6</sup>

In 1941 Horner<sup>7</sup> prepared ethyl oxindole-3-glyoxalate (V) by condensing ethyl oxalate and

(1) Gränacher and Mahal, *Helv. Chim. Acta*, **6**, 467 (1923).

(2) Aeschlimann, *J. Chem. Soc.*, 2902 (1926).

(3) Gränacher and Kouniniotis, *Helv. Chim. Acta*, **11**, 1241 (1928).

(4) Hill, Schultz and Lindwall, *THIS JOURNAL*, **52**, 769 (1930).

(5) Borsche and Jacobs, *Ber.*, **47**, 354 (1914).

(6) Camps, *Arch. Pharm.*, **237**, 687 (1889).

(7) Horner, *Ann.*, **548**, 117 (1941).