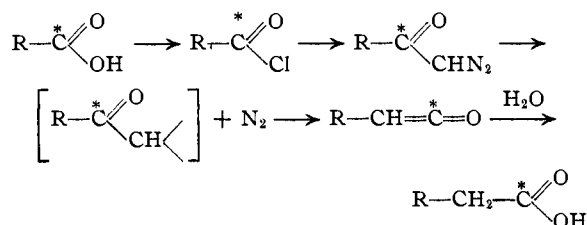


The Mechanism of the Arndt-Eistert Reaction¹

BY CLAYTON HUGGETT, RICHARD T. ARNOLD AND T. IVAN TAYLOR

The conversion of an acid to its next higher homolog by the Arndt-Eistert procedure is of considerable value to organic chemists. The most reasonable mechanism² for the reaction proposes the formation and decomposition of a ketene.



This mechanism readily explains the type of products formed under varying experimental conditions, and the analogy to the Curtius and Hofmann rearrangements has been recognized.³

From the above equation it is seen that the carbonyl carbon atom of the starting acid becomes the carbonyl carbon atom in the final product; the newly introduced carbon atom then occupies the alpha position.

We have found substantial evidence to support this formulation of the mechanism by using C¹³ isotopes as tracer elements. Heavy benzoic acid prepared by the carbonation of ordinary phenylmagnesium bromide with carbon dioxide⁴ containing a high per cent. of C¹³ was converted to phenylacetic acid by the method of Arndt and Eistert. The heavy isotope was found in the carbonyl group of the phenylacetic acid as shown by decarboxylation with copper chromite and quinoline.

The carbon dioxide from the heavy benzoic acid contained 2.51 per cent. C¹³ and that from the phenylacetic acid measured 2.53 per cent. C¹³. Within experimental error these values are identical and support the ketene mechanism.²

Of necessity this work has been discontinued but will be renewed when conditions permit.

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(1) For an excellent discussion see Bachmann and Struve, "Organic Reactions," Vol. I, J. Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(2) Eistert, *Ber.*, **68**, 208 (1935).

(3) Lane, Willenz, Weissberger and Wallis, *J. Org. Chem.*, **5**, 276 (1940).

(4) We are indebted to Dr. A. O. Nier for the heavy methane from which this was formed.

The Ionization Constant of Morpholine in Water¹

BY ALVIN R. INGRAM² AND W. F. LUDER

In connection with an investigation of the conductivity of morpholine solutions, it seemed desirable to know the strength of morpholine as a base. Accordingly, the ionization constant of morpholine in water was measured by the conductivity method.

Since great accuracy was not required, no special precautions were taken in the preparation of conductivity water. This, together with the low conductance of morpholine solutions, resulted in solvent corrections of several per cent. at the most dilute concentrations. Another source of error entered into the determination of Λ_0 . In order to find Λ_0 it was necessary to measure the conductance of morpholinium chloride. The slight hydrolysis of this salt was not taken into account in the extrapolation for its Λ_0 .

However, analysis of the results indicates that the value for the ionization constant of morpholine in water at 25° is 2.44×10^{-6} within the limits of error to which most ionization constants in the literature are given.

Experimental

Materials, Apparatus, and Procedure.—The bridge³ and procedure⁴ have been described previously. The temperature of the oil thermostat was kept at $25 \pm 0.01^\circ$ by an electronic relay. The water used was ordinary distilled water once redistilled and usually had a specific conductance of about 1×10^{-6} mho. Morpholine was dried over barium oxide and aluminum oxide, then fractionated three times off aluminum oxide, the constant boiling portion being used for runs. The best conductance for morpholine treated in this way was 6×10^{-10} mho. Morpholinium chloride (m. p. 177°) was prepared by passing dry hydrogen chloride over the surface of purified morpholine, washing the product with redistilled petroleum ether and diethyl ether, and pumping in a vacuum desiccator over phosphorus pentoxide.

Results.—Values of Λ are given in Tables I and II. Plots of $1/\Lambda$ against $c\Lambda$ for morpho-

(1) Abstracted from a portion of a thesis submitted by Alvin R. Ingram to the faculty of Northeastern University in partial fulfillment of the requirements for the M. S. degree, June, 1942.

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(3) W. F. Luder, *THIS JOURNAL*, **62**, 89 (1940).

(4) D. J. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32** 594 (1936).