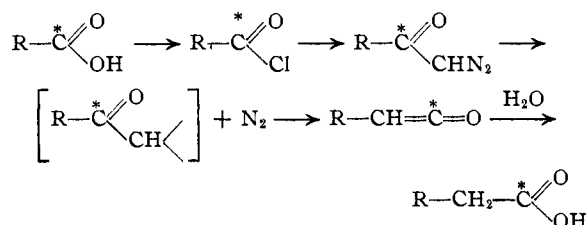


## The Mechanism of the Arndt-Eistert Reaction<sup>1</sup>

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 mechanism<sup>2</sup> 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.<sup>3</sup>

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 C<sup>13</sup> isotopes as tracer elements. Heavy benzoic acid prepared by the carbonation of ordinary phenylmagnesium bromide with carbon dioxide<sup>4</sup> containing a high per cent. of C<sup>13</sup> 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. C<sup>13</sup> and that from the phenylacetic acid measured 2.53 per cent. C<sup>13</sup>. Within experimental error these values are identical and support the ketene mechanism.<sup>2</sup>

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 Water<sup>1</sup>

BY ALVIN R. INGRAM<sup>2</sup> 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  $\Lambda_0$ . In order to find  $\Lambda_0$  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  $\Lambda_0$ .

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

### Experimental

**Materials, Apparatus, and Procedure.**—The bridge<sup>3</sup> and procedure<sup>4</sup> 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  $1 \times 10^{-6}$  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  $6 \times 10^{-10}$  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  $\Lambda$  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.

(2) Present address: General Chemical Defense Corporation, Point Pleasant, West Virginia.

(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).

TABLE I

MORPHOLINE IN WATER			
$C \times 10^3$	$\Lambda$	$C \times 10^3$	$\Lambda$
8.45	4.11	10.15	3.811
5.60	4.98	33.80	2.182
2.559	7.40	16.03	3.172
1.221	10.04	7.34	4.63
191.6	0.849	3.560	5.98
108.6	1.164	2.133	8.14
68.9	1.477	1.063	11.02
27.65	2.342		

TABLE II

MORPHOLINIUM CHLORIDE IN WATER			
$C \times 10^3$	$\Lambda$	$C \times 10^3$	$\Lambda$
56.25	98.6	0.861	111.8
22.49	103.7	48.1	99.6
8.47	108.2	22.02	104.1
4.56	109.9	6.55	108.0
2.341	111.0		

line and  $\Lambda$  against  $\sqrt{c}$  for morpholinium chloride indicate, by their deviations from the expected curves,<sup>5</sup> that the values of  $\Lambda$  for the most dilute points have been somewhat over-corrected for solvent conductance. The extrapolation to  $\Lambda_0$  for morpholinium chloride takes this into account, but may be a few per cent. in error because of hydrolysis. This determination seems to be the source of greatest error. However, it seems unlikely that it can be more than two or three per cent. Assuming it to be 3% the error in  $K$  would be slightly less, about 2.8%. The value of  $\Lambda_0$  was taken as 115.

Using this value and 261.5<sup>6</sup> for NaOH and 126.4<sup>7</sup> for NaCl,  $\Lambda_0$  for morpholinium hydroxide is 250. Plotting the straight line form of the Arrhenius conductance ratio equation for the ionization constant,  $1/\Lambda = c\Lambda/K\Lambda_0^2 + 1/\Lambda_0$ , the graphically determined slope  $1/K\Lambda_0^2$  gives a value of  $2.44 \times 10^{-6}$  for  $K$ .

(5) The ionization constant of morpholine is low enough so that in view of the two sources of error previously mentioned, it was considered unnecessary to use the more accurate forms of the  $1/\Lambda - c\Lambda$  plot proposed by Fuoss (THIS JOURNAL, 57, 488 (1935)) and Shedlovsky (J. Franklin Inst., 225, 739 (1938)).

(6) H. Jeffery and A. I. Vogel, Phil. Mag., 15, 395 (1933).

(7) D. A. MacInnes, T. Shedlovsky and L. G. Longworth, THIS JOURNAL, 54, 2758 (1932).

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## Action of Macerans Enzyme on a Component of Corn Starch

BY RALPH W. KERR

The origin of the Schardinger dextrins, when starch is treated in the presence of *B. Macerans*

or the enzyme prepared from this bacillus<sup>1</sup> has been a matter of speculation for many years. In another paper<sup>2</sup> the writer sought to show that, in procedures which might ordinarily be used to convert corn starch with this enzyme, the yield of Schardinger dextrins, precipitable with trichloroethylene, arose almost entirely from a degradation of the most permanently dispersed fraction of the starch, which latter amounts to approximately 55% of the total starch. It was concluded that these dextrins were probably formed by synthesis from the more simple configurations in this product.

We are now able to elaborate on these conclusions. In another communication<sup>3</sup> we discussed the isolation of an amylose in yields of 5 to 6% of starch, by crystallizing the product from a warm water extract of corn starch with butanol. The amylose quickly changes to an insoluble form, however, in concentrations over 1 g. per 100 cc. in water solution. In this condition it might be expected to be rather inert in the presence of starch splitting enzymes. It may, however, be held in a relatively stable solution at pH 6.0 at lesser concentrations, e. g., 0.30 g. per 100 cc.

A conversion of such a solution of the amylose was attempted adding 40 cc. of a *Macerans* enzyme preparation of 0.3 unit activity<sup>2</sup> to 2 l. of water containing 6 g. of the amylose in its soluble form. The conversion was made at pH 6.0 and 45° for forty-eight hours. The liquors were then concentrated by vacuum distillation to 400 cc. at 45° and allowed to stand at this temperature for another twenty-four hours at pH 6.0. Practically no insolubles were in evidence. The liquors were concentrated to 130 cc., a small amount of floc filtered off and 130 cc. of trichloroethylene added. The mixture was allowed to stand for forty-eight hours at room temperature, with intermittent stirring, and then for forty-eight hours in the refrigerator. The dextrins were filtered off, washed with ice water, then with methanol, dried and weighed: 4.2 g. of mixed dextrins, precipitable with trichloroethylene resulted, a yield of 70%. Further quantities precipitated when the mother liquors were concentrated.

Inasmuch as the crystalline amylose gives a conversion limit<sup>3,4</sup> of 93% maltose with  $\beta$ -amylase

(1) E. B. Tilden and C. S. Hudson, THIS JOURNAL, 61, 2900 (1939).

(2) R. W. Kerr, "On the Significance of the Degradation of Starch by Macerans Enzyme," presented at the 102nd meeting of the American Chemical Society, September, 1941.

(3) R. W. Kerr and G. M. Severson, "The Isolation of an Amylose in Crystalline Form," in press.

(4) R. W. Kerr, O. R. Trubell and G. M. Severson, Cereal Chemistry, 19, 64 (1942).