

for twenty-four hours each in two portions of 200 ml. of water saturated with butanol. The crystals were dehydrated and freed of butyl alcohol by prolonged standing in five successive portions of 200 ml. of absolute methanol, filtered, and the methanol evaporated in a vacuum desiccator. The yield was 2.14 g.

The subfraction procedure was repeated by adding 100 ml. of ethylenediamine to the sirupy, residual phase, poorer in ether and then adding 32 ml. of ether. The upper phase which separated was removed and the amylose crystals prepared as indicated above. The yield was 1.53 g. of thick platelets.

In the third step of the subfractionation procedure, 90 ml. of ethylenediamine was added followed by 29 ml. of ether. The yield was 1.45 g. of blunt needles.

Finally, the residual, lower phase from the third, phase separation procedure was treated with a large excess of ether to precipitate the remaining amylose. After crystallization from water-butyl alcohol, this subfraction formed well-shaped, thin needles which arranged themselves in star-like clusters and appeared very similar in shape to those described for the crystalline amyloses of tapioca and potato starches obtained by the addition of butyl alcohol to warm water extracts of the starches.<sup>4</sup> This yield was 1.82 g.

The subfraction technique was repeated several times and the results were the same as reported above. In one of these duplicate subfractionations, a small amount of needles (in water-butyl alcohol from the first butyl alcohol crystallization of the fourth subfraction) was added as seed to a solution of the first subfraction in water-butyl alcohol. On standing, however, platelet shaped crystals formed as usual. The complementary experiment was performed wherein platelets (the first subfraction) were added to a crystallization of the fourth subfraction. Needle-shaped crystals formed as usual.

Qualitatively the solution viscosity in ethylenediamine of the platelets, obtained by subfractionation of corn amylose sphero-crystals and from a warm water extraction of corn starch are of the same order of magnitude; also, those of the needles obtained from water extracts of tapioca starch and from the subfractionation of corn amylose are the same. The viscosity of the total butyl alcohol precipitate of corn starch in ethylenediamine is intermediate to those two ranges.

An analysis of the various subfractions obtained from corn amylose by the use of ethylenediamine—ether phase separation as well as a study of the application of the ethylenediamine—ether phase separation method as a fractionation procedure for whole starch is proceeding in our laboratories.

RESEARCH LABORATORIES

CORN PRODUCTS REFINING COMPANY

ARGO, ILLINOIS

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### $\alpha$ -Methoxycrotonic Acid

BY KARL PFISTER, C. A. ROBINSON AND MAX TISHLER

The recent publication of L. N. Owen<sup>1</sup> on the "Reactivity of  $\alpha$ -Bromo-crotonic Acid" prompts us to report at this time our results of a similar study. As indicated in our report, the conclusions are on the whole in agreement with those of Owen.

Our investigation began with an attempt to prepare tetrolic acid by the action of methanolic

(1) L. N. Owen, *J. Chem. Soc.*, 385 (1945).

potassium hydroxide on crotonic acid dibromide under conditions described by Reimer<sup>2</sup> for the preparation of phenylpropionic acid from cinnamic acid dibromide.

Under these conditions, crotonic acid dibromide was converted to  $\alpha$ -methoxycrotonic acid<sup>3</sup> in 80% yield (lustrous rods, m. p. 60–62°; calcd. for  $C_5H_8O_3$ : C, 51.72; H, 6.95; neut. equiv., 116.1. Found: C, 51.65; H, 6.83; neut. equiv., 115.2). The *p*-bromophenacyl ester derivative melts at 76–77°; calcd. for  $C_{11}H_{13}O_4Br$ : C, 49.84; H, 4.18. Found: C, 50.02; H, 4.10.  $\alpha$ -Methoxycrotonic acid decolorizes bromine and potassium permanganate rapidly. It is very soluble in water, ether and carbon disulfide but sparingly soluble in ligroin. Catalytic hydrogenation (palladium Norite catalyst) converted it into  $\alpha$ -methoxybutyric acid which was isolated and characterized by its *p*-bromophenacyl ester derivative (m. p. 69–70°; calcd. for  $C_{13}H_{15}O_4Br$ : C, 49.53; H, 4.80. Found: C, 49.26; H, 4.54). That the last mentioned compound is not the *p*-bromophenacyl ester of  $\beta$ -methoxybutyric acid was established by preparing the same ester of an authentic sample of  $\beta$ -methoxybutyric acid<sup>4</sup> and comparing the two. The *p*-bromophenacyl ester of  $\beta$ -methoxybutyric acid melts at 59–60° (found: C, 49.35; H, 4.72) and depresses the melting point of the isomeric  $\alpha$ -methoxy compound.

Identical treatment of  $\alpha$ -bromoisocrotonic acid with methanolic potassium hydroxide gave  $\alpha$ -methoxycrotonic acid in 87% yield. However, a much longer reaction time was required to completely remove the halogen from  $\alpha$ -bromocrotonic acid (70% yield of  $\alpha$ -methoxycrotonic acid). The difference in reaction rates of these two compounds may be due to the limited solubility of the potassium salt of the *trans* acid under the conditions of our experiments and may not reflect the relative reactivities of the halogen atoms in  $\alpha$ -bromocrotonic and  $\alpha$ -bromoisocrotonic acids.

As one would expect,  $\alpha$ -methoxycrotonic acid is hydrolyzed by boiling with dilute hydrochloric acid to  $\alpha$ -ketobutyric acid. The latter was identified by conversion to the known phenylhydrazone (m. p. 149–150°). The hydrolysis together with the preparation of the  $\alpha$ -alkoxy- $\alpha,\beta$ -unsaturated acids may find use as a convenient synthesis of aliphatic  $\alpha$ -keto acids.

(2) Reimer, *THIS JOURNAL*, 64, 2510 (1942).

(3) In connection with this reaction, it is of interest to note that treatment of diethyl  $\alpha,\alpha'$ -dibromosuccinate with sodium ethylate in ethanol yields some diethyl ethoxymalate. Cf. Michael and Maisch, *J. prakt. Chem.*, [2] 46, 235 (1892); Michael and Bucher, *Ber.*, 29, 1792 (1896).

(4) Prepared by the method of Purdie and Marshall, *J. Chem. Soc.*, 468 (1891).

RESEARCH LABORATORIES

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### Electrolyte Catalysis in the Ammonolysis of 9-Phenyl-9-chlorofluorene by Liquid Ammonia, Alkaline-Earth Nitrates

BY WILBUR F. ROPER,<sup>1</sup> ROBBIN C. ANDERSON AND GEORGE W. WATT

It has been shown that the ammonolysis of 9-phenyl-9-chlorofluorene by liquid ammonia is an autocatalytic reaction, the ammonium chloride produced acting as catalyst,<sup>2</sup> and, further, that this is not specific "acid catalysis"; but that electrolytes in general seem to catalyze the re-

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(2) Williamson, Anderson and Watt, *THIS JOURNAL*, 65, 49 (1943).