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.[4] 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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α-Methoxycrotonic Acid

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

The recent publication of L. N. Owen[1] on the "Reactivity of α-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 potassium hydroxide on crotonic acid dibromide under conditions described by Reimer[2] for the preparation of phenylpropiolic acid from cinnamic acid dibromide.

Under these conditions, crotonic acid dibromide was converted to α-methoxycrotonic acid[3] 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 $C_{13}H_{13}O_4Br$: C, 49.84; H, 4.18. Found: C, 50.02; H, 4.10. α-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 α-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 β-methoxybutyric acid was established by preparing the same ester of an authentic sample of β-methoxybutyric acid[4] and comparing the two. The *p*-bromophenacyl ester of β-methoxybutyric acid melts at 59–60° (found: C, 49.35; H, 4.72) and depresses the melting point of the isomeric α-methoxy compound.

Identical treatment of α-bromoisocrotonic acid with methanolic potassium hydroxide gave α-methoxycrotonic acid in 87% yield. However, a much longer reaction time was required to completely remove the halogen from α-bromocrotonic acid (70% yield of α-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 α-bromocrotonic and α-bromoisocrotonic acids.

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

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

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

[3] In connection with this reaction, it is of interest to note that treatment of diethyl α,α'-dibromosuccinate with sodium ethylate in ethanol yields some diethyl ethoxyfumarate. *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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RAHWAY, N. J.
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Electrolyte Catalysis in the Ammonolysis of 9-Phenyl-9-chlorofluorene by Liquid Ammonia, Alkaline-Earth Nitrates

BY WILBUR F. ROPER,[1] 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,[2] and, further, that this is not specific "acid catalysis"; but that electrolytes in general seem to catalyze the re-

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[1] Present address: C. A. S. Co. 96, U. S. Army.

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

action—some even more effectively than the ammonium salts.[3]

It was then decided to determine whether salts of other valence types would be as effective catalysts as the univalent compounds. Markova and Shatenshtein[4] have reported that calcium, barium and strontium nitrates increase the rate of ammonolysis of ethyl chloride in liquid ammonia but attribute this effect to some type of acid catalysis.

All materials were prepared and/or purified as described previously[2] except the barium, strontium and calcium nitrates. Reagent grade barium and strontium nitrates were recrystallized twice from water and dried thoroughly.

The concentration of these salts in reagent mixtures was controlled by using weighed amounts of the salts. Anhydrous calcium nitrate was found to be too deliquescent for solutions to be made up by direct weight. The anhydrous salt was stored over barium oxide in an atmosphere of ammonia. A definite and stable ammonate was not obtained, but reasonable accuracy could be attained in preparing solutions by analyzing a sample of the material for ammonia content just prior to making up the reagent mixtures.

The methods used in rate determinations were the same as those already described.[2] All experiments were carried out at 25.00 ± 0.02°.

Results

Because of the relative insolubility of the alkaline-earth chlorides in liquid ammonia,[5] the ammonium chloride formed in the ammonolysis tends to react with the catalyst to form a chloride precipitate. The presence of the second phase, which may or may not have some catalytic effect, and the uncertainty as to how rapid and how nearly complete the precipitation actually is made it impossible to calculate specific catalytic constants for these salts. However, the observed rates of reaction show clearly that the barium, calcium and strontium nitrates are more effective catalysts than the acids such as ammonium nitrate and ammonium chloride.

In Table I are summarized the results of typical experiments with various catalysts.

TABLE I

EFFECT OF NITRATES UPON THE AMMONOLYSIS OF 9-PHENYL-9-CHLOROFLUORENE

Nitrate	Init. concn., catalyst, mole/liter	Init. concn., RCl, mole/liter	Time, hr.	RCl reacted, mole/liter	Specific reaction rate, hr.$^{-1}$
Ammonium	0.0508	0.0759	2	0.0228	0.1784
	.0502	.0748	4	.0390	.1843
Calcium	.0500	.0750	2	.0332	.2923
	.0497	.0745	6	.0588	.2592
Barium	.0248	.0429	2	.0167	.2459
	.0247	.0748	2	.0275	.2279
	.0495	.0750	2	.0321	.2792
	.0251	.0760	6	.0492	.1767
	.0492	.0746	6	.0548	.2213
Strontium	.0492	.0749	2	.0323	.2822
	.0513	.0770	6	.0539	.2004

The values listed are averages of several independent determinations. The specific rate of reaction is that calculated from the simple first-order equation

$$dx/dt = k(a - x)$$

The value of k includes in this case the specific rate of the uncatalyzed reaction plus the catalytic effects of the various salts present.

The precipitation reaction

$$Ba(NO_3)_2 + 2NH_4Cl \longrightarrow BaCl_2 + 2NH_4NO_3$$

tends progressively to substitute ammonium nitrate for barium nitrate as the catalyst. The results in Table I show that conditions which favor this substitution—increased time of reaction, increased ratio of RCl to catalyst, etc.—result in a lower rate; and thus that barium nitrate has a greater effect than ammonium nitrate. A similar trend is observed with strontium and calcium nitrates.

Initially there is little difference in the effectiveness of the three alkaline earth nitrates; but as reaction proceeds, they tend to show divergence in the order of effectiveness $Ca^{++} > Ba^{++} > Sr^{++}$. This divergence may arise from variations in the specific catalytic activity of the three salts; but it may also be due, at least in part, to differences in the extent of precipitation of the chlorides or to small catalytic effects of the solid phases. Further experiments are planned to test these possibilities.

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[3] Williamson, Anderson and Watt, THIS JOURNAL, **66**, 376 (1944).

[4] Markova and Shatenshtein, *Compt. rend. acad. sci. U. R. S.S.*, **35**, 68 (1942).

[5] Franklin and Kraus, *Am. Chem. J.*, **21**, 1 (1899).

1-Acetyl-5,5-dimethylhydantoin

BY M. R. SALMON AND ALFRED Z. KOZLOWSKI

Biltz and Slotta[1] prepared 1-acetyl-5,5-dimethylhydantoin, m. p. 192°. This compound on methylation and deacetylation yielded 3,5,5-trimethylhydantoin, which had been synthesized by an unambiguous method.

Bucherer and Steiner,[2] apparently unaware of Biltz' prior description, acetylated 5,5-dimethylhydantoin under slightly different conditions and obtained another acetate, m. p. 123°, to which they also assigned the structure of 1-acetyl-5,5-dimethylhydantoin.

By following Bucherer's directions we have obtained the acetate described by Biltz and by following Biltz' directions we have obtained Bucherer's acetate, both in good yield and apparently uncontaminated. Both compounds are readily hydrolyzed by dilute alkali to 5,5-dimethylhydantoin. That the acetate of m. p. 192° is 1-acetyl-5,5-dimethylhydantoin follows from the fact that it dissolves readily in dilute alkali and is precipitated unchanged on acidification, as well as from Biltz' proof of structure.

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[1] Biltz and Slotta, *J. prakt. Chem.*, **113**, 233 (1926).

[2] Bucherer and Steiner, *ibid.*, **140**, 291 (1934).