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).

The acetate of m. p. 123° is so readily hydrolyzed that it is difficult to free it completely from acetic acid. Aqueous solutions become acid to test paper after standing a few minutes at room temperature. When this acetate is heated in a bath at 200° for twenty minutes, it rearranges with the formation of 1-acetyl-5,5-dimethylhydantoin and unidentified products.

We may formulate the acetate of m. p. 123° either as 3-acetyl-5,5-dimethylhydantoin or as 5,5-dimethylhydantoin-2-enolacetate. We prefer the latter because the structure of an enol acetate seems more consistent with the ease of hydrolysis and rearrangement.

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Determination of the Nature of the Volatile Base from the Rhizome of the Pitcher Plant *Sarracenia Purpurea*

BY A. WALTI*

Medicinal properties have repeatedly been ascribed to the rhizome of the pitcher plant, *Sarracenia purpurea*.[1] More recently Judovich[2] has prepared an aqueous distillate from the rhizome of the pitcher plant which has been used for the relief of spinal root pain.[3] The effect of the distillate of the pitcher plant rhizome on the isolated saphenous nerve of the cat has been investigated by Stewart and Hughes by the cathode ray oscillograph method. They found that it obliterated the potentials of the pain-carrying C fibers of the nerve but not those of the motor carrying fibers at the concentrations used.[4]

We have investigated the distillate of this plant rhizome which was obtained on steam fractionation of the powdered rhizome in the presence of caustic alkali and found it to yield a volatile base with an amino-like odor as previously mentioned by Bjorklund and Dragendorff.[5] On neutralization with hydrochloric or sulfuric acid, salts were formed which on crystallization were found to be identical with those of ammonium chloride and ammonium sulfate, respectively. The effects of ammonium chloride on the saphenous nerve when tested by the cathode ray oscillograph as well as the clinical results with ammonium chloride and ammonium sulfate on intractable pain reported by Bates and Judovich were in agreement with those previously obtained with the neutralized distillate of the pitcher plant rhizome.[6]

Experimental

A suspension was made of 500 g. of powdered pitcher plant rhizome, *Sarracenia purpurea*, in 1200 ml. of distilled water and 400 ml. of 30% sodium hydroxide. Steam was passed through the mixture until the last runnings of the distillate no longer gave a positive test for volatile base with litmus. The distillate was slightly turbid and had a distinct amine-like odor. It was neutralized with hydrochloric acid and concentrated at reduced pressure. The colored solution was treated with a little charcoal, filtered and concentrated further until crystallization occurred. The crystals were dissolved in little water, again treated with charcoal, filtered and alcohol was added until crystallization occurred. This crystallization was repeated. Recrystallization gave material which did not melt up to 320° and sublimed when heated in a small test-tube over a free flame.

Elementary analysis of the substance gave the following values. *Anal.* Calcd. for NH_4Cl: N, 26.2; Cl, 66.3. Found: N, 25.6; Cl, 64.6.

The crystalline substance yielded a flavianate, m. p. 289°, and that prepared from reagent ammonium chloride melted at 291°. A 5% solution of the isolated substance and one prepared from laboratory reagent ammonium chloride gave identical orange precipitates on treatment with an equal amount of Nessler reagent, and white precipitates with 10% phosphotungstic acid. It was evident, therefore, that the crystalline compound isolated from the neutralized distillate was ammonium chloride.

In another experiment, the alkaline distillate was neutralized with dilute sulfuric acid. The concentrated solution was clarified with little charcoal and concentrated till crystallization occurred. The perfectly white crystals gave the following analysis. *Anal.* Calcd. for $(NH_4)_2SO_4$: N, 21.21; S, 24.27. Found: N, 21.23; S, 23.92.

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[1] For review see J. S. Hepburn, *Am. J. Pharm.*, **100**, 675 (1928).

[2] B. D. Judovich, *Med. Rec.*, **141**, 583–585 (1935).

[3] Bates, Wand, B. D. Judovich, *Clin. Med. Surg.*, **46**, 205–207 (1939).

[4] W. B. Stewart, B. D. Judovich, T. Hughes and A. Walti, *Am. J. Physiol.*, **129**, 474 (1940).

[5] Bjorklund and Dragendorff, *Arch. Pharm.*, **169**, 93 (1864).

[6] W. Bates and B. D. Judovich, *Anesthesiology*, **3**, 663 (1942); B. D. Judovich, *ibid.*, **4**, 313 (1943).

NEW COMPOUNDS

Some Higher Alkyl Salicylates

Although a great many derivatives of salicylic acid have been prepared, there is scant mention in the chemical literature of the simple saturated alkyl salicylates in which the alkyl group contains more than five carbon atoms.[1] In order to study possible uses of these compounds we have prepared all of the straight-chain even-numbered alkyl salicylates from butyl to octadecyl, 2-ethylhexyl salicylate and the salicylic acid esters of 2-methoxyethanol (Methyl Cellosolve) and 2-ethoxyethanol (Cellosolve). Some of these esters were characterized as their 3,5-dinitrobenzoates and others as their 3,5-dinitro derivatives; neither derivative is very suitable for characterization because of the difficulty of crystallization, the low melting points, and the close proximity of the melting points of the

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[1] Sah and Ma, *Science Repts. Natl. Tsing Hua Univ., Ser. A*, **1**, 201 (1932); *Chem. Zentr.*, **103**, II, 3389 (1932); *C. A.*, **26**, 5929 (1932), have reported physical constants for carefully purified samples of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and isoamyl salicylate. Freeman and Haller, THIS JOURNAL, **60**, 2274 (1938), have done the same for *n*-amyl, *t*-amyl and 1-methylbutyl salicylate. Cleveland, U. S. Patent 1,911,551, claimed the use of an otherwise undescribed hexyl salicylate. Roger and Dvolaitskaya, *Recherches* (*Roure-Betrand fils*), **1**, 79 (1937); *C. A.*, **32**, 1241 (1938), prepared and characterized *n*-heptyl salicylate. Rule, Miles and MacGillivray, *J. Chem. Soc.*, **132**, 2274 (1929), prepared *d-s-β*-octyl salicylate. Segessemann, U. S. Patent 2,093,576, described the sulfonation of the otherwise undescribed 2-ethylhexyl salicylate Thomas, U. S. Patent 2,062,950, described dodecyl salicylate, characterized only by its saponification number.