only the method of Tchugaev will give fair yields of bornylene.[3]

Anhydrous potassium bornyl sulfate is much more stable than potassium cholesteryl sulfate and only after heating to relatively high temperatures (200°) can decomposition be induced. Rearrangement does occur and the main product of the reaction is camphene in about 60% yield. If water is present borneol is regenerated readily before decomposition can set in.

Experimental

Potassium Cholesteryl Sulfate.—The procedure described herein is adapted from a method previously reported[4] for estimating small amounts of cholesterol as pyridine cholesteryl sulfate.

Pyridine sulfur trioxide is prepared by adding 100 g. (1 mole) of sulfur trioxide to 200 g. (excess) of pyridine dissolved in 300 cc. of chloroform, in an ice-bath. The almost quantitative yield of pyridine sulfur trioxide is filtered off under anhydrous conditions, washed with chloroform and dried in a sulfuric acid desiccator.

Twenty-five grams of cholesterol is added to 100 cc. of anhydrous benzene with mechanical stirring and cooling using an ice-bath. A mixture of 25 cc. of acetic anhydride and 25 cc. of pyridine is added, followed by 25 g. of pyridine sulfur trioxide (excess), with vigorous stirring. The pyridine cholesteryl sulfate separates almost immediately. The reaction mixture is heated to 50° for thirty minutes with continual stirring. The mixture is cooled, an equal volume of petroleum ether is added and the mixture filtered. The residue which consists of pyridine cholesteryl sulfate mixed with some excess pyridine sulfur trioxide is transferred to an Erlenmeyer flask and treated with 8 g. of potassium hydroxide in 80 cc. of water, shaking vigorously for about fifteen minutes. The insoluble potassium cholesteryl sulfate separates at the top and is filtered off, washed with water and then with several portions of boiling anhydrous methyl alcohol. The residue is now transferred to a vacuum desiccator where the last traces of solvent are removed: yield 30 g.; m. p. 212° (dec.). A small portion was crystallized from 70% methyl alcohol. *Anal.* Calcd. for $C_{27}H_{45}OSO_3K$: K, 7.74; S, 6.35. Found: K, 7.88; S, 6.56.

Potassium Bornyl Sulfate.—Prepared as for potassium cholesteryl sulfate. Potassium bornyl sulfate should be precipitated in and washed with a limited volume of water for it is very water soluble; m. p. 220° (dec.). *Anal.* Calcd. for $C_{10}H_{17}OSO_3K$: K, 14.34; S, 11.76. Found: K, 14.31; S, 11.80.

Cholesterilene.—Twenty-five grams of anhydrous potassium cholesteryl sulfate is placed in a sealed tube from which the air has been evacuated. The tube is placed in an oven at 100° for one hour. A colorless liquid separates from the potassium acid sulfate. The tube is allowed to cool and the crystallized cholesterylene is recrystallized from alcohol: yield 14 g.; m. p. 79°. *Anal.* Calcd. for $C_{27}H_{44}$: C, 88.04; H, 11.96. Found: C, 87.74; H, 12.20.

Camphene.—Anhydrous potassium bornyl sulfate (100 g.) is placed in a distilling flask heated by means of an oil-bath. The temperature is raised to 200°. The salt decomposes and material begins to distill over. When no more distillate is obtained the distillate is fractionated. The main fraction distills from 158–162°, and crystallizes on cooling, m. p. 50°. *Anal.* Calcd. for $C_{10}H_{16}$: C, 88.23; H, 11.76. Found: C, 87.99; H, 11.90.

Cholesterol from Potassium Cholesteryl Sulfate.—Twenty-five grams of potassium cholesteryl sulfate is suspended in 100 cc. of water to which 1 drop of concd. sulfuric acid is added. The mixture is heated at 100° in a sealed tube or autoclave for one hour. The mixture is cooled, filtered and the residue is recrystallized from alcohol: yield 15 g.; m. p. 145°.

PEDIATRIC RESEARCH LABORATORY
JEWISH HOSPITAL OF BROOKLYN
BROOKLYN, NEW YORK
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The Preparation of Lead Tetraacetate

BY RALPH E. OESPER AND CLARA L. DEASY

Lead tetraacetate is usually prepared by warming red lead with acetic acid containing acetic anhydride sufficient to combine with the water formed[1]

$$Pb_3O_4 + 8HOAc \longrightarrow Pb(OAc)_4 + 2Pb(OAc)_2 + 4H_2O$$

Colson[1] (p. 891) found that a precipitate containing some tetraacetate is formed when chlorine is passed into a cold glacial acetic acid solution of lead diacetate

$$2Pb(OAc)_2 + Cl_2 \longrightarrow Pb(OAc)_4 + PbCl_2$$

We have made a systematic study of these procedures, varying the temperature, time of reaction and proportions of the reactants, and have found that improved yields result when these procedures are combined. Purification of the acetic acid by distillation over permanganate and then over phosphorus pentoxide raises the yield, but not enough to make this extra precaution profitable. The acetic anhydride content must not be unduly increased, nor may the total volume of the acetic acid–anhydride mixture be too drastically diminished.

Procedure.—The reaction is best carried out in a three-necked flask fitted with a gas-inlet tube, a thermometer and a mechanically driven stirrer (seal unnecessary). A mixture of 600 ml. of glacial acetic acid and 150 ml. of acetic anhydride is heated to 65°, the stirrer is started and a not

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[3] Tchugaev, *J. Russ. Phys.-Chem. Soc.*, **36**, 1039; *Chem. Centr.*, **76**, I, 94 (1905).

[4] Sobel, Drekter and Natelson, *J. Biol. Chem.*, **115**, 381 (1936); Drekter, Sobel and Natelson, *ibid.*, **115**, 391 (1936).

[1] Hutchinson and Pollard, *J. Chem. Soc.*, **63**, 1136 (1893); **69**, 212 (1896); Dimroth, Friedemann and Kämmerer, *Ber.*, **53**, 481 (1920); Dimroth and Schweizer, *Ber.*, **56**, 1375 (1923); Ruff, "Die Chemie des Fluors," Verlag von Julius Springer, Berlin, 1920, p. 41; Colson, *Compt. rend.*, **136**, 675 (1903); Hellmuth, Dissertation, Würzburg, 1930.

too rapid stream of dry chlorine led in. The red lead, 120 g. (dried at 150° for one to two hours) is introduced in five approximately equal portions, each addition being delayed until the color due to the previous portion has faded. The temperature is held at 65–80° throughout the reaction; higher temperatures decrease the yield. The reaction is complete in sixty to ninety minutes. The hot decolorized suspension is decanted promptly through a preheated filter. This filtrate, on cooling, will deposit about 65 g. of a material containing more than 90% tetraacetate.[2] The residual solid is returned from the filter to the reaction flask, and mechanically stirred for ten to fifteen minutes at 70–80° with 100 ml. of glacial acetic acid, or with a like volume of the cooled filtrate from a previous extraction. The hot suspension is decanted through a preheated filter, and the residue again extracted. About 33 g. of 90–95% tetraacetate is thus recovered, in addition to the original deposit, making a total yield of approximately 100 g. of high-grade tetraacetate. The contaminants (lead diacetate, lead chloride, acetic acid) ordinarily will not interfere in the use of the product. If pure tetraacetate is demanded, recrystallization from glacial acetic acid will serve, but the loss is considerable.

Dimroth and Schweizer reported a yield of 300–350 g. of crude tetraacetate from 600–650 g. of Pb_3O_4; Hellmuth claims 350 g. of purified product from this weight of red lead.[3] On a comparative basis our procedure yields a product containing approximately 500 g. of tetraacetate.

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[2] A typical sample contained 92.9% tetraacetate, 2.2% diacetate, 3.5% lead chloride, 1.4% acetic acid (by difference).

[3] Hellmuth's crude product contains 30–50% lead tetraacetate.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO
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The Entropy of Ionization in Solutions of Low Dielectric Constant

BY ELIJAH SWIFT, JR.

In a recent publication,[1] Bent and Keevil have reported figures derived from the conductances of some organic compounds in ether which indicate that the entropy of ionization at the temperature under consideration may have the same value for a number of compounds. Unfortunately, as they pointed out, the data were too few to warrant any definite statement to that effect.

There have been reported recently[2] some measurements in the same solvent of the conductance of sodium triphenylmethyl, a compound of somewhat smaller molecular diameter than those used by Bent and Keevil. In this case, the temperature coefficient of the equivalent conductance was zero between 0 and 25° within experimental error. Calculating ΔH in the same manner as was done by Bent and Keevil, it is found to be equal to -3.1 kcal., while $\Delta F = -15.1$ kcal. The resulting value of ΔS is -65.6 E. U., considerably higher than the values reported by Bent and Keevil for the compounds they studied ($\Delta S = -81, -83$ E. U.), but in fair agreement with the value calculated for sodium triphenylboron by Bent and Coolidge,[3] *i. e.*, -60 E. U. This indicates that a generalization about the constancy of ΔS in this solvent cannot be made, except perhaps in the case where the ions being compared are of about the same diameter.

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[1] H. E. Bent and N. B. Keevil, THIS JOURNAL, **60**, 193 (1938).

[2] E. Swift, Jr., *ibid.*, **60**, 1403 (1938).

[3] H. E. Bent and A. S. Coolidge, *ibid.*, **58**, 505 (1936).

GEORGE DAVIS SCIENCE HALL
KNOX COLLEGE
GALESBURG, ILLINOIS
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Polymers of Propylene from Isopropyl Alcohol and Boron Trifluoride

BY FRANK C. WHITMORE AND J. F. LAUCIUS

Although the action of boron trifluoride as a polymerizing agent was first observed in 1873[1] more than five decades elapsed before its use was exploited to any extent. Otto[2] reported the polymerization of ethylene and propylene with boron trifluoride and since then more than a score

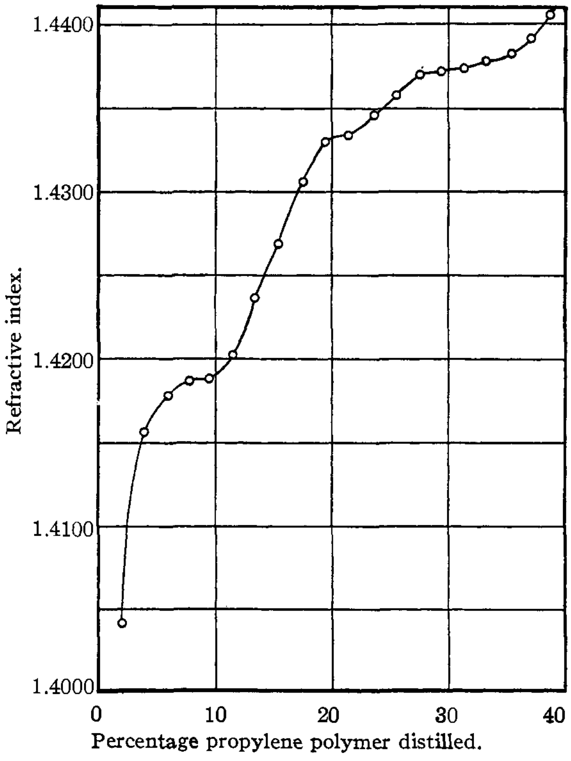

Fig. 1.

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[1] Butlerow and Gorianow, *Ann.*, **169**, 147 (1873).

[2] Otto, *Brennstoff-Chem.*, **8**, 321 (1927).