

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 Pb₃O₄; 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.

(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.

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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 recently² 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

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

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

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.

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

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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 1873¹ more than five decades elapsed before its use was exploited to any extent. Otto² reported the polymerization of ethylene and propylene with boron trifluoride and since then more than a score

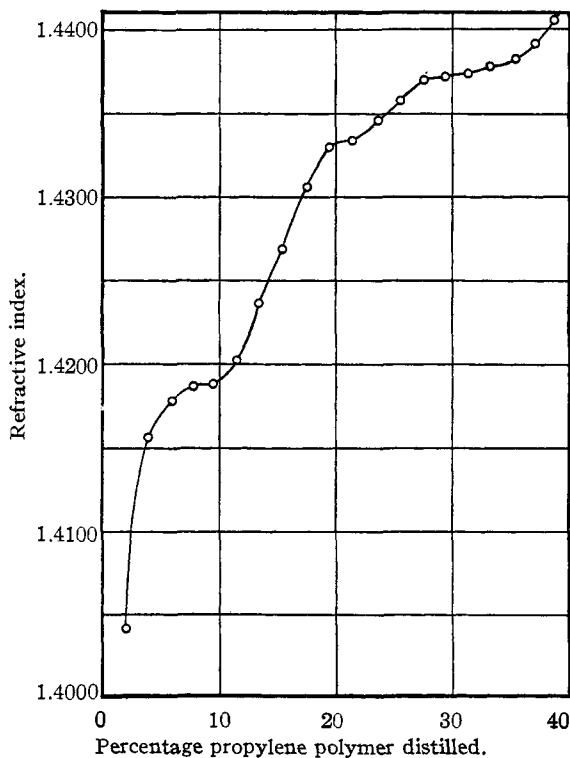


Fig. 1.

(1) Butlerow and Gorjanow, *Ann.*, **169**, 147 (1873).

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

of patents on such polymerization of olefinic compounds have appeared. In continuing the theoretical studies³ of olefin polymerization in this Laboratory, we have been led to investigate the action of boron trifluoride on alcohols, a type of reaction which has not been reported previously. This is of particular interest since this halide is believed to yield true polymerization products by its action on isobutylene at low temperatures.⁴

We have found that the action of boron trifluoride on isopropyl alcohol proceeds with the formation of polymerized products and from the reaction mixture we have isolated substantial yields of tetrapropylene.

Boron trifluoride (1400 g.) was dissolved in 2 kg. of isopropyl alcohol with external cooling and the resulting solution was heated in a loosely-

(3) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(4) I. G. Farbenindustrie, British Patent 401,297.

capped bomb at 100°. The reaction proceeded spontaneously with liberation of much boron trifluoride and other gases (propylene, the dimer, etc.). The contents of the bomb consisted of an upper layer of colorless polymer and a lower aqueous layer. The former was removed, washed free of acid, dried over anhydrous potassium carbonate and fractionated through a 12-plate distilling column of the type used in this Laboratory.⁵ Figure 1 shows the course of the distillation. The tetrapropylene, b. p. 94–105° at 30 mm., n_D^{20} 1.4358–1.4406, is about 20% of the 1200 g. of polymer formed from two kilograms of isopropyl alcohol. Investigation of the products is in progress.

(5) Whitmore and Lux, *THIS JOURNAL*, **54**, 3448 (1932).

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COMMUNICATIONS TO THE EDITOR

THE TOTAL SYNTHESIS OF THE SEX HORMONE EQUILENIN

Sir:

Although certain sex hormones such as estrone have been prepared from other naturally occurring compounds possessing similarities in structure, the total synthesis of none of them has yet been reported. We have now succeeded in accomplishing the total synthesis of the sex hormone equilenin, and in view of Marker's conversion of equilenin to estrone by reduction [*THIS JOURNAL*, **60**, 1897 (1938)] it follows that the total synthesis of both equilenin and estrone has been accomplished.

The reactions which were used are fairly obvious ones and the successful preparation of the hormone depended principally on developing the proper conditions for making the reactions proceed. As a matter of fact, some features of the method had been explored by other investigators without success. The starting point was the known 7-methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene, prepared from 1-naphthylamine-6-sulfonic acid (Cleve's acid).

An eleven-step synthesis converted this compound to equilenin. First of all this ketone was

condensed with methyl oxalate to give a 1-keto-2-glyoxalate derivative which by elimination of carbon monoxide yielded 7-methoxy-1-keto-2-carbomethoxytetrahydrophenanthrene. As early as 1932 Haworth [*J. Chem. Soc.*, 1125 (1932)] prepared the corresponding ethyl glyoxalate from 1-keto-tetrahydrophenanthrene but was unable to eliminate carbon monoxide without decomposing the compound. Under the proper conditions we were able to obtain the 2-carbomethoxy ketone in 89–91% yields. This compound readily was converted to the important intermediate, 7-methoxy-1-keto-2-methyl-2-carbomethoxytetrahydrophenanthrene (m. p. 84.5–86°) in excellent yield. From this point more or less standard procedures were employed to build up the five-membered ring. The Reformatsky reaction followed by dehydration and reduction of the unsaturated acid served to introduce an acetic acid group in the 1-position. As was expected, the product consisted of two racemic mixtures. These readily were separated into the *cis* (m. p. 228–230°) and the *trans* (m. p. 208–210°) 7-methoxy-1-acetic acid-2-methyl-2-carboxytetrahydrophenanthrene. Each of the acids was car-