

Dibutyltin Dicarboxylic Acid Esters

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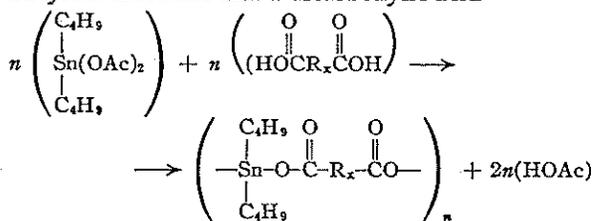
The preparation of a number of dibutyltin dicarboxylic acid esters, potentially useful in the synthesis of organometallic elastomers, is described. Dibutyltin oxide and dibutyltin diacetate were found to react readily with linear and cyclic dicarboxylic acids and anhydrides to form identical derivatives. Both reaction and structure studies indicate that the combining reaction is in the molar ratio of 1:1 regardless of the initial proportions used. Whereas such short chain aliphatic acids as succinic and adipic give soluble cyclic derivatives of low molecular weight, oxalic acid yields an insoluble, infusible product that has the characteristics of a hydrated salt. The cyclic terephthalic and the long chain sebacic acids, however, give linear polymers. The molecular weights vary from that of dimers to the order of 3000 for the sebacic acid product.

The work reported in this paper is part of a program to develop organometallic elastomers of chemically resistant and thermally stable properties. Although a considerable number of organometallic polymeric materials previously have been reported, only the organosilicon products are of wide significance as elastomers. Theoretically a number of other metals may react to form comparable and possibly superior type elastomers. It would be expected that group IV metals, especially tin and possibly titanium and zirconium, may conform in part to the basic type reactions of silicon as well as many of the reactions of carbon.¹ Tin, for example, does react similarly to carbon and silicon in many respects, but often in a manner peculiar to itself.²⁻⁷

It appeared probable that other metals, particularly those elements of even more metallic nature than silicon, would provide organometallic derivatives potentially capable of conversion to elastomers. Of the several metals offering favorable characteristics for reaction and polymer formation, tin appeared to have favorable possibilities. Such tin derivatives as the alkyl, aryl and alkoxy were well known. The dialkyl- and diaryl-tin oxides are insoluble and infusible, highly polymeric, amorphous materials that resemble metal oxides in their physical properties instead of being elastomeric like the silicones of similar chemical composition.

The present report deals with the reactions of dibutyltin oxide and dibutyltin diacetate with a varied series of dicarboxylic acids and anhydrides. These include adipic, succinic, sebacic, methyladipic, oxalic, terephthalic and itaconic acids or anhydrides, thus providing saturated and unsaturated, short and long chain, and ring-type acids for reaction and derivative evaluation. For the most part, the short chain derivatives such as the adipate and succinate are low molecular weight cyclic compounds of two to four alternating tin

and acid units. The terephthalate, however, is a chain-type product and the sebacate is a chain polymer of approximately 3000 molecular weight. The resulting products have been either hydrates or salts, cyclic polymers or linear polymers. Whether one employs dibutyltin diacetate or dibutyltin oxide in the reaction with a dicarboxylic acid or its anhydride, the reaction product is the same. The general type is illustrated by the reaction of dibutyltin diacetate and a dicarboxylic acid

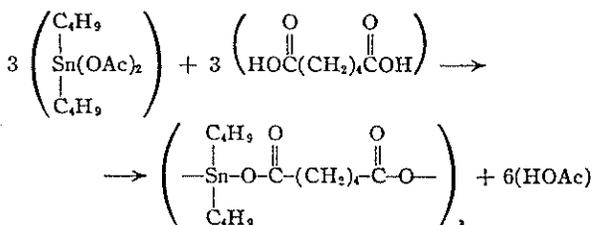


The R group may be a short or long chain of methylene groups with or without substituted groups, a ring compound or a combination of these.

The experimental work of this program has shown that in all cases, regardless of quantities used, the combining ratios are 1:1. This provides one of the conditions generally requisite for chain polymer formulation. This reaction ratio, however, would be essentially the same whether the resulting product is a chain or cyclic polymer. It has been found from these reactions that the directing factor as to whether the product has a chain or cyclic structure is the number of carbons between the reacting carboxyl groups.

The short chain acids such as adipic and succinic form cyclic dibutyltin compounds. The dibutyltin adipate product consists of three dibutyltin units alternately linked by three adipic acids. In the case of the succinate, four dibutyltins are similarly linked to form a cyclic tetramer. In neither compound is there any indication of free hydroxyl groups in the infrared spectrum.

The reaction of dibutyltin diacetate and adipic acid is considered to be as follows with three alternating tin and adipic groups forming a cyclic trimer



(1) J. G. A. Luijten and G. J. M. Van Der Kerk, "Investigations in the Field of Organotin Chemistry," Institute for Organic Chemistry, T.N.O., 79 Croesestraat, Utrecht, Holland.

(2) J. G. A. Luijten and G. J. M. Van Der Kerk, *J. Appl. Chem. (London)*, **4**, 301 (1954).

(3) Taichi Horada, "On the Metallo-Organic Compounds," The Institute of Physical and Chemical Research, Japan; November 29, 1938; October 25, 1939, V, VI, VII; September 30, 1940; October 31, (1940).

(4) Dietmar Seyferth and Eugene G. Rochow, *THIS JOURNAL*, **77**, 1302 (1955).

(5) Reuben G. Jones and Henry Gilman, *Chem. Rev.*, **54**, 835 (1954).

(6) N. V. Sidgwick, "Chemical Elements and their Compounds," Vol. 1, 1950, pp. 577-583.

(7) A. Cabours, *Ann.*, **114**, 244, 360, 364 (1860).

plastic, non-elastic, fully saturated product was obtained. No method was found for purification of the product.

Anal. Calcd. for $C_{13}H_{22}O_4Sn$: C, 43.25; H, 6.1; Sn, 32.91; neut. equiv., 180.4. Found: C, 40.33; H, 5.41; Sn, 28.59; neut. equiv., 188.

Dibutyltin 3-Methyladipate.—Molecular proportions of dibutyltin diacetate (5.03 g.) and 3-methyladipic acid (11.02 g.) were allowed to react at a gradual temperature rise in 300 ml. of xylene with azeotropic distillation until the by-product acetic acid was removed (91%). The xylene was then mostly removed by distillation and replaced by a 50/50

mixture of benzene and petroleum ether and warmed. The solution was cooled to -10° and left two days to crystallize. It was then filtered and washed with cold petroleum ether. The yield was 80% of crystalline material of m.p. 143-144.5°. The yield of product was 9.5 g. (78%).

Anal. Calcd. for $C_{15}H_{24}O_4Sn$: C, 46.07; H, 7.17; Sn, 30.08; neut. equiv., 195.4; mol. wt., 390.7. Found: C, 45.80; H, 7.30; Sn, 29.66; neut. equiv., 205; mol. wt., 800 (f.p. in benzene), 783 (Rast in camphor).

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