[CONTRIBUTION FROM CHEMICALS & PLASTICS DIVISION, Q.M.R. & E. COMMAND]

Dibutyltin Dicarboxylic Acid Esters

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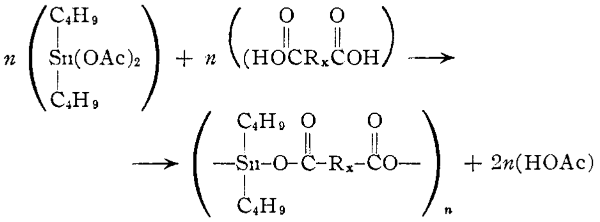
The preparation of a number of dibutyltin dicarboxylic acid esters, potentially useful in the synthesis of organometallic elastomers, is described. Dibutyltin oxide and dibutyltin diacetate were found to react readily with linear and cyclic dicarboxylic acids and anhydrides to form identical derivatives. 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



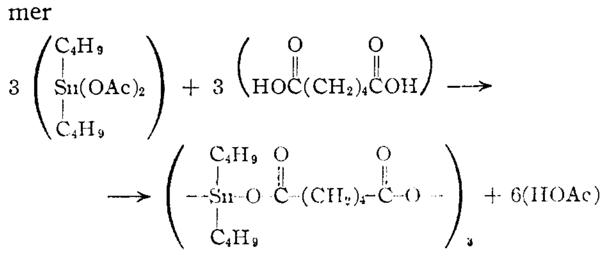
$$n\left(\begin{array}{c}C_4H_9\\ | \\ Sn(OAc)_2\\ | \\ C_4H_9\end{array}\right) + n\left(HO\overset{O}{\overset{\|}{C}}R_x\overset{O}{\overset{\|}{C}}OH\right) \longrightarrow \longrightarrow \left(-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\overset{O}{\overset{\|}{C}}-R_x-\overset{O}{\overset{\|}{C}}O-\right)_n + 2n(HOAc)$$

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



$$3\left(\begin{array}{c}C_4H_9\\ | \\ Sn(OAc)_2\\ | \\ C_4H_9\end{array}\right) + 3\left(HO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OH\right) \longrightarrow \longrightarrow \left(-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-\right)_3 + 6(HOAc)$$

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(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).

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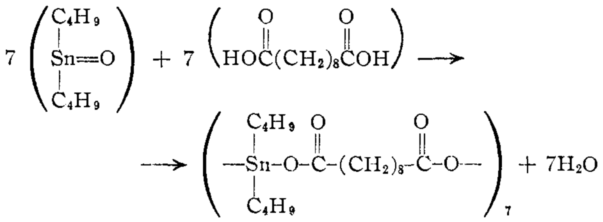
In the case of the succinic acid reaction with dibutyltin diacetate, a similar cyclic structure results but as a tetramer. The adipate was obtained in 85% yield as a crystalline product having a m.p. of 136–137° and a molecular weight of 1205. The succinate is also crystalline with 95% yield and a m.p. of 187–187.5° and molecular weight of 1420. The reactions may be carried out in benzene, toluene or xylene from moderate temperature to boiling, but preferably at slow boil to remove by-product water or acetic acid. These reactions and the resulting products have been characterized wherever possible by complete analytical data, molecular weight, neutralization equivalent and infrared analysis for free hydroxyl. The neutralization equivalent is essentially a saponification value and helps both in determining the number of acid groups in the product and the resulting reaction ratio. The infrared spectrum was employed for determining the presence or absence of free hydroxyl groups and probable structures of the products.

A somewhat complicated type of reaction takes place when oxalic acid is allowed to react with dibutyltin diacetate. These seem to react in a manner typical of many oxalic acid reactions.[7] The product is apparently a dibutyltin oxalate in the form of a monohydrate insoluble in all ordinary solvents. The powdery product does not melt but decomposes at 195°. Infrared analysis gives a strong test for the hydroxyl group.

In other similar reaction procedures the tendency to form cyclic derivatives has been overcome by using either a longer chain dicarboxylic acid or a ring type dicarboxylic acid. When sebacic acid is treated with either dibutyltin oxide or diacetate there is obtained in 96% yield a white waxy solid of m.p. 78–82°.



$$7\left((C_4H_9)_2Sn{=}O\right) + 7\left(HO\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OH\right) \longrightarrow \left(-\underset{C_4H_9}{\overset{C_4H_9}{Sn}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-\right)_7 + 7H_2O$$

From the reaction and analytical data and its molecular weight, it is concluded that the product is a chain polymer of the order of 3000 molecular weight, comprising seven units of dibutyltin sebacate. Terephthalic acid and dibutyltin oxide or diacetate were found to react to give practically 100% yield of dibutyltin terephthalate. The product in this case, however, is insoluble in all ordinary solvents and does not melt up to 245°. It is assumed that this is a high molecular weight chain-type polymer.

The further reactions of dibutyltin oxide or diacetate with varied type dicarboxylic acids give only cyclic structures generally similar to those of the adipate and succinate. The 3-methyladipic acid which is heated with dibutyltin oxide in xylene with azeotropic distillation gave an 80% yield of crystalline dibutyltin 3-methyladipate, m.p. 142–143°. The product is a cyclic dimer with no indication of free hydroxyl in the infrared spectrum. Dibutyltin diacetate was similarly allowed to react with itaconic acid. This unsaturated acid provided the possibility not only of a chain or cyclic reaction product by means of the dicarboxylic but also by subsequent reaction through the vinyl or unsaturated group of the acid. The resulting dibutyltin itaconate is waxy or plastic, non-elastic and fully saturated.

Experimental

Dibutyltin Adipate.—A solution of 16.7 g. (0.048 mole) of dibutyltin diacetate, 6.9 g. (0.047 mole) of adipic acid and 100 ml. of xylene was heated at slow temperature rise with azeotropic distillation to 136°. At this time 95% of the by-product acetic acid had distilled over. When practically all the xylene had distilled, 50 ml. of benzene was added and the solution left to crystallize at −10°. The yield after purification was 15.4 g. (85%) of dibutyltin adipate crystals of m.p. 136–137°.

Anal. Calcd. for $C_{14}H_{26}O_4Sn$: C, 44.60; H, 6.90; Sn, 31.51; neut. equiv., 188.4; mol. wt., 376.7. Found: C, 44.55; H, 7.10; Sn, 31.36; neut. equiv., 183.0; mol. wt., 1205.

Dibutyltin Sebacate.—A mixture of 8.3 g. (0.033 mole) of dibutyltin oxide, 6.8 g. (0.033 mole) of sebacic acid and 300 ml. of benzene was heated under reflux with a Dean–Stark trap for two hours. The benzene was then removed under vacuum. Due to the extreme solubility of the product, no satisfactory purification was accomplished. The yield was 13.9 g. (96%) of a white waxy solid of m.p. 78–82° and molecular weight of approximately 3000.

Anal. Calcd. for $C_{18}H_{34}O_4Sn$: C, 49.92; H, 7.86; Sn, 27.43; neut. equiv., 216.4; mol. wt., 432.7. Found: C, 50.10; H, 7.96; Sn, 27.52; neut. equiv., 216.0; mol. wt., 3000 (Rast in camphor) and 2950 (f.p. in benzene).

Dibutyltin Succinate.—Dibutyltin oxide 10.0 g., (0.040 mole), 4.03 g. (0.039 mole) of succinic anhydride and 300 ml. of xylene were heated under reflux for four hours, cooled and the precipitate separated by filtration, washed with absolute alcohol and recrystallized from benzene. This gave 13.3 g. (95%) of crystalline dibutyltin succinate of m.p. 187–187.5°. Analytical and physical data, including molecular weight (Rast), indicate the product is a cyclic tetramer.

Anal. Calcd. for $C_{12}H_{22}O_4Sn$: C, 41.29; H, 6.31: Sn, 34.02; neut. equiv., 169.4; mol. wt., 348.7 Found: C, 41.23; H, 6.51; Sn, 34.02; neut. equiv., 164; mol. wt., 1430 (Rast in camphor).

Dibutyltin Oxalate.—To a solution of 4.07 g. (0.045 mole) of oxalic acid in 300 ml. of a 50/50 mixture of xylene and dioxane was added 15.8 g. (0.045 mole) of dibutyltin diacetate. The solution was heated under azeotropic distillation until 95% of the theoretical acetic acid was recovered. The resulting insoluble product was removed by filtration and soxhlet extracted with dioxane. It is insoluble in all solvents and begins to decompose at 195°. The yield was 13.5 g. (95%) of an indicated monohydrate of dibutyltin oxalate.[7]

Anal. Calcd. for $C_{10}H_{18}O_4Sn \cdot H_2O$: C, 35.43; H, 5.91; Sn, 35.10. Found: C, 35.27; H, 6.10; Sn, 35.37.

Dibutyltin Terephthalate.—Dibutyltin diacetate 15.14 g., (0.04 mole) was allowed to react in 1:1 ratio with 7.17 g. (0.043 mole) of terephthalic acid in 250 ml. of toluene with azeotropic distillation. The reaction went with difficulty and only 68.03% of by-product acetic acid was recovered. The solid product was filtered off and soxhlet extracted with N,N-dimethylformamide, giving 17.0 g. (100%) of insoluble product that was not further purified. The material does not melt up to 245°. With the *p*-carboxyl groups of terephthalic acid being in a relatively fixed position, it would be expected that cyclization would be prevented and a chain derivative produced.

Anal. Calcd. for $C_{16}H_{22}O_4Sn$: C, 48.40; H, 5.55; Sn, 29.92; neut. equiv., 188.4. Found: C, 46.92; H, 5.51; Sn, 30.45; neut. equiv., 213.

Dibutyltin Itaconate.—Dibutyltin diacetate (26.407 g.) was treated with 9.789 g. of itaconic acid in 300 ml. of benzene with heating for 1.5 hours and subsequent distillation until 100% by-product acetic acid was removed. After evaporation of residual solvent under vacuum, a waxy or 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 $C_{15}H_{28}O_4Sn$: 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).

NATICK, MASSACHUSETTS

[CONTRIBUTED FROM THE RESEARCH LABORATORIES OF THE DOW CORNING CORPORATION]

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part III. The Addition to Non-terminal Olefins in the Presence of Chloroplatinic Acid

BY JOHN C. SAAM AND JOHN L. SPEIER

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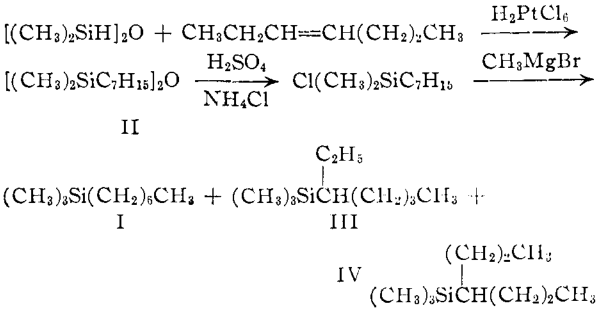
In the presence of chloroplatinic acid, trichlorosilane methyldichlorosilane or dimethylchlorosilane and heptene-3 formed *n*-heptylchlorosilanes in good yields. Symmetrical tetramethyldisiloxane and heptene-3 formed 1,3-di-*n*-heptyltetramethyldisiloxane along with smaller amounts of the 3- and 4-heptyl isomers.

The unexpected formation of *n*-pentylsilanes from pentene-2 and methyldichlorosilane or trichlorosilane in the presence of chloroplatinic acid, ruthenium chloride or platinum-on-charcoal has recently been described.[1] The novelty of this result prompted an investigation of the addition of various silicon hydrides to heptene-3 where the terminal position of the olefin is more remote from the double bond and is less subject to inductive or resonance effects.

Refluxing trichlorosilane with heptene-3 in the presence of chloroplatinic acid resulted in excellent yields of *n*-heptyltrichlorosilane. The product was converted with excess methylmagnesium bromide to the known heptyltrimethylsilane (I)[2] and compared with an authentic sample prepared from trimethylchlorosilane, *n*-heptyl chloride and sodium.[3] A gas–liquid phase chromatogram and an infrared spectrum of the trimethyl derivative of the adduct revealed that it was free of isomers and identical with the authentic sample. Likewise, methyldichlorosilane and dimethylchlorosilane reacted with heptene-3 in the presence of chloroplatinic acid to form only the *n*-heptylsilanes in good yields, and in each case the products were converted to *n*-heptyltrimethylsilane (I) which was identical with the authentic sample and free of isomers.

One siloxane, *sym*-tetramethyldisiloxane, was found to yield a mixture of 1,3-diheptyltetramethyldisiloxane, (II). The mixture was converted to the heptyltrimethylsilanes by employing the flood reaction.[4]



$$[(CH_3)_2SiH]_2O + CH_3CH_2CH{=\!=}CH(CH_2)_2CH_3 \xrightarrow{H_2PtCl_6}$$

$$\underset{\text{II}}{[(CH_3)_2SiC_7H_{15}]_2O} \xrightarrow[NH_4Cl]{H_2SO_4} Cl(CH_3)_2SiC_7H_{15} \xrightarrow{CH_3MgBr}$$

$$\underset{\text{I}}{(CH_3)_3Si(CH_2)_6CH_3} + \underset{\text{III}}{(CH_3)_3Si\overset{C_2H_5}{\overset{|}{C}}H(CH_2)_3CH_3} + \text{IV}\ (CH_3)_3Si\overset{(CH_2)_2CH_3}{\overset{|}{C}}H(CH_2)_2CH_3$$

A gas–liquid phase chromatogram of the heptyltrimethylsilanes revealed three components, the major component being identical with *n*-heptyltrimethylsilane (I). The two minor components were identical to the authentic mixed 3- and 4-heptyltrimethylsilanes which were prepared by the addition of trichlorosilane to heptene-3 in the presence of acetyl peroxide[5] followed by treatment of the adduct with excess methylmagnesium bromide. The results of the addition of various silicon hydrides to heptene-3 are summarized in the table.

These results and others[1] indicated a strong tendency for the chlorosilyl group of the silicon hydride to add to the terminal position of the olefin, even when the double bond was as remote as two carbon atoms from the terminal position. This tendency appeared to have been somewhat weakened when the silicon hydride was a siloxane.

A plausible explanation of these results could require a nucleophilic attack at the double bond by a hydride ion, brought about by the catalyst. The resulting 3- or 4-secondary carbanion (A) would tend to acquire a more stable configuration by transmitting the negative charge to the terminal position through the transition states B or B′. Transition state B is a series or a cascade of "α-hydrogen bonds"[6] involving the protons along the chain; whereas transition state B′ is a five- or six-membered cyclic in which a terminal proton is

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[1] J. L. Speier, J. A. Webster and G. H. Barnes, THIS JOURNAL, **79**, 974 (1957).

[2] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. VanStrien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, *ibid.*, **68**, 475 (1946), report b.p. 184° at 760 mm., n^{20}_D 1.4201, d^{20}_4 0.7506.

[3] J. L. Speier, *ibid.*, **74**, 1003 (1952).

[4] E. A. Flood, *ibid.*, **55**, 1735 (1933).

[5] J. L. Speier, R. Zimmerman and J. Webster, *ibid.*, **78**, 2278 (1956); L. H. Sommer, E. Pietruza and F. C. Whitmore, *ibid.*, **69**, 188 (1947).

[6] M. M. Kreevoy and H. Eyring, *ibid.*, **79**, 5121 (1957).