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Abstract

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STEPWISE FORMATION OF COMPOUNDS WITH A STANNOXANE BOND AND REACTIVE TERMINAL GROUPS

The study of the stannoxane bond has begun only in recent years. Among individual compounds of this type, several dimers are known (^{1}), and a tetramer of the following structure was first obtained by M. M. Koton and G. M. Kiseleva (^{2}):
C_2H_5O—$[Sn(C_4H_9)_2OSn(OC_2H_5)_2O]_4$—$OC_2H_5$.

The use of hydrolysis of compounds $R_2Sn(OCOCH_3)_2$, as well as the polycondensation reaction between dibutyltin diacetate and dibutyldibutoxytin for obtaining individual compounds, does not lead to the desired result, since mixtures are formed in this case (^{3}). However, as we have already briefly reported earlier (^{4}), hydrolysis of organotin salts of organic acids with a calculated amount of water in the presence of diazoalkanes proceeds according to the equation:

$$2R_2Sn(OOCCH_3)_2 + 2CH_2N_2 + H_2O \rightarrow CH_3COO\cdot Sn(R)_2OSn(R)_2OOCCH_3 +$$

$$+2CH_3COOCH_3 + 2N_2.$$

This procedure makes it possible: a) to carry out the formation of individual compounds in stages; b) to obtain linear compounds with active terminal groups, creating the possibility of carrying out further steps.

In the present work, the sequence of the following transformations is described: monomer (I) → dimer (II) → tetramer (III) → octamer (IV) → hexadecamer (V), characterized by elemental analysis, infrared spectra, determination of molecular weight, boiling, melting, and decomposition temperatures (Table 1). By varying the amount of water and diazomethane, the reaction can, if desired, be stopped at the formation of individual compounds with a specified molecular weight. Thus, for example, from the monomer (dibutyltin diacetate*) a dimer (ω,ω-diacetate of tetrabutyldistannoxane) was obtained, and from the same monomer a tetramer (ω,ω-diacetate of octabutyltetrastannoxane).

When the temperature is raised to 40–45°, it is possible to obtain individual stannoxanes with still higher molecular weight. The method found apparently has general significance—it can be carried out when two hydrolyzable groups (residues of an organic acid) are present in compounds of the type $R_2El(OOCR)_2$ or $El(OOCR)_4$. In a recently published article (5), we obtained plumboxanes in this way.

Compounds with a stannoxane bond were used as stabilizers for polyvinyl chloride and other chlorine-containing polymers (6).

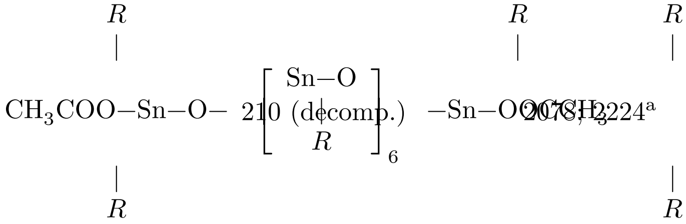
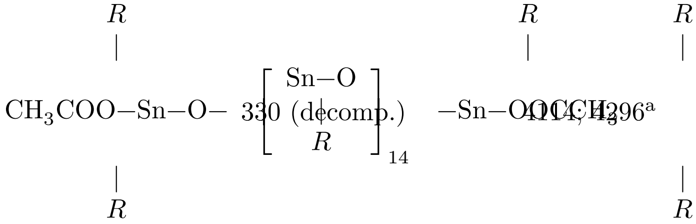
Experimental Part

1. ω,ω-Diacetate of tetrabutyldistannoxane. To a solution of 16.25 g (0.043 mole) of dibutyltin diacetate in 120 ml of dry acetone, 0.8 ml (0.044 mole) of water is added and, dropwise over 15 min, 1.84 g (0.044 mole; 8% excess) of diazomethane in 73 ml of ether. The diazomethane is rapidly decolorized, and gas is evolved.

* Everywhere n-C_4H_9.

Table 1

Compound	Temp., °C	Molecular weight, found	Molecular weight, calc.
$CH_3COO{-}\underset{R}{\overset{R}{Sn}}{-}OOCCH_3$	146–147/10 (2) (b.p.)	341.6[a] 347.5[b]	350.9
$CH_3COO{-}\underset{R}{\overset{R}{Sn}}{-}O{-}\underset{R}{\overset{R}{Sn}}{-}OOCCH_3$	58–60 (m.p.)	591; 624[a] 588; 602[b]	599.9
$CH_3COO{-}\underset{R}{\overset{R}{Sn}}{-}O{-}\left[\begin{array}{c}Sn{-}O\\ R\end{array}\right]_2{-}\overset{R}{Sn}{-}\underset{R}{\overset{R}{}}OOCCH_3$	137–138 (m.p.)	1100; 1146[a] 1072; 1079[b] 1069; 1110[c]	1097.8

Compound	Temp., °C	Molecular weight, found	Molecular weight, calc.
 $CH_3COO-\underset{R}{\overset{R}{Sn}}-O-\left[\underset{R}{Sn}-O\right]_6-\underset{R}{\overset{R}{Sn}}-OOCCH_3$	210 (decomp.)	2078; 2224[a]	2093.5
 $CH_3COO-\underset{R}{\overset{R}{Sn}}-O-\left[\underset{R}{Sn}-O\right]_{14}-\underset{R}{\overset{R}{Sn}}-OOCCH_3$	330 (decomp.)	4114; 4296[a]	4084.8

[a] —by terminal groups; [b] —cryoscopically in benzene; [c] —by depression of the m.p. of stilbene; R = n-C_4H_9.

The solvent is removed in vacuo; the residue, a yellowish liquid, crystallizes on cooling to 0°. The crystals are filtered off and washed on the filter with a small amount of cold hexane. This gives 10.8 g (82.9%) of a substance with m.p. 56—58°. ω,ω-Diacetate of tetrabutyldistannoxane is readily soluble in all organic solvents, and its recrystallization is associated with large losses.

Thus, from a solution of 3 g of the substance in 1.5 ml of hexane, 1 g of crystalline precipitate with m.p. 58—60° separated.

$C_{20}H_{42}O_5Sn_2$. Found, %: C 39.68; 39.74; H 6.89; 6.99; Sn 40.05
Calculated, %: C 40.04; H 7.06; Sn 39.56

2. ω,ω-Diacetate of octabutyltetrastannoxane.
a) To a solution of 19.7 g (0.033 mole) of ω,ω-diacetate of tetrabutyldistannoxane in 70 ml of dry acetone are added 0.5 ml (0.028 mole) of water and, dropwise over 20 min, 1.39 g (0.033 mole) of diazomethane in 58.5 ml of ether. The diazomethane is rapidly decolorized, and gas is evolved. The colorless solution is evaporated in vacuo to approximately half its volume; the crystals that separate are filtered off and dried in vacuo. This gives 15.2 g (84.3%) of ω,ω-diacetate of octabutyltetrastannoxane with m.p. 137—138° (with decomposition).

Found, %: C 39.50, 39.77; H 7.04, 7.07; Sn 42.41

The product obtained was subjected to analysis without additional purification. It can be dissolved in chloroform and, by slow addition of hexane or ether, a crystalline precipitate can again be obtained. The melting point does not change.

b) To a solution of 16.7 g (0.048 mole) of dibutyltin diacetate in 50 ml of dry acetone are added 1.5 ml (0.083 mole) of water and, dropwise over 15 min.

3.028 g (0.072 mole) of diazomethane in 130 ml of ether. After half an hour the colorless solution is evaporated in vacuo to approximately one half; the crystals that separate are filtered off and dried in vacuo. This gives 8.5 g (65.1%) of the ω,ω-diacetate of octabutyltetrastannoxane, m.p. 137–138° (with decomposition).

$C_{36}H_{78}O_7Sn_4$. Found, %: C 39.26, 39.40; H 7.14, 7.24; Sn 42.78, 42.63
Calculated, %: C 39.35; H 7.15; Sn 43.20

The ω,ω-diacetate of octabutyltetrastannoxane is readily soluble in chloroform in the cold, and on heating in benzene, alcohol, and carbon tetrachloride. It is moderately soluble on heating in hexane, acetone, and methyl ethyl ketone.

3. ω,ω-Diacetate of hexadecabutyloctastannoxane. To a solution of 5.0 g (0.0046 mole) of the ω,ω-diacetate of octabutyltetrastannoxane in 400 ml of dry methyl ethyl ketone are added 0.3 ml (0.0166 mole) of water and 0.2022 g (0.0048 mole) of diazomethane in 7.5 ml of ether. After 6 hr the colorless solution is evaporated in vacuo to approximately one half; the precipitate that separates is filtered off and dried in vacuo. This gives 3.0 g (63%) of the ω,ω-diacetate of hexadecabutyloctastannoxane with decomposition temperature about 210°.

$C_{68}H_{150}O_{11}Sn_8$. Found, %: C 39.03, 39.08; H 7.19, 7.22; Sn 45.48, 45.51
Calculated, %: C 39.08; H 7.24; Sn 45.44

The substance is readily soluble on heating in chloroform and benzene, and moderately soluble in acetone, methyl ethyl ketone, and hexane.

4. ω,ω-Diacetate of dotriacontabutylhexadecastannoxane. To a solution of 5.2 g (0.0047 mole) of the ω,ω-diacetate of octabutyltetrastannoxane in 250 ml of dry methyl ethyl ketone are added 0.1 ml (0.0055 mole) of water and a solution of 0.3058 g (0.0073 mole) of diazomethane in 14 ml of ether. Diazomethane at 37–40° is decolorized within 2 hr. On cooling, a precipitate (0.93 g) separates, which is filtered off.

The solution is evaporated in vacuo to approximately 1/3. This gives 2.3 g (47.5%) of the hexadecamer with decomposition temperature above 330°.

Found, %: C 38.68, 38.80;
H 7.16, 7.24; Sn 46.67, 46.82
$C_{132}H_{294}O_{19}Sn_{16}$.
Calculated, %: C 38.82;
H 7.25; Sn 46.50

Fig. 1. Infrared spectra of ω,ω-diacetates (from top to bottom) of tetrabutyldistannoxane, octabutyltetrastannoxane, hexadecabutyloctastannoxane, and dotriacontabutylhexadecastannoxane.

Figure 1: Fig. 1. Infrared spectra of ω,ω-diacetates (from top to bottom) of tetrabutyldistannoxane, octabutyltetrastannoxane, hexadecabutyloctastannoxane, and dotriacontabutylhexadecastannoxane.

The substance is moderately soluble in hot xylene.

The spectra of the compounds obtained (Fig. 1) with the stannoxane bond were measured in the region from 2000 to 400 cm^{-1} on an H-800 infrared spectrophotometer (Hilger); the samples were prepared as pastes in Vaseline oil.

Since the spectrum of Vaseline oil has strong absorption bands at 1460 and 1380 cm^{-1}, the curves in this region in Fig. 1 are shown by dashed lines. In the spectra of all the compounds investigated there are bands in the region 1640-1580 cm^{-1}, which are attributed to symmetric stretching vibrations of the carboxylate ion; moreover, for the last three members of the series of substances studied, the carboxylate-ion band lies in the region of 1608 cm^{-1}, and its intensity decreases as the molecular weight increases. The spectrum of tetrabutyl-distannoxane ω,ω-diacetate differs sharply from the spectra of the other members of the series. In particular, in the indicated region of 1600 cm^{-1} it shows two intense bands, 1640 and 1580 cm^{-1}, which are assigned to vibrations of the carboxylate ion. The presence of two bands in this region had previously been observed in the spectra of some organotin and organolead salts of organic acids ([7]). The reasons for such splitting of the band in this region are not clear; it is possible that it is due to different packing of the ions in the crystal lattice of the salt.

Fig. 1. Infrared spectra of ω,ω-diacetates (from top to bottom) of tetrabutyldistannoxane, octabutyltetrastannoxane, hexadecabutyloctastannoxane, and dotriacontabutylhexadecastannoxane.

The two very intense bands in the regions of 640 and 478 cm^{-1} in the spectrum of tetrabutyl-distannoxane ω,ω-diacetate should be assigned to different deformation vibrations of the carboxylate ion ([8]), and the strong band at 670 cm^{-1}— to deformation vibrations of the CH_2 group in the butyl radical bonded to the tin atom ([8]).

The band at 670 cm^{-1} is observed in the spectra of all the compounds studied. The intensity of the bands at 640 and 478 cm^{-1}, however, decreases very strongly as the number of $-Sn(R)_2O - Sn(R)_2$ units in the molecule of the substance increases; at the same time, in the region of 600-400 cm^{-1} a series of intense bands appears, which are assigned to vibrations of the Sn—C and Sn—O—Sn bonds ([9]).

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