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Synthesis of mixed organotin compounds via dialkylstannyl derivatives of sulphomaleic anhydride

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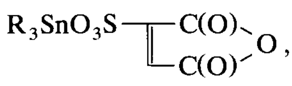
Abstract

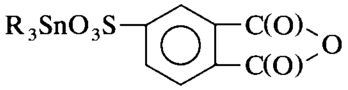
A few mixed organotin compounds which combine two different organotin moieties (R_2Sn and R'_2Sn or R_2Sn and R'_3Sn) in the same molecule have been synthesized using trialkylstannyl- and new dialkylstannyl derivatives of sulphomaleic anhydride as starting materials.

Keywords: Tin; Stannyl; Alkyl

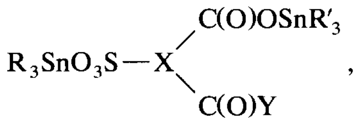
1. Introduction

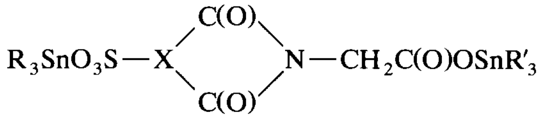
Recently [1] we synthesized and characterized the trialkyltin derivatives of sulphomaleic and 4-sulphophthalic anhydrides with the following formulas:

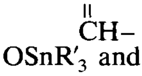




On the basis of these compounds, by the addition of some nucleophilic agents (alcohols, amines, trialkyltin oxides and others) to reactive anhydride cycle, we prepared numerous mixed trialkyltin compounds [2] of the following general formulas:







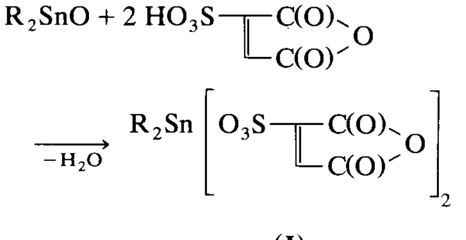
X = $-\underset{\underset{\text{CH}-}{\|}}{\text{C}}-$, o-C_6H_3; Y = OH, OR, NH_2, NR_2, $OSnR'_3$ and others

This is a very suitable way to prepare both mixed organotin and mixed organometallic compounds, i.e. combining R_nM– and R_nM'– or R'_nM'– moieties in the same molecule. One example (trialkylstannyl-trialkylgermyl-containing compound) was described in a recent paper [1].

In the present paper, we describe the preparation of a series of dialkylstannyl derivatives of sulphomaleic anhydride, i.e. having two anhydride heterocycles in the same molecule, and also the synthesis of new mixed dialkyltin compounds.

2. Results and discussion

Dialkylstannyl derivatives of sulphomaleic anhydride were prepared by acid-base reactions of sulphoanhydride with appropriate dialkyltin oxides in polar solvent:



(I)

R = Me (a), Et (b), Bu (c), n.Okt (d), cyclo-Hex (e)
Acetonitrile sulphoanhydride and organotin products are disolvable in well is suitable solvent to carry out all reactions. Thus, we have synthesized new dialkylstan-

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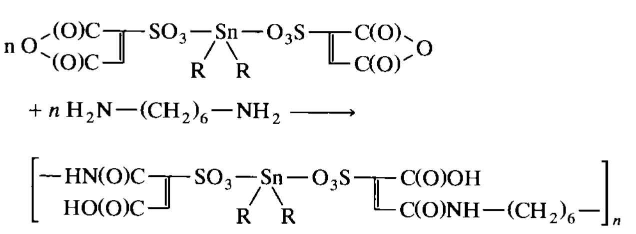
nyl derivatives **Ia–e**: *O,O′*-dimethylstannyl-bis-[(oxysulphonyl)maleic anhydride] (**Ia**), *O,O′*-diethylstannyl-bis-[(oxysulphonyl)maleic anhydride] (**Ib**), *O,O′*-dibutylstannyl-bis-[(oxysulphonyl)maleic anhydride] (**Ic**), *O,O′*-dioktylstannyl-bis-[(oxysulphonyl)maleic anhydride] (**Id**), *O,O′*-dicyclohexylstannyl-bis-[(oxysulphonyl)maleic anhydride] (**Ie**).

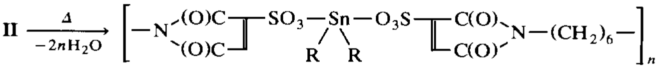
With two anhydride heterocycles, the derivatives **I** can be classified as bifunctional compounds. Our interest lies in the easy opening either anhydride cycles under the action of bifunctional nucleophilic agents, such as diamines. This enables the chain growth to occur and condensation polymeric products obtained. Thus, the compounds **Ic** and hexamethylenediamine interact readily at room temperature giving a colourless insoluble precipitate. Considering the elemental analysis and IR data for this solid, the reaction can be represented in accordance with the universally adopted scheme:



(II)

(2)

At the next stage, compound **II** was subjected to imidization by heating in vacuo at 130–150°C and freezing out the liberated water:



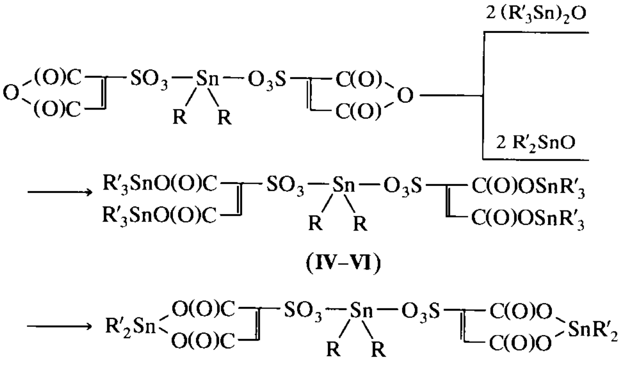
(III)

(3)

The single band ν(NH) present in the IR spectrum of **II** (3400 cm^{-1}) is missing in the spectrum of **III**, suggesting that the imide-cycles were formed at the expense of water elimination.

The synthetic route described below permits the synthesis of mixed organotin compounds (i.e. compounds with two equally alkylated organotin moieties in the same molecule with various alkyl groups at each tin atom: R_3Sn– and R'_3Sn [2] or R_2Sn= and R'_2Sn=) as well as twice-mixed organotin compounds (i.e. compounds containing two differently alkylated organotin groups along with various organic moieties around the tin atoms: R_3Sn– and R'_2Sn=).

We demonstrate here several synthetic variations which are distinguished by the structure of the starting compounds. As an illustration, a few model mixed dialkylstannyl-dialkylstannyl-derivatives and twice-mixed dialkylstannyl-trialkylstannyl-derivatives have been prepared in accordance with Eqs. (4) and (5):

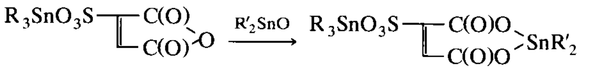


(VII)

(4)

R = Me, R′ = Bu (**IV**); R = Et, R′ = Bu (**V**); R = Bu, R′ = Et (**VI**) and (**VII**)

In this way we have synthesized tetrakis-tributyltin{*O,O′*-dimethylstannyl)-bis-[(oxysulphonyl)maleate]} (**IV**), tetrakis-tributyltin{*O,O′*-(diethylstannyl)-bis-[(oxysulphonyl)maleate]} (**V**), tetrakis-triethyltin{*O,O′*-(dibutylstannyl)-bis-[(oxysulphonyl)maleate]} (**VI**) and bis-diethyltin{*O,O′*-(dibutylstannyl)-bis-[(oxysulphonyl)maleate]} (**VII**).



(VIII, IX)

(5)

R = Et, R′ = Bu (**VIII**);
R = Bu, R′ = Et (**IX**).

According to Eq. (5), we have obtained dibutyltin *O*-(triethylstannyl)oxysulphonylmaleate (**VIII**) and diethyltin *O*-(tributylstannyl)oxysulphonylmaleate (**IX**).

3. Experimental details

Trialkyltin- and dialkyltin oxides were prepared by the alkali hydrolysis of corresponding trialkyltin chloride or dialkyltin dichloride in ethanol [3]. Sulphomaleic anhydride and their trialkylstannyl derivatives were prepared as described in our recent paper [1].

The IR spectra were obtained with a Perkin-Elmer 577 spectrometer using Nujol mulls (KBr). In spite of our efforts, it was impossible to record the spectra of **Ia–e** and **VII–IX** with fairly high resolution particularly in the 1500–1000 cm^{-1} region (powerful absorption).

Because original sulphomaleic anhydride and its organotin derivatives are hygroscopic, all reactions were carried out under a dry atmosphere and in dry acetonitrile. Sealed capillary tubes were used for the determination of melting points. In most cases, the melting points were equal to the decomposition points. Yields, melting points, analytical data and main IR bands for the new organotin compounds obtained are given in Table 1.

3.1. Preparation of compounds Ia–e

Typically, a solution of sulphomaleic anhydride in 50 ml of acetonitrile was added dropwise during 0.5 h to a stirred suspension of dialkyltin oxide (3 g) in 50 ml of acetonitrile while keeping the anhydride oxide molar ratio at 2:1. The mixture was refluxed for 5–6 h with stirring and cooled to room temperature. Minor amounts of R_2SnSO_4 (up to 0.3 g) were filtered off as by-product. The azeotrope and then a basic quantity of the remaining solvent were distilled off with a Dean-Stark funnel from the filtrate. The residue obtained was evaporated off under reduced pressure and kept in vacuo at 70°C for 3 h to isolate the following products (Table 1): **Ia** (5.96 g; 11.8 mmol); **Ib** (5.33 g; 10.0 mmol); **Ic** (5.61 g; 9.5 mmol); **Id** (4.89 g; 7.0 mmol); **Ie** (5.16 g; 8.1 mmol).

3.2. Preparation of product II and its imidization

A solution of hexamethylenediamine (0.40 g; 3.4 mmol) in 20 ml acetonitrile was added dropwise during 0.5 h to a stirred solution of **Ic** (2.0 g; 3.4 mmol) in 30 ml of acetonitrile. The mixture was stirred for 1 h at room temperature, the colourless precipitate was separated on a glass filter, washed with acetone (3 × 5 ml) and dried in vacuo at 70°C for 1 h to yield the polymeric product **II** (2.35 g; 3.2 mmol; 94%, melted over the range 135–145°C). IR: 3400 cm^{-1} [ν(NH)]. Found: C, 37.33; H, 6.84; S, 9.20; Sn, 17.41. $C_{22}H_{36}N_2O_{12}S_2Sn$ calcd.: C, 37.57; H, 5.16; S, 9.12; Sn, 16.88%.

The product **II** (1.2 g; 1.7 mmol) was heated in vacuo with slowly increasing temperature up to 150°C in a definite time (10–15 h); the water released (0.062 g; 3.4 mmol) was removed in a trap (−178°C) to obtain the polymeric product **III** (1.13 g; 1.7 mmol; 100%, melted over the range 110–155°C) as a yellowish amorphous residue. IR: the band [ν(NH)] was absent. Found: C, 38.60; H, 4.44; S, 9.23; Sn, 18.10. $C_{22}H_{32}N_2O_{10}S_2Sn$ calcd.; C, 39.60; H, 4.83; S, 9.61; Sn, 17.79%.

3.3. Preparation of mixed organotin compounds IV–IX

Typically, a solution of tributyltin or triethyltin oxides or a suspension of diethyltin oxide in 20 ml of acetonitrile was added during 0.5 h to a stirred solution of selected compound **I** (1 g) in 30 ml of acetonitrile while keeping the organotin oxide/organotin anhy-

Table 1
Characterization date for new organotin compounds

Compound	Yield (%)	M.p. (°C) [a]	Formula	Anal. (Found (calcd.) (%))				IR bands (max., cm^{-1})			
				C	H	S	Sn	ν(C=O)	$\nu(SO_2)$		ν(Sn–C)
									Asymmetric	Symmetric	
Ia	65	80–85	$C_{10}H_8O_{12}S_2Sn$	23.52 (23.88)	2.10 (1.60)	11.38 (12.75)	22.95 (23.59)	1770, 1705	1270–1160 [b]		520
Ib	60	70–75	$C_{12}H_{12}O_{12}S_2Sn$	27.17 (27.14)	3.08 (2.28)	11.82 (12.07)	22.29 (22.35)	1830, 1770	1270–1160 [b]		550, 520
Ic	79	65–70	$C_{16}H_{20}O_{12}S_2Sn$	32.58 (32.73)	4.03 (3.43)	10.54 (10.92)	20.54 (20.21)	1725, 1705	1280, 1240, 1205	1150	555, 520
Id	84	Wax	$C_{24}H_{36}O_{12}S_2Sn$	41.45 (41.22)	5.43 (5.15)	8.50 (9.15)	16.51 (16.99)	1730, 1705	1300–1140 [b]		520
Ie	81	88–95	$C_{20}H_{24}O_{12}S_2Sn$	36.95 (37.58)	4.56 (3.78)	9.50 (10.03)	18.64 (18.56)	1770, 1710	1260–1160 [b]		530
IV	65	75	$C_{58}H_{116}O_{14}S_2Sn_5$	39.72 (41.10)	6.63 (6.90)	3.32 (3.78)	35.64 (35.01)	1570– 1540 [b]	1220	1140	780 [c] 520
V	58	65–70	$C_{60}H_{120}O_{14}S_2Sn_5$	40.92 (41.82)	7.13 (7.02)	3.79 (3.72)	34.02 (34.44)	1570– 1540 [b]	1220	1140	520
VI	86	105–109	$C_{40}H_{80}O_{14}S_2Sn_5$	33.54 (33.30)	6.04 (5.59)	4.52 (4.44)	41.13 (41.14)	1580– 1550 [b]	1250	1150	530
VII	64	90–95	$C_{24}H_{40}O_{14}S_2Sn_3$	29.26 (29.63)	4.85 (4.14)	6.21 (6.59)	35.21 (36.60)	1640, 1580	1240–1150 [b]		530
VIII	80	155–175	$C_{18}H_{34}O_7SSn_2$	33.66 (34.21)	6.05 (5.42)	4.38 (5.07)	37.55 (37.55)	1700, 1570	1280–1130 [b]		520
IX	67	80–83	$C_{20}H_{38}O_7SSn_2$	36.59 (36.40)	6.10 (5.80)	4.38 (4.86)	35.77 (35.97)	1730, 1710, 1680	1270–1140 [b]		530

[a] With decomposition.
[b] With unsatisfactory resolution.
[c] ρ(Sn–Me).

dride molar ratio at 2:1. The reaction mixtures were refluxed at 80–85°C with continuous stirring. After cooling to room temperature, precipitate solids were filtered off, washed with ether (5 ml) and dried in vacuo to give the products **IV–VII**. Analytical samples were obtained by recrystallization of these precipitates from ethanol. In this way, the following compounds were isolated as colurless or light-beige amorphous solids (Table 1): **IV** (2.2 g; 1.3 mmol); **V** (1.9 g; 1.1 mmol); **VI** (2.1 g; 1.46 mmol) and **VII** (0.94 g; 0.96 mmol).

A similar procedure starting with dialkyltin oxide and *O*-trialkylstannyloxysulphonylmaleic anhydrides [1] (1 g), while keeping the molar ratio of the reagents at 1:1, gave the products **VIII** (1.35 g; 2.1 mmol) and **IX** (1.15 g; 1.74 mmol) (Table 1).

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