

## ORGANOTIN DERIVATIVES OF ALKANEDISULFONIC ACIDS

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The preparation of dibutyltin and tributyltin alkanedisulfonates from alkyltin oxides and the corresponding alkanedisulfonic acids has been studied. The products, obtained in 56–74% yield, were tested as biocides against bacteria, yeasts, and moulds as well as fungicides against wood rot and their activity was compared with that of bis(tributyltin) oxide.

The relatively low solubility in water of many common organotin biocides excludes their application in cases where water as solvent is necessary or desirable. This problem can be overcome by using organotin derivatives of alkanesulfonic acids. Dibutyltin and tributyltin derivatives of alkanemonosulfonic acids were prepared by reaction of the free acids with dibutyltin oxide (DBTO) and bis(tributyltin) oxide (TBTO), respectively, or by treatment of their silver salts with dibutyltin chloride (DBTC) and tributyltin chloride (TBTC), respectively, in an alcohol as solvent<sup>1</sup>. These compounds are high-melting and some of them are hygroscopic. In our present work we describe the synthesis of similar derivatives from alkanedisulfonic acids.

Alkanedisulfonic acids were prepared from their sodium salts, obtained by reaction of the corresponding dibromoalkanes with sodium sulfite. The arising sodium bromide was removed by crystallization; however, with increasing number of methylene groups in the molecule the effectivity of this purification decreased because of similar solubility of the two salts.

In this way we prepared sodium salts of the type  $\text{NaO—O}_2\text{S—(CH}_2\text{)}_m\text{—SO}_2\text{—ONa}$ , where  $m = 1$  (ref.<sup>2</sup>),  $m = 2$  (refs<sup>3–5</sup>),  $m = 3$  (ref.<sup>5</sup>), and  $m = 4–6$  (refs<sup>5,6</sup>). The isolation *via* barium salts was possible only for compounds with  $m = 1–3$  (refs<sup>2,5</sup>); the free acids were liberated with sulfuric acid. Free acids with  $m = 4–6$  were obtained by reaction of the sodium salts with anhydrous hydrogen chloride in absolute ethanol<sup>5,6</sup>. We have now elaborated the preparation of free acids with  $m = 1–6$  by passing aqueous solutions of the corresponding sodium salts through column of a strongly acidic ion-exchange resin.

## EXPERIMENTAL

**Chemicals.** Dibutyltin oxide (DBTO) 97% was obtained from Metal and Thermit Chemicals, U.S.A., bis(tributyltin) oxide (TBTO) 96% was a Schering (G.F.R.) product, tributyltin ethane-monosulfonate was our own preparation. The dibromoalkanes ( $m = 1-6$ ) were of "purum" quality (Aldrich, U.S.A.), the ion-exchange resins used were Dowex 50 W  $\times$  8 (BDH, GB), Amberlite CG-120 I<sup>+</sup>, Ostion KS 0806, 0807 (Lachema, Czechoslovakia), particle size 0.04 to 0.08 mm (200–400 mesh).

**Apparatus.** Determination of melting points and molecular weight (Rast method) was done on a Boetius block (G.D.R.), gradient 4°C . min<sup>-1</sup>. Infrared spectra were measured in KBr and Nujol on a UR-20 (Carl Zeiss, G.D.R.) spectrometer.

## Free Alkanedisulfonic Acids

A solution of the sodium sulfonate (0.025 mol) in distilled water (about 50 ml) was passed twice through a glass column (diameter 20 mm, height 200 mm; at the bottom equipped with a glass frit and a stopcock) filled with an ion-exchange resin (100 g). The resin was then washed with distilled water to neutral reaction (litmus), the eluates were concentrated *in vacuo* and the residue was kept over phosphorus pentoxide at 100–150°C and 13.3 Pa (0.1 Torr) for about 6 h. If water was still present, several drops of thionyl chloride were added, the mixture was heated to 100°C for 1 h and the drying *in vacuo* was repeated<sup>5</sup>. Yields of the acids were 88–95%. The acids were well identified by their di-(*m*-toluidine) salts (DMTS) of reproducible melting points<sup>6</sup> (Table I).

## Dibutyltin Derivatives of Alkanedisulfonic Acids

The title compounds were prepared according to the equation

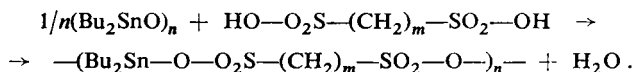


TABLE I

Alkanedisulfonic acids HO—O<sub>2</sub>S—(CH<sub>2</sub>)<sub>m</sub>—SO<sub>2</sub>—OH

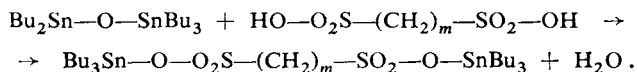
<i>m</i>	Mol. wt.	<i>x</i> H <sub>2</sub> O <sup>a</sup>	M.p., °C <sup>b</sup>	DMTS <sup>c</sup> , m.p., °C		Ref.
				determ.	published	
1	176	<i>x</i>	— (90)	230	241	2,3
2	190	2	97–172 (112)	222	230	5,6
3	204	2	120–124 (—)	215	222	5,6
4	218	—	84–144 (—)	205	214	4,6
5	232	—	20–22 (—)	177	187	6
6	246	—	75–78 (—)	163	158	6

<sup>a</sup> Hydrate. <sup>b</sup> Published data for the acid (hydrate). <sup>c</sup> DMTS di-(*m*-toluidine) salt.

A solution of the alkanedisulfonic acid (0.025 mol) in distilled water (after reaction with the ion-exchange resin) was evaporated and dried *in vacuo* as described above. Methanol (50 ml) and DBTO (6.25 g; 0.025 mol) were added and the stirred mixture was heated to the boil in a high beaker or Erlenmeyer flask until the solution became homogeneous<sup>1</sup>. Methanol was added in two portions (50 ml each) and the solution was concentrated to 15–20 ml. After addition of another portion of methanol (50 ml), the hot solution was filtered and the filtrate was stripped of the solvent at 120°C and 1.33 kPa (10 Torr). The residue was crystallized from methanol (charcoal) and dried *in vacuo*. The products were obtained in 60–74% yield as white crystals melting above 300°C. Tin<sup>8,7</sup> and sulfur<sup>9</sup> content was determined by titration. Molecular weight was determined by the method of Rast with camphor as solvent and azobenzene as standard. Analytical data for the products, together with the yields, are given in Table II.

#### Tributyltin Derivatives of Alkanedisulfonic Acids

The synthesis was performed according to the equation:



The compounds were prepared from TBTO (15.0 g; 0.025 mol), either in the same manner as the dibutyltin derivatives or in toluene with azeotropic removal of the arising water. The reaction mixture was processed as described in the preceding experiment except that the drying *in vacuo* was performed only at 60–80°C since at higher temperatures glassy products were often obtained; yield 56–60%. Analytical data and yields are summarized in Table III.

Infrared spectra confirmed the presence of  $-\text{SO}_2-\text{O}-$  groups (bands at 1 120 and 1 640  $\text{cm}^{-1}$ ) as well as traces of free acids<sup>1,10</sup> (bands at 1 050 and 1 200  $\text{cm}^{-1}$ ). In comparison with the previously published values<sup>1</sup> the corresponding band maxima were somewhat shifted.

#### Thermal and Biocidal Tests

The dibutyltin derivatives were tested as thermal stabilizers in foils of unplasticized and plasticized PVC on a band stabilimeter at 180°C, using commercial stabilizers as standards<sup>11</sup>.

TABLE II  
Dibutyltin alkanedisulfonates ( $\text{Bu}_2-\text{Sn}-\text{O}-\text{O}_2\text{S}-(\text{CH}_2)_m-\text{SO}_2-\text{O}-$ )<sub>n</sub>

m	Mol. wt.	Value n (Rast)	Yield g (%)	Calculated/found	
				% Sn	% S
1	407	20	7.5 (73.7)	29.16/27.02	15.75/16.83
2	421	18	7.8 (74.1)	28.19/27.50	15.23/15.60
3	435	18	7.8 (71.7)	27.28/26.25	14.74/15.33
4	449	17	8.0 (71.3)	26.42/26.18	14.28/14.07
5	463	18	7.7 (66.5)	25.62/25.11	13.84/13.00
6	477	15	7.2 (60.4)	24.87/24.25	13.44/13.60

Considering the possible use in wood rotproofing and antimicrobial treatment of polyamide fibres, we tested the tributyltin derivatives against bacteria (*Escherichia coli*, *Staphylococcus aureus*), yeasts (*Candida albicans*, *Candida tropicalis*) and moulds (*Aspergillus niger*), as well as against wood-rotting fungi (*Coniophora puteana*, *Corolius versicolor*)<sup>12,13</sup> in agar by the "poisoned medium" method in concentrations 0.001 and 0.0001% using TBTO as standard<sup>14</sup>. The results are given in Table IV.

## RESULTS AND DISCUSSION

The dibutyltin and tributyltin alkanedisulfonates were successfully obtained by reaction of DBTO and TBTO with the corresponding alkanedisulfonic acids (prepared from their sodium salts by treatment with ion-exchange resins in alcohol or toluene). The yields were 56–74% the losses being mainly due to crystallization of the crude products. The obtained compounds are well soluble in water and some ( $m = 1, 2$ ) are even slightly hygroscopic.

The dibutyltin alkanedisulfonates are mostly oligomers. It was very difficult to determine their molecular weight because their very low solubility in common organic solvents prevented to use more precise methods. From this point of view, the values obtained by the Rast method are only informative.

Compared with common commercial thermal PVC stabilizers, the dibutyltin derivatives exhibited only low effectivity and they are thus not suitable for stabilization of chlorinated plastics.

The tributyltin alkanedisulfonates are monomers. They show relatively high antimicrobial activity against bacteria, yeasts and moulds as well as against wood-rotting fungi, comparable with TBTO. Although they are effective as possible antimicrobial additives to polyamide fibers, they do not withstand the relatively high polymerization temperatures in the melt (220–260°C); in this respect the dibutyltin derivatives are more stable but their activity is by an order of magnitude lower.

TABLE III

Tributyltin alkanedisulfonates  $\text{Bu}_3\text{—Sn—O—O}_2\text{S—(CH}_2\text{)}_m\text{—SO}_2\text{—O—Sn—Bu}_3$

$m$	Mol. wt.	M.p. °C	Yield g (%)	Calculated/found	
				% Sn	% S
1	754	135	11.4 (60.2)	31.47/30.08	8.50/9.00
2	768	92	12.2 (63.3)	30.90/30.00	8.35/8.41
3	782	88	11.1 (56.7)	30.33/29.65	8.20/8.07
4	796	83	11.8 (59.4)	29.81/29.13	8.05/7.88
5	810	70	12.2 (60.0)	29.29/28.88	7.91/7.61
6	824	52	12.5 (60.7)	28.79/28.05	7.78/7.17

However, both types of derivatives have an adverse effect on the plasticizing process in the melt and therefore they are more suitable for the antimicrobial treatment of foils, plates and rods.

The synthesized compounds are well soluble in water, better than derivatives of alkanemonosulfonic acids. The exact solubility data have not been hitherto measured. For practical purposes their 3–10% aqueous solutions are used.

In more detail have been investigated only derivatives such as trimethyltin ethanesulfonate and tributyltin ethanesulfonate which have found use as fungicides for wood rotproofing and are produced on industrial scale<sup>15</sup>. These compounds are liquids that are not easily purified because they decompose when distilled even *in vacuo*<sup>15</sup>. Although TBTO is very effective, it decomposes on longer storage and deposits (neat or its solutions) DBTO.

There is hitherto no standard test for determination of the biological activity; a non-standard agar block test<sup>12,13</sup> may be used, however, it is rather laborious and the results are given as an interval between two values (growth and inhibition of the rot) in  $\text{kg m}^{-3}$ . The values for TBTO are 0.20–0.70 and for TBTES ( $\text{Bu}_3\text{SnOSO}_2\text{Et}$ ) 0.58–1.18  $\text{kg m}^{-3}$ , the activity being thus comparable. The  $\text{DL}_{50}$  value for TBTO is estimated<sup>15</sup> to be similar to that for TBTO, about 150–200  $\text{mg kg}^{-1}$  (rat).

We used a faster and less laborious comparative non-standard agar surface test (poisoned medium method) where the biological activity of the compound was assessed from the inhibition zone area<sup>14</sup>. The obtained results were then compared with the activity of TBTO (taken as 100%) as well as TBTES. As shown in Table IV, the tributyltin alkanedisulfonates exhibit a significant activity. At the same time the

TABLE IV  
Biocidal and fungicidal activity (in %) of tributyltin alkanedisulfonates  $\text{Bu}_3\text{—Sn—O—O}_2\text{S—}(\text{CH}_2)_m\text{—SO}_2\text{—O—Sn—Bu}_3$  (concentration 0.0001%, activity of TBTO = 100%)

Test organism	Substance						
	1	2	3	4	5	6	TBTES <sup>a</sup>
<i>Escherichia coli</i>	62	66	65	65	60	62	48
<i>Staphylococcus aureus</i>	56	55	55	53	50	50	37
<i>Candida albicans</i>	52	52	50	55	47	46	35
<i>Candida tropicalis</i>	50	53	53	53	50	50	38
<i>Aspergillus niger</i>	40	44	42	40	40	40	30
<i>Coniophora puteana</i>	80	88	82	77	60	60	70
<i>Corolius versicolor</i>	81	90	80	80	75	73	73

<sup>a</sup> TBTES := tributyltin ethanesulfonate.

results indicate that the activity is about proportional to the tin content in the molecule (for TBTO about 40%, TBTES 30%, disulfonate with  $m = 2$  about 31%); the same effect was observed with PVC-stabilizers and some biocides<sup>14</sup>.

The tributyltin derivatives exhibit good biological activity in aqueous and aqueous-alcoholic solutions. Their advantage is that they are well soluble and can be stored for a long time. They can be used for treatment of polyamide products, stone, for impregnation of wood and as an additive to aqueous solution of paints and varnishes.

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