APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 143–147 (1993)

N-Tributyltin mesylimide—a new water-soluble fungicide

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In addition to the known water-soluble tributyltin compounds, *N*-tributyltin mesylimide [$Bu_3SnN(SO_2Me_2)_2$] was prepared and proposed as a fungicide for water-based preservative formulations. The aqueous solubility of the new compound is in the range of 11.0–11.4% w/w at 25 °C and its activity towards moulds (*Aspergillus niger*) is near that for tributyltin oxide. The compound has an average toxicity ($LD_{50} = 740$ mg kg^{-1}).

Keywords: Tributyltin, aqueous solubility, fungicide, *Aspergillus niger*

INTRODUCTION

Tributyltin compounds have been widely used as wood preservatives for many years since they were introduced in the late 1950s.[1] At present, there are plenty of wood preservative formulations based upon tributyltin oxide, tributyltin phosphate and others,[2] all of which have a very low solubility in water and need to be used with organic solvents. It is self-evident that using water instead of more expensive, flammable, volatile and, in some instances, toxic organic solvents is preferable. This problem can be avoided by using water-soluble tributyltin compounds, and numerous attempts to prepare such compounds have appeared.[3-13] To date, those compounds having the highest aqueous solubility have been found to be the tributyltin alkanemonosulphonates (TBTS), Bu_3SnOSO_2R (R = Me, Et)[9, 14] and the bis(tributyltin) alkanedisulphonate (TBTS-bis), $Bu_3SnOSO_2(CH_2)_nSO_2OSnBu_3$ ($n = 1$–6).[12] These latter compounds are readily soluble in water, even more soluble than derivatives of alkanemonosulphonic acids.

In the course of our work on the synthesis of biologically active triorganotin compounds,[15-22] we describe in this paper *N*-tributyltin mesylimide (TBTM), $Bu_3SnN(SO_2Me)_2$, a new water-soluble organotin fungicide.

EXPERIMENTAL

Commercial bis(tributyltin)oxide (TBTO), $Bu_3SnOSnBu_3$, was subjected to distillation under reduced pressure prior to use. Mesylimide, $(MeSO_2)_2NH$, was prepared and purified according to a previously published procedure.[23]

The IR spectrum was obtained with a Perkin–Elmer 577 spectrometer as a Nujol mull (KBr). The ^1H NMR spectrum of TBTM was recorded on a Tesla BS 487C spectrometer with hexamethyldisiloxane as an internal standard.

Preparation of TBTM

TBTM was prepared by the reaction of $(Bu_3Sn)_2O$ (3.42 g; 5.7 mmol) with $(MeSO_2)_2NH$ (1.99 g; 11.5 mmol) in hexane or toluene (100 cm^3). The mixture was refluxed for about 5 min and the toluene–water azeotrope was fractionated off using a Dean and Stark trap. The major quantity of the solvent was then distilled off under atmospheric pressure and the residue was kept under reduced pressure at 90 °C for about 15 min. Crude TBTM, $Bu_3SnN(SO_2Me)_2$, was obtained as colourless, slightly hygroscopic, heavy oil and purified by vacuum distillation. The yield was approximately 80% (5.26 g; 9.2 mmol); b.p. 168–170 °C/0.5 mm Hg, 197 °C/3 mm Hg; m.p. 24–25 °C (under a dry atmosphere). IR: 1085 cm^{-1} [$\nu_{sym}(SO_2)$]; 1260 cm^{-1} [$\nu_{as}(SO_2)$]; 515 cm^{-1} [$\nu_{sym}(Sn{-}C)$]; 550 cm^{-1} [$\nu_{as}(Sn{-}C)$]. ^1H NMR (CCl_4): δ 1.40–2.19 (m, 27H, $3C_4H_9$), 3.36 (s, 6H,

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0268-2605/93/020143-05 $07.50

Received 9 April 1992
Accepted 19 October 1992

$2CH_3$). Calcd for $C_{14}H_{33}NO_4S_2Sn$: C, 36.38; H, 7.19; N, 3.03; S, 13.83; Sn, 25.68%; mol. wt, 462.19. Found: C, 36.42; H, 7.16; N 2.95; S, 13.77; Sn, 26.02%; mol. wt 449 (cryoscopy in benzene). TBTM is soluble in hydrocarbons, aromatics and carbon tetrachloride.

In a similar procedure *N*-tricyclohexyltin mesylimide has also been prepared, $(cyclo\text{-}C_6H_{11})_3SnN(SO_2Me)_2$, m.p. 204–207 °C (with decomp.) (toluene–hexane). IR: 1050, 1090 cm^{-1} [$\nu_{sym}(SO_2)$]; 1245 cm^{-1} [$\nu_{as}(SO_2)$]; 515 cm^{-1} [$\nu_{sym}(Sn—C)$]; 555 cm^{-1} [$\nu_{as}(Sn—C)$]. Calcd for $C_{20}H_{39}NO_4S_2Sn$: C, 44.46; H, 7.27; N, 2.59; S, 11.87; Sn, 21.97%. Found: C, 44.41; H, 7.24; N, 2.70; S, 11.69; Sn, 22.01%.

Fungicidal testing for TBTM

The fungicidal activity of TBTM was determined by the roll-culture method.[24, 25] In conformity with this method a solution of TBTM in alcohol was introduced into Chapek–Dox full nutrient medium at different concentrations and poured into Petri dishes to be hardened. Concentrations of TBTM in the medium were chosen so as to increase in the order 0.2, 0.5, 1, 2, 5, 10, 25, 50 ppm (mg dm^{-3}) etc., up to 150 ppm. The cured surface of the medium was inoculated by a suspension of spores. To prepare this suspension, a mixture of nine test organisms (*Aspergillus orysae* (*Ahlburg*) *Cohn.*, *Asp. niger van Tieghem*, *Asp. terreus Thom*, *Chaetomium globosum Kunze*, *Paecilomyces varioti Bainier*, *Penicillum funiculosum Thom.*, *Pen. chrysogenum Thom*, *Pen. cyclopium Westling*, *Trichoderma viride Pers. ex Fr.*) at the age of 14–28 days after re-sowing and at a total concentration of about 1×10^6 spores per cm^3 (each mould species equally) was used in accordance with USSR State Standard (GOST 9.051-75). The Petri dishes, inoculated with fungi, with different contents of TBTM, were then incubated at 22 ± 2 °C and at a constant humidity of 90% for the period of 28 days. After incubation the cultures were observed for growth. Only samples with complete suppression of growth were considered. All tests were performed in triplicate.

The biological activity of TBTM was assessed from the value of the minimum fungicide concentration (MFC) of the compound.[24–26] The MFC value is defined as the lowest concentration of the compound under test causing complete inhibition of visible growth of the fungi relative to the control.

Determination of the aqueous solubility of TBTM

About 15 g of TBTM was placed in a suitable vessel with distilled water (100 cm^3). The contents of the vessel were then shaken at a given temperature in a liquid-filled thermostat provided with a shaking mechanism. Suitable aliquots (3–5 cm^3) of aqueous solutions were withdrawn from the vessel periodically and concentrations of TBTM in solutions were measured alkalimetrically (titration with phenolphthalein as the indicator). In parallel, the tin content in aliquots was determined gravimetrically as SnO_2 by wet combustion of the aliquot in concentrated nitric/sulphuric acids. Hydrogen peroxide was added to the mixture in the later stages and the non-organic residue was then subjected to calcination. The shaker, combined with a thermostat, was stopped for a period of 15 min each time before taking an aliquot.

Determination of acute oral toxicity of TBTM

The mammalian toxicity of TBTM has been determined by D. B. Gelashvili (Lobachevsky State University, Nizhny Novgorod) under USSR State Standard (GOST 12.1.007-76) protocol.

For acute oral studies with mice of mass 20–22 g, the animals were exposed to TBTM in the form of a vegetable-oil solution at dose intervals between 70 and 1200 mg kg^{-1}. Each portion, of volume 0.5 cm^3, including pure oil as control, was injected by a syringe into the stomach. Lethal results were observed at periods from one to seven days. The total observation time was 14 days. No deaths were observed in controls. The value of LD_{50} was calculated to be 740 (655.8–824.2) mg kg^{-1} by the probit-analysis method of Litchfield and Wilcoxon[27].

RESULTS AND DISCUSSION

An ordinary acid–base reaction was used for the preparation of TBTM (Eqn [1]):

$$(Bu_3Sn)_2O + 2(MeSO_2)_2NH \xrightarrow[-H_2O]{} 2Bu_3SnN(SO_2Me)_2 \qquad [1]$$

Table 1 Aqueous solubility of TBTM at 25 °C

Mode of determination	Concentration of TBTM found in aqueous solution After 1 day		After 2 days		After 3 days		After 4 days		After 5 days	
	$g\,dm^{-3}$	% w/w	$g\,dm^{-3}$	% w/w	$g\,dm^{-3}$	% w/w	$g\,dm^{-3}$	% w/w	$g\,dm^{-3}$	% w/w
Alkaline titration	106.2	10.3	108.2	10.5	117.4	11.4	115.5	11.2	116.5	11.3
Wet acidic combustion	103.1	10.0	106.2	10.3	115.5	11.2	113.4	11.0	115.5	11.2

The product, purified by vacuum distillation, was crystallized slowly by storage at room temperature under a dry atmosphere. However, the solidified product becomes liquid in humid air.

N-Tricyclohexyltin mesylimide was prepared using tricyclohexyltin hydroxide in accordance with Eqn [1] while keeping the molar ratio of the reagents at 1:1.

TBTM is readily soluble in non-polar solvents (hexane, benzene, carbon tetrachloride) and exists as a monomer in benzene solution. This is characteristic for compounds of the type R_3SnX having a typically covalent interaction between the R_3Sn moiety and X in organic solutions. As is seen from the ^1H NMR-spectrum of TBTM in carbon tetrachloride, all protons of the mesylimide group are quite equivalent (there is a sharp and intensive singlet) and, hence, a direct tin–nitrogen bond seems to exist in the dissolved molecules.

Another situation probably arises on dissolving TBTM in water. It is known that the organotin species present in aqueous solutions of water-soluble trialkyltin compounds is the hydrated trialkyltin cation $[R_3Sn(H_2O)_2]^+$, where R = Me[28–32] or Bu.[33] In confirmation of this, ^{119}Sn NMR studies of aqueous solutions of TBTS show the presence of $[Bu_3Sn(H_2C)_2]^+$.[33] So, it would be expected that the same hydrated cation, along with counterion $[N(SO_2Me)_2]^-$ is formed in an aqueous solution of TBTM.

The aqueous solubility of TBTM was found to be 11.2% w/w at 25 °C (Table 1) with good agreement between two different analytical methods. As indicated in Table 1, a saturated solution of TBTM can be obtained by the third day of shaking; after that the concentration of the organotin is constant. To change from a volume concentration ($g\,dm^{-3}$) to a weight concentration (% w/w), the relative density of the saturated solution of TBTM in water at 25 °C was found as the weight ratio of samples of the latter and distilled water, taken in equal volumes. The measurement was repeated three times with different equal volumes and the value of the relative density was taken as the mean value:

$$\frac{7.2460\text{ g}}{7.0300\text{ g}} = 1.031;$$

$$\frac{10.7443\text{ g}}{10.4110\text{ g}} = 1.032;$$

$$\frac{14.5379\text{ g}}{14.1144\text{ g}} = 1.030$$

Mean value of $d_{25}^{25} = 1.031$

The fungicidal activity of TBTM was tested on a mixture of nine different mould species according to USSR State Standard and one comparative fungus *Aspergillus niger* as in a previous report.[26] The results are given in Table 2.

Table 2 Evaluation of the fungicidal activity of TBTM after 28 days of incubation[a]

Test organisms	Concentration of TBTM (ppm = $mg\,dm^{-3}$) 0 (control)	0.2	0.5	1	2	5	10	25	50	75	100	150
Mixture of nine fungi	3+	3+	3+	3+	3+	3+	2+	2+	+	−	−	−
Aspergillus niger	3+	2+	±	−	−	−	−					

[a] Key: 3+, abundant growth (no inhibition); 2+, modrate growth; +, slight growth; −, no visible growth (complete inhibition).

Table 3 Comparative data on some properties of TBTM and several other tributyltin analogues

Tributyltin compound	Aqueous solubility (% w/w)	MFC towards *Aspergillus niger* (ppm)	Acute oral toxicity, LD_{50} (mg kg^{-1})	Tin content (%)
TBTM, $Bu_3SnN(SO_2Me)_2$	11.2	1.0	740	25.71
TBTO, $B_3SnOSnBu_3$ (industrial fungicide)	0.001–0.002[9, 11]	0.5–1.0[12, 13]	194–200[34, 35]	39.87
TBTS, Bu_3SnOSO_2Et (water-soluble analogue)	1–3;[35] 3.1–3.2[9]	30% of TBTO[12]	150–200[12, 35]	30.85
TBTS-bis, $Bu_3SnOSO_2(CH_2)_nSO_2OSnBu_3$ (water-soluble analogue)	3–10[12]	40% of TBTO[12]	150–200[12]	31.51

As is seen from Table 2, the MFC value for TBTM is 75 ppm for the standard mixture of fungi and only 1 ppm towards the individual fungus *Aspergillus niger*.

Finally, data reported in Table 3 suggest some points in favour of TBTM compared with several other tributyltin analogues.

CONCLUSION

The results obtained show that *N*-tributyltin mesylimide has the highest aqueous solubility among tributyltin compounds. It has also a not-very-high toxicity, on conjunction with a lower content of tin (or tributyltin moiety) in the molecule, as against the comparison compounds in Table 3. The fungicide activity value for TBTM is estimated to be comparable with that for TBTO, 1.0 ppm (*Aspergillus niger*). It would thus appear possible to use this compound as an active substance in a water-based preservative for various materials (wood, paper or cardboard, textiles, etc.).

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