

SOME METALLIC DERIVATIVES OF BENZENESELENOL

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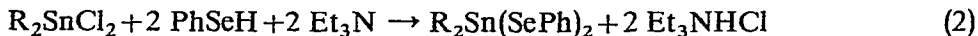
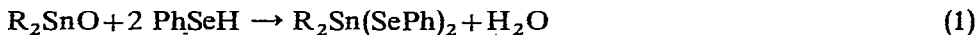
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SUMMARY

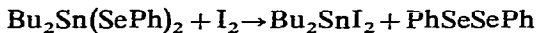
The organotin benzeneselenolates $R_3SnSePh$ ($R = Ph, Bu$), $R_2Sn(SePh)_2$ ($R = Me, Et, Bu$) have been prepared and characterized. Cleavage of the Sn-Se bond is observed with a variety of reagents. The compounds $CuSePh$, $AgSePh$, and $Ni(SePh)_2 \cdot 3H_2O$ have also been prepared.

The metallic and organometallic derivatives of alkane- and arenethiols are relatively well documented¹, but few papers have been published describing analogous selenium derivatives. Organometallic derivatives of Group IV such as $Me_3SiSePh^2$, $RSeMe$ ($R = Me_3Si, Me_3Ge, Me_3Sn, SiH_3, GeH_3, Si_2H_5$) and $R(SeMe)_2$ ($R = Me_2Si, Me_2Ge, Me_2Sn, SiH_2$)³, $Me_3SnSePh^4$, $Me_2Sn(SePh)_2^4$, $Bu_3SnSeBu^5$, and $Ph_3SnSePh^6$ are known. By applying the techniques used to prepare organotin thiol derivatives¹, it has been possible to prepare analogous benzeneselenol derivatives



$Me_2Sn(SePh)_2$, $Bu_2Sn(SePh)_2$ and $Bu_3SnSePh$ were prepared by method (1) and $Et_2Sn(SePh)_2$ and $Ph_3SnSePh$ by method (2).

Some reactions of these compounds have been studied. In all the reactions cleavage of the Sn-Se bond was observed in preference to the selenium acting as a donor, or tin as an acceptor, or cleavage of the Sn-C bond. Iodine, in carbon tetrachloride, quantitatively cleaved the Sn-Se bond, and this reaction, analogous to that observed in similar sulfur compounds⁷, can be used for titrimetric estimation of the selenium compound, see Table 1. The products from the reaction were isolated and identified.



No reaction was observed when MeI was added to $Bu_3SnSePh$ or $Bu_2Sn(SePh)_2$. Methyl iodide cleaves the Sn-S bond in $Bu_2Sn(SMe)_2$ and analogous compounds with SMe groups⁸, but does not react with $Bu_2Sn(SR)_2$, $R = Ph$ or C_6F_5 ⁸.

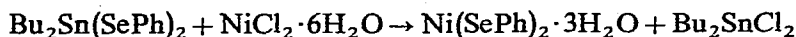
There was no trace of adduct formation when $Bu_2Sn(SePh)_2$ was dissolved in methanol, benzonitrile, dimethylformamide, triethylamine, or dimethyl sulfoxide, but hydrolysis occurred when a stoichiometric amount of water was added. The hydrated oxide $Bu_2SnO(H_2O)_x$ was recovered in high yields.

TABLE 1

REACTIONS WITH IODINE

Compound	(mmoles)	I ₂ (mmoles)
Bu ₂ Sn(SePh) ₂	0.137	0.134
	0.137	0.135
Bu ₃ SnSePh	0.054	0.027
	0.135	0.068
Et ₂ Sn(SePh) ₂	0.116	0.115
	0.116	0.113
Me ₂ Sn(SePh) ₂	0.250	0.246
	0.208	0.208

Cleavage of the Sn-Se bond was also observed in the reactions with metal halides in methanol solution.



AgSePh and CuSePh (together with PhSeSePh) were prepared similarly from AgNO₃ and Cu(NO₃)₂ · 3H₂O. Analogous reactions are observed with Bu₂Sn(SPh)₂⁸. This method can be used for preparing metallic derivatives of benzeneselenol, although various other methods which may be more convenient are known, such as the reaction of Al(SePh)₃ with metal halides⁹. No reaction was observed between Bu₂Sn(SePh)₂ and BCl₃ or PCl₃, although the compound B(SePh)₃ has been reported¹⁰, there is no apparent report of P(SePh)₃.

When attempts were made to purify Ph₃SnSePh by vacuum sublimation, decomposition occurred.



Although the compound Me₂Sn(SePh)₂ was obtained pure on distillation, as is shown by its reaction with iodine, it decomposed too readily to be chemically analysed commercially in contrast with the previous observation of a low melting solid which is not reported to be unstable⁴. The compounds AgSePh and CuSePh decomposed thermally to Ag at 150° and Cu_{2-x}Se at 190° respectively.

The reactions of R₂Sn(SePh)₂ and Bu₃SnSePh are very similar to those ob-

TABLE 2

TIN-SULFUR AND TIN-CARBON STRETCHING FREQUENCIES (cm⁻¹)

Compound	ν(Sn-C)		ν(Sn-Se)	
	ν _{asym}	ν _{sym}	ν _{asym}	ν _{sym}
Bu ₂ Sn(SePh) ₂	515	472	305	275
Bu ₃ Sn(SePh)	515	471		295
Et ₂ Sn(SePh) ₂	520	469	328	309
Ph ₃ Sn(SePh)	271			339
Me ₂ Sn(SePh) ₂	512	470	305	285

served for similar sulfur containing compounds⁸. Cleavage of the Sn-Se, or Sn-S, bond is the main reaction observed and the Se (or S) shows no donor properties and the Sn no acceptor properties.

The infrared spectra of the compounds show the expected frequencies of the functional groups. By comparison the Sn-C and Sn-Se frequencies^{13,14} can be deduced and are shown in Table 2.

EXPERIMENTAL

All reagents used were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany. Infrared spectra were recorded on a Perkin-Elmer 457, as mulls or thin films. X-ray diffraction data were obtained on Phillips Norelco X-ray powder pattern diffractometer using Fe-K_α radiation with a Mn filter. Analytical data and physical properties of the new compounds isolated are shown in Table 3.

TABLE 3

ANALYSES AND PHYSICAL PROPERTIES OF NEW COMPOUNDS

Compound	Color	M.p. (°C) or b.p. (°C/mm)	n _D ²⁰	Analyses			
				Calcd.		Found	
				C	H	C	H
Bu ₃ SnSePh	Orange	141/0.3	1.5501	48.5	7.2	48.4	7.1
Bu ₂ Sn(SePh) ₂	Red-orange	200/0.5	1.6269	44.0	5.2	44.4	5.6
Et ₂ Sn(SePh) ₂	Red-orange	112/0.5	1.6005	39.3	4.1	39.0	4.2
Me ₂ Sn(SePh) ₂	Pale yellow	46-48/0.6 ^a	1.6054				
Ni(SePh) ₂ ·3H ₂ O	Grey	d.250		34.1	3.9	34.2	3.0
CuSePh	Brown	d.150		32.8	2.3	33.1	2.7
AgSePh	Yellow	d.200		27.3	1.9	27.3	1.9
Ph ₃ SnSePh·4Me ₂ Co	White	99-101		58.5	6.0	58.7	4.8

^a Lit.⁴ m.p. 32-33°.

Preparations

(Phenylseleno)tributyltin was obtained by reaction of (Bu₃Sn)₂O (10.0 mmoles) and PhSeH (20.0 mmoles) in 20.0 ml of MeOH. The product (80.5% yield) was purified by vacuum sublimation.

Bis(phenylseleno)dibutyltin was prepared similarly from Bu₂SnO (20.0 mmoles) and PhSeH (40.0 mmoles), yield 63%.

Bis(phenylseleno)dimethyltin was prepared similarly from Me₂SnO (20.0 mmoles) and PhSeH (40.0 mmoles), yield 39%. This compound was analysed by titration with iodide (see Table 1), but was too unstable for professional elemental analysis.

Bis(phenylseleno)diethyltin was obtained from Et₂SnCl₂ (20.0 mmoles) and PhSeH (40.0 mmoles) in 20 ml of MeOH, in the presence of 40.0 mmoles of Et₃N.

$\text{Et}_3\text{NH}^+\text{Cl}^-$ filtered off corresponded to 90% reaction, but after vacuum distillation only 79% of $\text{Et}_2\text{Sn}(\text{SePh})_2$ was obtained.

Phenylselenotriphenyltin was prepared similarly from Ph_3SnCl and PhSeH . Found m.p. 88° , lit.⁹ m.p. 88° , when this compound was purified by vacuum sublimation some PhSeSePh formed, which was separated from Ph_3SnSePh by TLC, found m.p. 61° , lit. 61° . On recrystallization from Me_2CO , $\text{Ph}_3\text{Sn}(\text{SePh}) \cdot 4\text{Me}_2\text{CO}$ was recovered.

Reactions

Reactions with iodine. The results are summarized in Table 1, of the reactions studied in CCl_4 solution. The iodine solution was added until the starch blue color persisted for 2 min. The products $(\text{PhSe})_2$ and Bu_3SnI , Bu_2SnI_2 , or Me_2SnI_2 were separated after evaporation of the solvent by TLC and identified by their m.p.'s or b.p.'s ($\text{PhSe})_2$ m.p. 61° , lit. $59-60^\circ$, Me_2SnI_2 m.p. $41-43^\circ$ lit.¹² 44° , Bu_2SnI_2 b.p. $92/0.3$ mm, lit.¹¹ $145/6$ mm; Bu_3SnI $111/0.3$ mm, lit.¹² $168/8$ mm.

Reactions with metal ions. These reactions were studied using stoichiometric amounts of reactants $\text{Bu}_2\text{Sn}(\text{SePh})_2$ and the metal salt (20.0 mmoles) in 10 ml of MeOH. The metal selenophenolate was filtered off and washed with various solvents. Thus $\text{Ni}(\text{SePh})_2 \cdot 3\text{H}_2\text{O}$ was prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AgSePh from AgNO_3 , and CuSePh together with $(\text{PhSe})_2$ from $\text{Cu}(\text{NO}_3)_2$. The presence of H_2O in $\text{Ni}(\text{SePh})_2 \cdot 3\text{H}_2\text{O}$ was detected in its IR spectrum.

Reactions with water. When 20.0 mmoles H_2O and 20.0 mmoles $\text{Bu}_2\text{Sn}(\text{SePh})_2$ were mixed in 25 ml of MeOH, a 79% yield of $\text{Bu}_2\text{SnO}(\text{H}_2\text{O})$ was recovered after 3 days at room temperature. Hydrolyses occurred very slowly in PhCN , DMF, DMSO and Et_3N , but when a stoichiometric amount of H_2O was added rapid hydrolysis ensued.

No reaction occurred between $\text{Bu}_2\text{Sn}(\text{SePh})_2$ and BCl_3 , PCl_3 (in n-hexane), or MeI (in MeOH, CCl_4 , neat) or Bu_3SnSePh and MeI (in MeOH, CCl_4 , neat).

Thermal decompositions. Samples of AgSePh and CuSePh were heated in a vacuum sublimator at $150^\circ \pm 10^\circ$, 0.15 ± 0.05 mm or $190^\circ \pm 5^\circ$, 0.5 ± 0.3 mm for 24 h respectively. The solid products were identified by X-ray powder patterns as Ag (ASTM4-0783) and Cu_{2-x}Se (ASTM6-0680).

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