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SOME METALLIC DERIVATIVES OF BENZENESELENOL

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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 documented[1], 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 derivatives[1], it has been possible to prepare analogous benzeneselenol derivatives

$$R_2SnO + 2\ PhSeH \rightarrow R_2Sn(SePh)_2 + H_2O \qquad (1)$$

$$R_2SnCl_2 + 2\ PhSeH + 2\ Et_3N \rightarrow R_2Sn(SePh)_2 + 2\ Et_3NHCl \qquad (2)$$

$Me_2Sn(SePh)_2$, $Bu_2Sn(SePh)_2$ 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 compounds[7], can be used for titrimetric estimation of the selenium compound, see Table 1. The products from the reaction were isolated and identified.

$$Bu_2Sn(SePh)_2 + I_2 \rightarrow Bu_2SnI_2 + PhSeSePh$$

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 groups[8], 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)*
$Bu_2Sn(SePh)_2$	0.137	0.134
	0.137	0.135
$Bu_3SnSePh$	0.054	0.027
	0.135	0.068
$Et_2Sn(SePh)_2$	0.116	0.115
	0.116	0.113
$Me_2Sn(SePh)_2$	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.

$$Bu_2Sn(SePh)_2 + NiCl_2 \cdot 6H_2O \rightarrow Ni(SePh)_2 \cdot 3H_2O + Bu_2SnCl_2$$

AgSePh and CuSePh (together with PhSeSePh) were prepared similarly from $AgNO_3$ and $Cu(NO_3)_2 \cdot 3H_2O$. Analogous reactions are observed with $Bu_2Sn(SPh)_2$[8]. 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 halides[9]. No reaction was observed between $Bu_2Sn(SePh)_2$ and BCl_3 or PCl_3, although the compound $B(SePh)_3$ has been reported[10], there is no apparent report of $P(SePh)_3$.

When attempts were made to purify $Ph_3SnSePh$ by vacuum sublimation, decomposition occurred.

$$2\ Ph_3SnSePh \rightarrow Ph_3SnSnPh_3 + PhSeSePh$$

Although the compound $Me_2Sn(SePh)_2$ 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 unstable[4]. The compounds AgSePh and CuSePh decomposed thermally to Ag at 150° and $Cu_{2-x}Se$ at 190° respectively.

The reactions of $R_2Sn(SePh)_2$ and $Bu_3SnSePh$ are very similar to those ob-

TABLE 2

TIN–SULFUR AND TIN–CARBON STRETCHING FREQUENCIES (cm^{-1})

<table>
<tr><th><i>Compound</i></th><th colspan="2"><i>ν(Sn–C)</i></th><th colspan="2"><i>ν(Sn–Se)</i></th></tr>
<tr><th></th><th>ν_{asym}</th><th>ν_{sym}</th><th>ν_{asym}</th><th>ν_{sym}</th></tr>
<tr><td>$Bu_2Sn(SePh)_2$</td><td>515</td><td>472</td><td>305</td><td>275</td></tr>
<tr><td>$Bu_3Sn(SePh)$</td><td>515</td><td>471</td><td colspan="2">295</td></tr>
<tr><td>$Et_2Sn(SePh)_2$</td><td>520</td><td>469</td><td>328</td><td>309</td></tr>
<tr><td>$Ph_3Sn(SePh)$</td><td>271</td><td></td><td colspan="2">339</td></tr>
<tr><td>$Me_2Sn(SePh)_2$</td><td>512</td><td>470</td><td>305</td><td>285</td></tr>
</table>

served for similar sulfur containing compounds[8]. 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*
$Bu_3SnSePh$	Orange	141/0.3	1.5501	48.5	7.2	48.4	7.1
$Bu_2Sn(SePh)_2$	Red-orange	200/0.5	1.6269	44.0	5.2	44.4	5.6
$Et_2Sn(SePh)_2$	Red-orange	112/0.5	1.6005	39.3	4.1	39.0	4.2
$Me_2Sn(SePh)_2$	Pale yellow	46-48/0.6[a]	1.6054				
$Ni(SePh)_2 \cdot 3H_2O$	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
$Ph_3SnSePh \cdot 4Me_2Co$	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 $(Bu_3Sn)_2O$ (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 Bu_2SnO (20.0 mmoles) and PhSeH (40.0 mmoles),yield 63%.

Bis(phenylseleno)dimethyltin was prepared similarly from Me_2SnO (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 Et_2SnCl_2 (20.0 mmoles) and PhSeH (40.0 mmoles) in 20 ml of MeOH, in the presence of 40.0 mmoles of Et_3N.

$Et_3NH^+Cl^-$ filtered off corresponded to 90% reaction, but after vacuum distillation only 79% of $Et_2Sn(SePh)_2$ 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, $Ph_3Sn(SePh)\cdot 4Me_2CO$ 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 $(PhSe)_2$ 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 $(PhSe)_2$ m.p. 61°, lit. 59–60°, Me_2SnI_2 m.p. 41–43° 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 $Bu_2Sn(SePh)_2$ and the metal salt (20.0 mmoles) in 10 ml of MeOH. The metal selenophenolate was filtered off and washed with various solvents. Thus $Ni(SePh)_2\cdot 3H_2O$ was prepared from $NiCl_2\cdot 6H_2O$, AgSePh from $AgNO_3$, and CuSePh together with $(PhSe)_2$ from $Cu(NO_3)_2$. The presence of H_2O in $Ni(SePh)_2\cdot 3H_2O$ was detected in its IR spectrum.

Reactions with water. When 20.0 mmoles H_2O and 20.0 mmoles $Bu_2Sn(SePh)_2$ were mixed in 25 ml of MeOH, a 79% yield of $Bu_2SnO(H_2O)$ 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 $Bu_2Sn(SePh)_2$ 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 sublimer at 150° ± 10°, 0.15 ± 0.05 mm or 190° ± 5°, 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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