Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

o-AMINOPHENOL, *o*-PHENYLENEDIAMINE AND *o*-AMINOTHIOPHENOL DERIVATIVES OF DIBUTYLTIN(IV)

R. C. MEHROTRA and B. P. BACHLAS
University of Rajasthan, Jaipur (India)

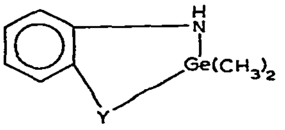
(Received January 27th, 1972)

SUMMARY

The reactions of dibutyltin oxide with *o*-aminophenol, *o*-phenylenediamine and *o*-aminothiophenol in dry toluene have been studied.

INTRODUCTION

Recently, Wieber and Schmidt[1,2] reported the preparation of dimethylgermanium derivatives of type (I) by the reactions of *o*-aminophenol, *o*-aminothiophenol and *o*-phenylenediamine with dimethylgermanium dichloride in the presence of triethylamine.



(I)

In order to examine the possibility of obtaining similar derivatives of dibutyltin, we undertook a study of the reactions of dibutyltin oxide with *o*-aminophenol, *o*-phenylenediamine and *o*-aminothiophenol in 1/1 and 1/2 molar ratio.

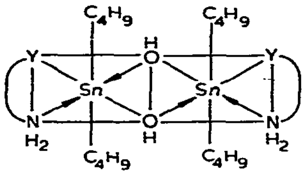
RESULTS

The reactions with 1/1 molar ratios in dry refluxing toluene can be represented as follows:

$$o\text{-}H_2NC_6H_4YH + (C_4H_9)_2SnO \rightarrow (C_4H_9)_2Sn(o\text{-}H_2NC_6H_4Y)(OH)$$

(where Y = O, NH and S)

No water appears to be liberated even when the reaction is carried out in the higher boiling xylene. The products were analysed, and their IR spectra recorded (see Tables 1–3). The IR data indicate the presence of a bridging hydroxy group, in addition to chelation through the phenolic oxygen, amino, or mercapto group. Thus the following octahedral structure (II) is tentatively proposed for these products:



(where Y=O , NH and S)

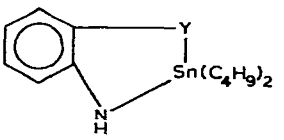
(II)

When heated under reduced pressure, the compounds (II) gave tin heterocyclic derivatives, for which structure (III) is proposed on the basis of analyses and IR spectra.

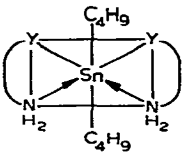
The reactions of dibutyltin oxide with *o*-aminophenol and *o*-aminothiophenol, in 1/2 molar ratios, were carried out in dry refluxing toluene. Water distilled out in the form of toluene/water azeotrope. The reactions can be represented as follows:

$$(C_4H_9)_2SnO + 2\,o\text{-}H_2NC_6H_4YH \longrightarrow (C_4H_9)_2Sn(o\text{-}H_2NC_6H_4Y)_2 + H_2O$$

The products were analysed (see Table 1) and then IR spectra (see Table 3) were recorded as Nujol mulls and also neat. On the basis of the available data, structure (IV) is proposed.



(III)



(IV)

TABLE 1

PREPARATION, PROPERTIES AND ANALYSES OF DIBUTYLTIN(IV) DERIVATIVES

	Reactants (*g*)	*Molar ratio*	*Yield* (*g*) *and nature of the products*	*Analyses found (calcd.)* (%) *Sn*	*N*	*Mol.wt.*[a] *found* (*calcd.*)
1	$(C_4H_9)_2SnO$(2.48) + (o-$OHC_6H_4NH_2$)(1.09)	1/1	3.2, Brown solid, $(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)(OH)$	33.20 (33.24)	3.82 (3.92)	380 (357)
2	$(C_4H_9)_2SnO$(2.48) + (o-$OHC_6H_4NH_2$)(2.18)	1/2	4.0, Brown solid, $(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)_2$[b]	26.29 (26.43)	6.20 (6.23)	460 (449)
3	$(C_4H_9)_2SnO$(2.48) + (o-$H_2NC_6H_4NH_2$)(1.08)	1/1	2.5, Brown flaky substance, $(C_4H_9)_2Sn(HNC_6H_4NH_2)(OH)$[b]	33.23 (33.44)	7.62 (7.89)	345 (355)
4	$(C_4H_9)_2SnO$(2.48) + (o-$H_2NC_6H_4SH$)(1.25)	1/1	3.2, Lemon yellow liquid $(C_4H_9)_2Sn(o\text{-}NH_2C_4H_4S)(OH)$[b]	31.21 (31.73)	3.62 (3.74)	388 (374)
5	$(C_4H_9)_2SnO$(2.48) + (o-$H_2NC_6H_4SH$)(2.50)	1/2	4.1, Yellow liquid 183°/1.5 mm $(C_4H_9)_2Sn(o\text{-}NH_2C_6H_4S)_2$	24.45 (24.67)	5.68 (5.82)	490 (481)

[a] In benzene. [b] Compounds are soluble in organic solvents and are monomeric in refluxing benzene.

TABLE 2

EFFECT OF HEAT ON THE (1/1) DERIVATIVES OF DIBUTYLTIN (IV) WITH *o*-AMINOPHENOL, *o*-AMINOTHIOPHENOL AND *o*-PHENYLENEDIAMINE

	Compounds (g) decomposition temperature (°C/mm)	*Yield (g) and nature*	*Analyses found (calcd.) (%)*		*Mol.wt.[a] found (calcd.)*
			Sn	*N*	
1	$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)(OH)$ (1.3), 120 (0.1)	0.7, Brown solid, $(C_4H_9)_2Sn(o\text{-}OC_6H_4NH)$	34.75 (34.90)	4.01 (4.11)	310 (340)
2	$(C_4H_9)_2Sn(o\text{-}H_2NC_6H_4NH)(OH)$ (1.5), 130 (0.1)	0.7, Pink solid $(C_4H_9)_2Sn(o\text{-}NHC_6H_4NH)$[b]	34.85 (35.02)	9.15 (8.26)	345 (339)
3	$(C_4H_9)_2Sn(o\text{-}H_2NC_6H_4S)(OH)$ (1.5), 135 (2.0)	0.9, Lemon yellow liquid, 135°/2 mm $(C_4H_9)_2Sn(o\text{-}NHC_6H_4S)$[b]	33.20 (33.35)	3.89 (3.93)	370 (356)

[a] In benzene. [b] Compounds are soluble in organic solvents and are monomeric in refluxing benzene.

Infrared spectra of dibutyltin(IV) derivatives (cm^{-1})*

$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)(OH)$:[a] 3360 s, 3300 s, 3050 w, 2960 vs, 2865 vs, 1590 m, 1520 (sh), 1510 m, 1460 s, 1370 s, 1285 s, 1268 s, 1228 w, 1215 w, 1145 m, 1085 w, 1071 m, 1038 w, 920 w, 895 m, 961 w, 845 w, 810 m, 765 w, 745 s, 735 s (doublet), 665 s, 590 m, 563 s, 488 (sh), and 443 m.

$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH)$:[a] 3470 m, 2950–2860 vs, 1600 m, 1535 s, 1500 (sh), 1470 s, 1380 s, 1325 w, 1280 m, 1263 m, 1228 w, 1151 m, 1111 vw, 1073 w, 958 w, 914 w, 863 m, 743 s, 668 s, 588 w, 565 m, and 523 s.

$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)_2$:[a] 3365 s, 3292 s, 2960 vs, 2860 vs, 1590 m, 1530 vs, 1465 s, 1415 w, 1365 m, 1315 s, 1275 vs, 1228 w, 1177 w, 1144 m, 1084 w, 1073 w, 1030 m, 923 m, 894 s, 844 m, 828 w, 763 m, 743 s, 737 s, 665 m, 585 m, 558 m, and 483 vw.

$(C_4H_9)_2Sn(o\text{-}HNC_6H_4NH_2)(OH)$:[a] 3410 vs, 3390 vs, 3300 m, 3200 m, 2970 s, 2870 vs, 1640 s, 1601 s, 1500 vs, 1460 s, 1420 w, 1380 s, 1320 w, 1278 s, 1195 vw, 1158 m, 1118 vw, 1070 m, 1030 w, 1002 w, 928 m, 883 m, 860 m, 850 m, 820 (br), 750 s, 725 vw, 665 s, 590 s, 560 s, 528 w, and 435 (br).

$(C_4H_9)_2Sn(o\text{-}SC_6H_4NH_2)_2$:[b] 3457 m, 3357 m, 3057 w, 2957 vs, 2912 s, 2862 s, 2852 s, 1601 vs, 1472 w, 1457 w, 1442 w, 1372 m, 1357 m, 1332 w, 1298 m, 1248 m, 1178 w, 1155 m, 1072 s, 1045 vw, 1022 m, 958 m, 875 m, 865 (sh), 840 w, 742 vs, 690 s, 672 m, 590 m, 550 vw, 535 w, 515 w, and 445 m.

EXPERIMENTAL

Where relevant, moisture was rigorously excluded. Molecular weight determination was carried out with a semimicro ebulliometer (Gallenkamp) with ther-

---

* [a] Spectra were recorded in nujol mull. [b] Infrared spectrum was recorded with neat liquid.

TABLE 3

SPECTROSCOPICALLY SIGNIFICANT ABSORPTIONS OF DIBUTYLTIN(IV) DERIVATIVES (cm^{-1})[a]

	Compounds	$\nu(Sn{-}C)$	$\nu(Sn{-}O)$	$\nu(Sn{-}N)$	$\nu(Sn{-}OH)$	$\Delta\nu(C{-}O)$	$\nu\left(Sn\begin{smallmatrix}\diagup O\diagdown\\ \diagdown O\diagup\end{smallmatrix}Sn\right)$	$\Delta\nu(NH_2)$
1	$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)(OH)$	565 s	565 s, 590 m	488 (sh)	443 m	30	810 m	10
2	$(C_4H_9)_2Sn(o\text{-}H_2NC_6H_4NH)(OH)$	560 s	665 s 590 s	528 w	435 w(br)		820 m	10
3	$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH)$	565 m, 523 s	668 s, 588 w	523 s		20		10
4	$(C_4H_9)_2Sn(o\text{-}NHC_6H_4NH)$	560 s, 535 s	665 s, 590 s	523 w				10
5	$(C_4H_9)_2Sn(o\text{-}OC_6H_4NH_2)_2$	558 m	665 m, 585 m	483 vs		75		10
6	$(C_4H_9)_2Sn(o\text{-}SC_6H_4NH_2)_2$	590 m		515 w				15

[a] s=strong, m=medium, w=weak, sh=shoulder, br=broad.

mistor sensing. Solvents were dried by standard procedures. *o*-Aminophenol and *o*-phenylenediamine were recrystallised from suitable solvents, and *o*-aminothiophenol was distilled (126°/6 mm). Dibutyltin oxide (Nitto Kasei, Japan) was used without purification. The IR spectra of the compounds were recorded on a Perkin–Elmer 337 spectrophotometer fitted with KBr optics.

Reaction of dibutyltin oxide with o-aminophenol

To a toluene solution of dibutyltin oxide was added a calculated amount of the ligand, and the mixture was refluxed under a fractionating column at 120°. The excess of solvent and any azeotrope was fractionated out. Residual toluene was removed under reduced pressure at the room temperature, and the product was finally dried at 0.1 mm. Results of other similar experiments are listed in Tables 1 and 2.

ACKNOWLEDGEMENT

Thanks are due to Dr. V. K. Mathur for determining the IR spectra.

REFERENCES

1 M. Wieber and M. Schmidt, *Z. Naturforsch. B*, 18 (1963) 849.
2 M. Wieber and M. Schmidt, *Angew. Chem.*, 75 (1963) 1116.