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PREPARATION OF MONOALKYLTIN(IV) COMPOUNDS BY THE REACTION OF ORGANIC TIN(II) COMPOUNDS WITH n-ALKYL HALIDES

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Summary

Reactions of $Sn(OR)_2$ compounds ($R = CH_3\overset{|}{C}{=}CCOCH_3$, $CH_3\overset{|}{C}{=}CHCO_2Et$, $Ph\overset{|}{C}{=}CHCOPh$, and o-$C_6H_4CO_2Et$) with n-alkyl iodides, $R'I$ (R' = Me, Et, n-Bu), gave Sn^{IV} compounds of type $R'Sn(OR)_2I$.

We have reported the preparation of some monomeric organic tin(II) compounds containing Sn—OC bonds [1—3] and their reactions with n-alkyl halides [4]. More recently, Bos and his co-workers [5] have reported the reaction between tin(II) bis(acetylacetonate) and methyl iodide with the formation of methylbis(acetylacetonato)tin(IV) iodide. As an extension of studies on organic tin(II) compounds, it was thought worthwhile to investigate the behavior of tin(II) compounds toward n-alkyl halides. This paper deals with the preparation of monoalkyltin(IV) compounds by the reaction of organic tin(II) compounds of the type $Sn(OR)_2$ [$R = CH_3\overset{|}{C}{=}CHCOCH_3$, $CH_3\overset{|}{C}{=}CHCO_2CH_2CH_3$, $C_6H_5\overset{|}{C}{=}CHCOC_6H_5$, o-$C_6H_4CO_2CH_2CH_3$, C_6H_5, CH_3CO] with n-$R'X$ [$R' = CH_3$, CH_3CH_2, n-C_4H_9, X = I, Br, Cl].

Results and discussion

As shown in Table 1, tin(II) bis(acetylacetonate) reacted easily with methyl iodide to give methylbis(acetylacetonato)tin(IV) iodide. A similar but slower reaction took place also between tin(II) bis(2-carboethoxyphenoxide), tin(II) bis(1,3-diphenyl-1,3-propanedionate), or bis(ethylacetoacetato)tin(II) and methyl iodide. The oxidative addition products were identified from the data of elemental and spectral analyses (Tables 2 and 3).

On the other hand, no reaction occurred between tin(II) phenoxide or acetate and methyl iodide at 43° for 7 h. The difference in behavior of tin(II) compounds may be explained by the fact that tin(II) phenoxide and acetate are highly associated solids with intermolecular tin—oxygen bridging, while the

TABLE 1

REACTION OF $Sn(OR)_2$ WITH n-ALKYL HALIDES

Reactants		Reaction conditions		Products	
$Sn(OR)_2^a$	R'X	time (h)	temp. (°C)	$\overset{I}{RSn}(OR)_2$	Yield (%)
$Sn(acac)_2$	CH_3I	1.5	43	$CH_3\overset{I}{Sn}(acac)_2$	86
$Sn(dbzm)_2$	CH_3I	7	43	$CH_3\overset{I}{Sn}(dbzm)_2$	57
$Sn(ceph)_2$	CH_3I	3	43	$CH_3\overset{I}{Sn}(ceph)_2$	53
$Sn(etacac)_2$	CH_3I	9	43	$CH_3\overset{I}{Sn}(etacac)_2$	55
$Sn(acac)_2$	C_2H_5I	1.5	73	$C_2H_5\overset{I}{Sn}(acac)_2$	56
$Sn(acac)_2$	n-C_4H_9I	5	90	n-$C_4H_9\overset{I}{Sn}(acac)_2$	70

[a] acac = $CH_3\underset{O-}{C}{=}CHCOCH_3$; dbzm = $C_6H_5\underset{O-}{C}{=}CHCOC_6H_5$, ceph = o-$C_2H_5CO_2C_6H_4O-$; etacac = $CH_3\underset{O-}{C}{=}CHCO_2C_2H_5$.

other tin(II) compounds bearing carbonyl functions, such as tin(II) bis(acetylacetonate), bis(ethylacetoacetato)tin(II), and tin(II) bis(2-carboethoxyphenoxide), are monomeric in benzene.

Tin(II) bis(acetylacetonate) also reacted with ethyl iodide and n-butyl iodide to give the corresponding alkyltin(IV) compounds. However, no reaction occurred with n-butyl bromide or chloride under the same reaction conditions, as is clear from the yield of the n-butyl halides recovered. Therefore, the oxidative addition reaction may be utilized for preparing various monoalkyltin(IV) iodides.

TABLE 2

ANALYTICAL AND PHYSICAL DATA FOR ALKYLTIN(IV) DERIVATIVES

Alkyltin(IV) deriv.	M.p. (°C) or b.p. (°C/mmHg)	Mol. wt. Found (calcd.)	Anal. Found (calcd.) (%) Sn	C	H	I
$CH_3\underset{I}{Sn}(acac)_2^b$	118	444 (459)	25.46 (25.81)	28.41 (28.79)	3.60 (3.74)	27.78 (27.68)
$CH_3\underset{I}{Sn}(dbzm)_2$	215—218	688[a] (707)	16.50 (16.79)	52.23 (52.65)	3.74 (3.56)	17.90 (17.95)
$CH_3\underset{I}{Sn}(ceph)_2$	150—153	582[a] (591)	19.60 (20.08)	38.21 (38.61)	3.68 (3.58)	21.40 (21.47)
$CH_3\underset{I}{Sn}(etacac)_2$	122—125/10^{-4}	509 (519)	23.04 (22.90)	29.85 (30.10)	4.06 (4.08)	24.22 (24.47)
$C_2H_5\underset{I}{Sn}(acac)_2$	74—75.2	478 (473)	25.09 (25.10)	29.63 (30.05)	4.04 (4.05)	26.63 (26.84)
n-$C_4H_9\underset{I}{Sn}(acac)_2$	86.3—88	515 (501)	24.01 (23.71)	33.89 (33.55)	4.60 (4.63)	25.17 (25.35)

[a] Molecular weight determined by ebulliometry. [b] Lit. [6] m.p. 115—116°C.

TABLE 3

IR AND NMR DATA FOR ALKYLTIN(IV) DERIVATIVES

Alkyltin(IV) deriv.	IR (cm^{-1})			NMR[b]				
	$\nu(Sn-C)$	$\nu(Sn-O)$	$\nu(C=O)$	$\delta(CH_3C)$	$\delta(CH=)$	$\delta(Sn-CH_3)$	$J(^{117}Sn-CH)$	$J(^{119}Sn-CH)$
$CH_3\underset{\substack{\vert \\ I}}{Sn}(acac)_2^a$	534	432	1570	2.04	5.52	1.10	113	117
$CH_3\underset{\substack{\vert \\ I}}{Sn}(dbzm)_2$	545		1540			1.57 (in $CDCH_3$)	114	120
$CH_3\underset{\substack{\vert \\ I}}{Sn}(ceph)_2$	538		1585			1.57 (in benzene)	112	117
$CH_3\underset{\substack{\vert \\ I}}{Sn}(etacac)_2$	535	432	1585	1.98	4.98	1.15	114	118
$C_2H_5\underset{\substack{\vert \\ I}}{Sn}(acac)_2$	509	430	1570	2.02	5.42			
$n\text{-}C_4H_9\underset{\substack{\vert \\ I}}{Sn}(acac)_2$	605	432	1580	2.01	5.46			

[a] Lit. [7]: 2.05 (CH_3C), 5.56 (CH) and 1.21 (CH_3Sn) ppm (in $CHCl_3$ soln.). [b] δ(ppm), J(cps).

Experimental

All experiments were carried out under dry nitrogen atomosphere. Melting points and boiling points are uncorrected. IR spectra were recorded using Nujol mulls or liquid films with Hitachi EPI-S2 and EPI-L spectrometers. NMR spectra were measured on a Varian A-60 spectrometer, using CCl_4 as solvent, unless otherwise stated. Chemical shifts, δ(ppm), were given relative to internal TMS. The molecular weights were determined cryoscopically in benzene at concentrations of 0.5—1.0 g/30 ml, unless otherwise stated. The elemental analyses were carried out with Yanagimoto CHN corder, model MT-2.

Materials. Alkyl halides and solvents were purified by distillation after drying over calcium chloride or oxide.

Tin(II) bis(2-carboethoxyphenoxide) was prepared from tin(II) ethoxide and ethyl salicylate and recrystallized from n-hexane—benzene solution: yield 61.4%, white crystals, m.p. (dec.) 102—110°. IR (Nujol); 1679 and 1620 [ν(C=O)], 596 and 587 [ν(Sn—O)]. NMR (benzene); 0.97 3H, triplet, CH_3), 3.99 (2H, quartet, CH_2). Mol. wt. 437(449). Anal. Found; Sn (total), 26.42; Sn^{II}, 25.80. $SnO_6C_{18}H_{18}$ calcd.: Sn, 26.42%.

The other tin(II) compounds were prepared by procedures described in the literature [1—2]. Tin(II) phenoxide and acetate were prepared by a modified procedure of Morrison [8]. These products were identified from the data of their Sn analyses and IR spectra.

Reaction of tin(II) bis(acetylacetonate) with methyl iodide

Methyl iodide (0.1 mole) was added to tin(II) bis(acetylacetonate) (0.1 mole) over a period of ca. 1 h at 5—10°. The mixture then was kept at 43° under the conditions given in Table 1. Unreacted methyl iodide was removed under reduced pressure and the residue was recrystallized from n-hexane—benzene.

Reaction of bis(ethylacetoacetato)tin(II) with methyl iodide

The reaction of bis(ethylacetoacetato)tin(II) (0.2 mole) with an excess of methyl iodide (24 ml) was carried out similarly. A viscous liquid was obtained by distillation under reduced pressure.

Reaction of tin(II) bis(1,3-diphenyl-1,3-propanedionate) with methyl iodide

Tin(II) bis(1,3-diphenyl-1,3-propanedionate) (0.2 mole) was treated with an excess of methyl iodide (20 ml). Removal of the unconverted iodide left a solid residue which was recrystallized from n-hexane—benzene as a pale yellow powder.

A similar procedure was used for the reaction of tin(II) bis(2-carboethoxyphenoxide) (0.02 mole) with methyl iodide (20 ml).

Analysis

Tin contents were determined by chelate titration with ethylenediamine tetraacetic acid for total tin and iodometry for tin in the 2+ oxidation state.

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