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

REACTION OF DIPHENYLTIN WITH ALKYL HALIDES
NUCLEAR MAGNETIC RESONANCE SPECTRA OF METHYLTIN AND ETHYLTIN COMPOUNDS

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(Received July 19th, 1967)

In continuation of studies on the reaction between alkyl halides and dialkyltin[1], alkyl halides were reacted with diphenyltin, $(Ph_2Sn)_m$[2,3], and various phenyltin halides and alkylated phenyltin halides were obtained as shown in eqn. (1). These halides were identified as the tetra-substituted phenylalkyltin compounds, obtained by treating the reaction mixture with a Grignard reagent having an alkyl residue different from that of the starting materials (eqn. (2)) (Table 1).

TABLE 1

REACTION OF DIPHENYLTIN WITH ALKYL HALIDE

Alkyl halide (RX)	*Reaction time (h)*	*Solvent*	*Yield of products (%)*				
			Ph_3SnX	*Ph_2RSnX*	*$PhRSnX_2$*	*PhR_2SnX*	*Ph_2SnX_2*
MeI	3	benzene	17.7	26.5	13.8	3.7	2.6
EtI	10		29.0	17.1	5.4	10.2	2
n-PrI	10	tetrahydrofuran	28.2	10.6	5.2	14.9	trace
n-BuI	10	tetrahydrofuran	34.0	8.3	4.9	11.5	2
EtBr	10		14.3	4.9	4.0	1	4.2
n-PrBr	10		13.8	13.2	3.5	3.0	1
n-BuBr	10		20.1	28.8	6.1	5.0	1

$$(Ph_2Sn)_m + RX \longrightarrow Ph_3SnX + Ph_2RSnX + PhRSnX_2 + PhR_2SnX + Ph_2SnX_2 \quad (1)$$

$$\xrightarrow{R'MgX} Ph_3R'Sn + Ph_2RR'Sn + PhRR'_2Sn + PhR_2R'Sn + Ph_2R'_2Sn \quad (2)$$

(R = Me, R′ = n-Bu)
(R = Et, n-Pr, n-Bu, R′ = Me)
(X = I, Br)

Alkyldiphenyltin halide, Ph_2RSnX, was assumed to be produced via an addition reaction with ring-demembering (eqn. (3))[1]. Other products such as Ph_3SnX, $PhRSnX_2$, PhR_2SnX and Ph_2SnX_2, would be formed via the disproportionation reaction (eqn. (4)) and both the addition and the disproportionation reactions could proceed competitively.

$$(Ph_2Sn)_m+RX \begin{cases} \rightarrow [\text{Addition}]\ Ph_2RSnX & (3) \\ \rightarrow [\text{Disproportionation}]\ \begin{matrix} Ph_3SnX,\ PhRSnX_2 \\ PhR_2SnX,\ Ph_2SnX_2 \end{matrix} & (4) \end{cases}$$

Disproportionation occurred readily in the reaction of diphenyltin with alkyl iodide but in the reaction of dialkyltin with alkyl iodide only the addition reaction took place[1]. The lability of the phenyl–tin bonding would be consistent with the ready cleavability of the bond by iodine[4–6] and hydrochloric acid[7].

Four possible pathways of the disproportionation, A, B, C and D, are to be considered.

$$(Ph_2Sn)_m+RX \rightarrow Ph_2SnX_2 \xrightarrow{(Ph_2Sn)_m} Ph_3SnX+Sn \qquad (A)$$

$$Sn+RX \rightarrow R_2SnX_2 \xrightarrow{(Ph_2Sn)_m} PhR_2SnX+PhRSnX_2+Ph_3SnX \qquad (B)$$

$$(Ph_2Sn)_m \rightarrow [Ph_3Sn\text{-}] \xrightarrow{RX} Ph_3SnX \qquad (C)$$

$$Ph_2RSnX+RX \nrightarrow Ph_3SnX+PhRSnX_2+PhR_2SnX \qquad (D)$$

In sequence A, the diphenyltin chain is disrupted and the fragment takes halogen atoms from the alkyl halide to give diphenyltin dihalide which reacts with an excess of diphenyltin to yield triphenyltin halide and metallic tin. This was proved to be the case, when a mixture of diphenyltin diiodide and excess of diphenyltin was heated at 140° and triphenyltin iodide and metallic tin were obtained according to eqn. (5).

$$\frac{2}{m}(Ph_2Sn)_m+Ph_2SnI_2 \xrightarrow[10\text{ h}]{140^\circ} 2\ Ph_3SnI+Sn \qquad (5)$$

Kuivila and Jukusik[8] reported the formation of triphenyltin chloride and stannous chloride by the reaction of diphenyltin dichloride with diphenyltin according to the following equation. In this case, however, excess diphenyltin dichloride was used.

$$Ph_2Sn+2\ Ph_2SnCl_2 \xrightarrow[5\text{ h}]{130-140^\circ} 2\ Ph_3SnCl+SnCl_2$$

The metallic tin produced in sequence A could be taken up by alkyl halide to give dialkyltin dihalide which reacts with diphenyltin to yield dialkylphenyltin halide, alkylphenyltin dihalide and triphenyltin halide (sequence B). This route was also shown to be feasible by heating a mixture of di-n-butyltin diiodide and diphenyltin (eqn. (6)). The yields given under each compound are based on the total tin atoms of the diiodide and the diphenyltin consumed.

$$(Ph_2Sn)_m+Bu_2SnI_2 \xrightarrow[10\text{ h}]{140^\circ}$$

$$\begin{matrix} PhBu_2SnI & + & PhBuSnI_2 & + & Ph_3SnI & + & Ph_2SnI_2 & + & Ph_3SnSnPh_3 \\ (42\%) & & (5\%) & & (6\%) & & (5\%) & & (7\%) \end{matrix} \qquad (6)$$

In sequence C, the ring form of diphenyltin is converted into an open-chain compound in which the terminal of the chain constitutes a triphenyltin species [Ph_3Sn-]. On disruption, this terminal group takes a halogen atom from the alkyl halide to give triphenyltin halide. Attempts to confirm and determine this species in the form of triphenyltin iodide by the iodine method[1] were abandoned since not only Sn–Sn, but also Sn–Ph bondings were cleaved easily by iodine, even at room temperature. It is known that thermal decomposition of diphenyltin yields hexaphenylditin together with tetraphenyltin and metallic tin[8,9]. The formation of a triphenyltin fragment could be considered to occur *en route* to tetraphenyltin from diphenyltin. This might be supported by the fact that hexaphenylditin, a dimeric form of triphenyltin species, has been formed by the pyrolysis of diphenyltin[9]. Treatment of hexaphenylditin with methyl iodide at 140° afforded triphenyltin iodide (eqn. (7)), showing that the triphenyltin species takes an iodine atom from the alkyl iodide to give triphenyltin iodide.

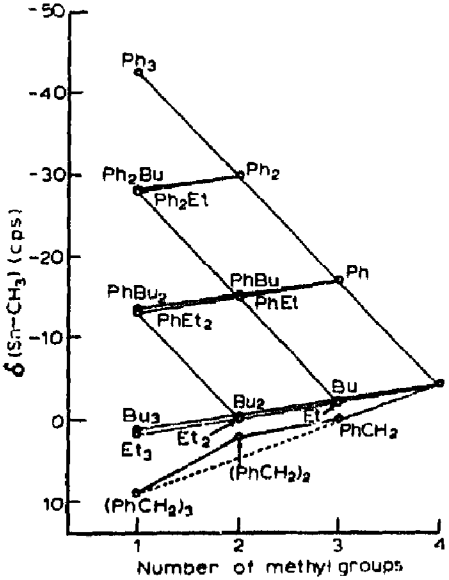
$$Ph_3SnSnPh_3 + MeI \xrightarrow[3\ h]{140°} Ph_3SnI \qquad (7)$$

In order to test the feasibility of sequence D, methyldiphenyltin iodide was heated in the presence of alkyl iodide under the same reaction conditions, but the whole of the iodide was recovered unchanged. The random distribution between phenyl and alkyl groups in the products as expressed in sequence D, therefore, can thus be excluded.

Triphenyltin halide can be produced, therefore, from diphenyltin via sequences A, B, C and eqn. (7). It is not clear which sequence predominates.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Nuclear magnetic resonance spectra of tetra-substituted methyltin derivatives (RR'R''SnMe) having phenyl, ethyl, n-butyl or benzyl groups as the substituents have now been obtained. It was shown that chemical shifts and coupling constants of tetra-substituted methyltin compounds are related linearly to the number of sub-



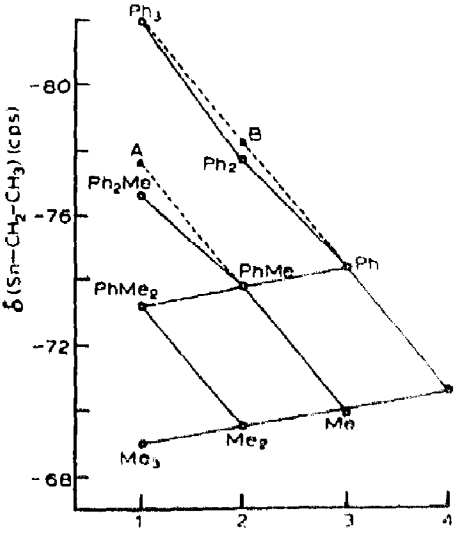


Fig. 1. Chemical shift of methyl protons in the methyl group of tetra-substituted methyltin compounds.
Fig. 2. Chemical shift of methyl protons in the ethyl group of tetra-substituted ethyltin compounds.

stituents. Systematic studies of the NMR spectra of tetra-substituted methyltin and ethyltin compounds have not so far been reported except for some work on organotin hydrides[10–14] or halides[15,16]. The chemical shifts of methyl protons in tetra-substituted methyltin and ethyltin compounds are listed in Table 2. These shifts [δ(Sn–CH$_3$) and δ(Sn–CH$_2$–CH$_3$)] vary linearly with the number of substituents as shown in Figs. 1 and 2. Methyl protons of methyl groups are more shielded than those of ethyl groups. The slope of the lines represents the shielding constant (σ_i) of each substituent. The chemical shifts of tetra-substituted methyltin compounds are calculated from eqn. (8)[17] where −4.2 cps is the chemical shift of methyl protons in tetramethyltin, and σ_i is the shielding constant of the *i*th group. The shielding constants of phenyl, ethyl, *n*-butyl and benzyl groups for methyl protons of methyl groups are 12.8, −2.1, −1.8 and −4.4 cps, respectively.

TABLE 2

CHEMICAL SHIFTS OF METHYL PROTONS IN METHYLTIN AND ETHYLTIN GROUPINGS

Negative δ-values in cps at 60 Mc give the signal at low field to tetramethylsilane

Compound	δ(Sn–CH$_3$) (cps)		δ(Sn–CH$_2$–CH$_3$) (cps)	
	Obs.	*Calcd.*	*Obs.*	*Calcd.*
Me_4Sn[18]	−4.2			
Me_3EtSn	−2.0	−2.1	−69.0	−68.8
Me_3BuSn	−2.4	−2.4		
Me_2Et_2Sn	0.0	0.0	−69.5	−69.4
Me_2Bu_2Sn	−0.4	−0.6		
$MeEt_3Sn$	1.9	2.1	−69.9	−70.0
$MeBu_3Sn$	1.4	1.2		
Et_4Sn[19]			−70.6	
$PhMe_3Sn$	−16.9	−17.0		
$PhMe_2EtSn$	−15.0	−14.9	−72.9	−73.2
$PhMe_2BuSn$	−15.2	−15.2		
$PhMeEt_2Sn$	−13.0	−12.8	−73.5	−73.8
$PhMeBu_2Sn$	−13.6	−13.4		
$PhEt_3Sn$			−74.5	−74.4
Ph_2Me_2Sn	−29.8	−29.8		
$Ph_2MeEtSn$	−27.9	−27.7	−76.6[a] −77.4[b]	−77.6
$Ph_2MeBuSn$	−28.2	−28.0		
Ph_2Et_2Sn			−77.7[a] −78.0[b]	−78.2
Ph_3MeSn	−42.4	−42.6		
Ph_3EtSn			−81.9	−82.0
$(PhCH_2)_3MeSn$	9.0	9.0		
$(PhCH_2)_2Me_2Sn$	2.2	4.6		
$(PhCH_2)Me_3Sn$	0.1	0.2		

[a] Chemical shift of a single peak assigned to both methyl and methylene protons.

[b] Chemical shift determined from the coupling constant $J(^{117/119}Sn\text{–}CH_2\text{–}CH_3)$.

$$\delta(\mathrm{Sn{-}CH_3}) = -4.2 - \sum_i \sigma_i \tag{8}$$

The same treatment was carried out for $\delta(\text{Sn-CH}_2\text{-CH}_3)$, and shielding constants (σ_i') of phenyl and methyl substituents for methyl protons of ethyl groups

$$\delta(\text{Sn-CH}_2\text{-CH}_3) = -70.6 - \sum_i \sigma_i' \qquad (9)$$

were found to be 3.8 and −0.6 cps, respectively. The chemical shift of methyl protons in the ethyl group of tetraethyltin is −70.6 cps. $\delta(\text{Sn-CH}_3)$ and $\delta(\text{Sn-CH}_2\text{-CH}_3)$ of tetra-substituted methyltin and ethyltin compounds calculated from eqns. (8) and (9), respectively, using these constants, are in good agreement with the observed data (Table 2). Chemical shifts of methylene protons in ethyl groups could not be measured owing to the complexity of the peaks.

Since methyl protons are much more shielded by a phenyl group than by an alkyl group, the number of phenyl groups bonded to the tin atom in methyltin derivatives can very easily be determined by the chemical shift of methyl protons.

As for benzylmethyltin derivatives, the chemical shift of methyl protons in dibenzyldimethyltin is very different from the expected value. If the substituent effect were additive, the value would have fallen on the interpolated (dotted) line, the slope of which is equal to the σ_i-value of the benzyl group (Fig. 1).

It can be seen from Fig. 3 that the tin–methyl proton coupling constant of methyltin derivatives $[J(^{117/119}\text{Sn-CH}_3)]$ changes linearly with the number of phenyl, methyl, ethyl, n-butyl or benzyl groups, independently of other substituents. This indicates that the "additivity rule"[20] is applicable for these derivatives and can be expressed as eqn. (10):

$$J(^{117}\text{Sn-CH}_3)(\text{MeXYZSn}) = \zeta_X + \zeta_Y + \zeta_Z \qquad (10)$$

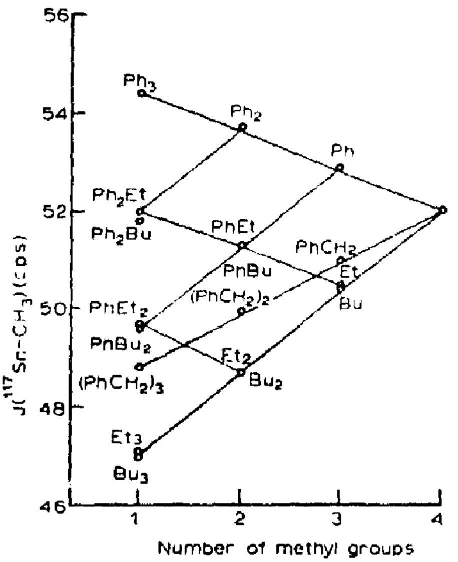


Fig. 3. Coupling constant of tin–methyl protons in the methyl group.

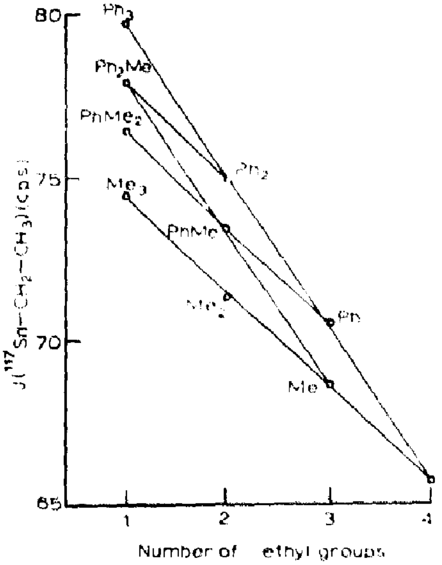


Fig. 4. Coupling constant of tin–methyl protons in the ethyl group.

TABLE 3

EMPIRICAL PARAMETERS, ζ_X, OF THE SUBSTITUENT X FOR COUPLING CONSTANTS

	ζ_X *(cps)*				
$X =$	*Me*	*Et*	*n-Bu*	*Ph*	*PhCH$_2$*
$J(^{117}Sn\text{-}CH_3)$	17.3	15.7	15.7	18.1	16.2
$J(^{119}Sn\text{-}CH_3)$	18.1	16.4	16.4	18.9	17.0
$J(^{117}Sn\text{-}CH_2\text{-}CH_3)$	24.8	21.9		26.6	
$J(^{119}Sn\text{-}CH_2\text{-}CH_3)$	26.0	23.1		27.7	
$J(^{117}Sn\text{-}CH_2\text{-}Ph)$	20.1				18.9
$J(^{119}Sn\text{-}CH_2\text{-}Ph)$	20.9				19.7

TABLE 4

COUPLING CONSTANTS FOR METHYLTIN AND ETHYLTIN GROUPINGS

Compound	$J(^{117}Sn\text{-}CH_3)$ *(cps)*		$J(^{119}Sn\text{-}CH_3)$ *(cps)*		$J(^{117}Sn\text{-}CH_2\text{-}CH_3)$ *(cps)*		$J(^{119}Sn\text{-}CH_2\text{-}CH_3)$ *(cps)*	
	Obs.	*Calcd.*	*Obs.*	*Calcd.*	*Obs.*	*Calcd.*	*Obs.*	*Calcd.*
Me_4Sn[18]	52.0		54.3					
Me_3EtSn	50.5	50.3	52.8	52.6	74.4		77.9	
Me_3BuSn	50.4	50.3	52.6	52.6				
Me_2Et_2Sn	48.7	48.7	50.9	51.0	71.3	71.5	75.0	75.1
Me_2Bu_2Sn	48.7	48.7	50.9	51.0				
$MeEt_3Sn$	47.1		49.3		68.6	68.6	72.0	72.2
$MeBu_3Sn$	47.0		49.3					
Et_4Sn					65.7		69.2	
$PhMe_3Sn$	52.9	52.7	55.2	55.1				
$PhMe_2EtSn$	51.3	51.1	53.5	53.4	76.4	76.2	79.9	79.7
$PhMe_2BuSn$	51.3	51.1	53.5	53.4				
$PhMeEt_2Sn$	49.7	49.5	51.9	51.7	73.4	73.3	76.9	76.8
$PhMeBu_2Sn$	49.6	49.5	51.9	51.7				
$PhEt_3Sn$					70.5	70.4	74.0	73.9
Ph_2Me_2Sn	53.7	53.5	55.8	55.8				
$Ph_2MeEtSn$	52.0	51.9	54.2	54.2	77.9	78.0	81.4	81.4
$Ph_2MeBuSn$	51.8	51.9	54.0	54.2				
Ph_2Et_2Sn					74.9	75.1	78.5	78.5
Ph_3MeSn	54.4		56.6					
Ph_3EtSn					79.7		83.2	

TABLE 5

COUPLING CONSTANTS OF BENZYLMETHYLTIN COMPOUNDS

Compound	$J(^{117}Sn\text{-}CH_3)$ *(cps)*		$J(^{119}Sn\text{-}CH_3)$ *(cps)*		$J(^{117}Sn\text{-}CH_2\text{-}Ph)$ *(cps)*		$J(^{119}Sn\text{-}CH_2\text{-}Ph)$ *(cps)*	
	Obs.	*Calcd.*	*Obs.*	*Calcd.*	*Obs.*	*Calcd.*	*Obs.*	*Calcd.*
$(PhCH_2)_4Sn$[21]					56.8		59.0	
$(PhCH_2)_3MeSn$	48.7		50.9		57.9	57.9	60.2	60.3
$(PhCH_2)_2Me_2Sn$	49.9	49.7	52.2	52.1	59.2	59.1	61.5	61.5
$(PhCH_2)Me_3Sn$	51.0	50.8	53.4	53.2	60.4		62.7	

where ζ_X is an empirical parameter associated with substituents X, but independent of Y and Z (Table 3). A similar trend was observed with $J(^{117}Sn-CH_2-CH_3)$(Fig. 4) and $J(^{117}Sn-CH_2-Ph)$. The same treatment has been carried out for $J(^{119}Sn-CH_3)$, $J(^{119}Sn-CH_2-CH_3)$ and $J(^{119}Sn-CH_2-Ph)$. The agreement between the observed and the calculated coupling constants is satisfactory (Tables 4 and 5).

EXPERIMENTAL

Analytical procedure

The determination and separation of all distillable products were carried out by gas chromatography with helium flowing at 40 ml/min through a stainless-steel column of 3 m × 4 mm o.d. packed with "High Vacuum Silicon Grease" at a column bath temperature of 200°. Retention times of the products are summarized in Table 6.

TABLE 6

ANALYSES AND RETENTION TIMES OF TETRA-SUBSTITUTED METHYLTIN COMPOUNDS

Compound	*Retention time (min)*[a]	% *C*		% *H*	
		Found	*Calcd.*	*Found*	*Calcd.*
$PhMe_2EtSn$	3.6	47.48	47.13	6.46	6.33
$PhMeEt_2Sn$	5.2	49.24	49.12	6.78	6.74
Ph_2Me_2Sn	16.3				
$Ph_2MeEtSn$	22.9	57.13	56.83	6.05	5.72
$PhMe_2PrSn$	5.2	49.18	49.14	6.79	6.75
$PhMePr_2Sn$	8.7	52.81	52.66	7.42	7.47
$Ph_2MePrSn$	28.6	58.20	58.05	6.27	6.05
$PhMe_2{}^nBuSn$	6.4	50.73	50.95	7.17	7.08
$PhMeBu_2Sn$	21.4	55.22	55.42	7.95	8.06
$Ph_2MeBuSn$	36.9	56.27	59.18	6.64	6.43

[a] The conditions of gas chromatography are described in the analytical procedure.

The main products of each experiment were isolated analytically pure by preparative gas chromatography through a stainless-steel column of 0.75 m × 6 mm o.d. packed with "Thermol-3" (Simazu Co. Ltd.) at a column bath temperature of 170°. All new compounds were characterized by infrared spectra, elemental analyses and NMR spectra.

The NMR spectra of all compounds were recorded at a fixed frequency of 60 Mcps on a Varian A-60 spectrometer. All samples were used as 10% solutions in $CDCl_3$, and tetramethylsilane was used as an internal standard throughout. In order to determine the peaks and the distance between peaks on resonances accurately, the spectra were enlarged if necessary. The chemical shifts, δ, and the coupling constants, J, have an error of ±0.3 cps.

The peaks associated with the ethyl group were too complex to be analysed. The highest of all the peaks, however, was assigned to a main peak of the triplet of methyl protons in ethyl groups[19,22,23], except that of Ph_3EtSn the chemical shift of which was determined by the centre of the coupled satellite peaks of $^{117/119}Sn-CH_2-CH_3$. The shift was in good agreement with the extrapolated value. In the spectra of both Ph_2Et_2Sn and $Ph_2EtMeSn$, ethyl protons gave a single peak as a result of the close approach of both shifts of the methyl and methylene protons in the ethyl group. This made it difficult to measure precisely the real chemical shift of the methyl protons. The shift of the single peak is slightly different from the extrapolated values (A and B, respectively, in Fig. 2). The value A (and B) coincided with the chemical shift of the methyl protons in this compound determined from the satellite peaks of $^{117/119}Sn-CH_2-CH_3$.

Reaction of diphenyltin with alkyl halide

Diphenyltin was prepared from diphenyltin dihydride by the method of Neumann and König[2,3]. In all experiments, four equimolar amounts of alkyl halide were used for diphenyltin prepared from an equimolar amount of diphenyltin dihydride. Reactions were carried out in a nitrogen atmosphere. Yields of products are based on the tin atom of the starting diphenyltin.

A representative procedure was as follows. A mixture of 2.73 g (0.010 mole calculated on the basis of Ph_2Sn) of diphenyltin, 7.36 g (0.040 mole) of n-butyl iodide and 3.0 ml of tetrahydrofuran was heated in a sealed glass bottle at 140° for 10 h. The reaction mixture was filtered to give 0.55 g (20 %) of unchanged diphenyltin and a trace of metallic tin; the filtrate was treated with 0.06 mole of methyl magnesium iodide (prepared from 9.0 g of methyl iodide) and distilled *in vacuo* to give 0.88 g of a liquid containing 0.29 g (8.3 %) of n-butylmethyldiphenyltin, 0.37 g (11.5 %) of di-n-butylmethylphenyltin, 0.14 g (4.9 %) of n-butyldimethylphenyltin, 0.06 g (2 %) of dimethyldiphenyltin and a trace of di-n-butyldimethyltin. The distillation residue was separated by elution chromatography to give 1.24 g (34.0 %) of methyltriphenyltin and a trace of hexaphenylditin.

Reaction of diphenyltin with diphenyltin diiodide

A mixture of 0.69 g (0.0026 mole) of diphenyltin, 0.86 g (0.0016 mole) of diphenyltin diiodide[24] and 3.0 ml of benzene was heated in a sealed glass bottle at 140° for 10 h. The reaction mixture was dissolved in 100 ml of tetrahydrofuran and 0.27 g (35 %) of metallic tin was separated by filtration. The solvent in the filtrate was distilled and 1.19 g (53 %) of triphenyltin iodide, m.p. 121–122°, was obtained. Yields are based on the consumed tin atoms of both starting materials.

Reaction of diphenyltin with di-n-butyltin diiodide

A mixture of 1.95 g (0.0071 mole) of diphenyltin, 1.72 g (0.0035 mole) of di-n-butyltin diiodide and 3.0 ml of benzene was heated in a sealed glass bottle at 140° for 10 h. The product was dissolved in benzene and the solution filtered to remove 1.60 g of unchanged diphenyltin. The filtrate was treated with 0.03 mole of methyl magnesium iodide (prepared from 4.3 g of methyl iodide) and distilled *in vacuo* to give 0.97 g of liquid containing 0.42 g (42 %) of di-n-butylmethylphenyltin, 0.04 g (5 %) of n-butyldimethylphenyltin, 0.05 g (5 %) of dimethyldiphenyltin and 0.45 g of di-n-butyldimethyltin. From the distillation residue, 0.07 g (6 %) of methyltriphenyltin and 0.08 g (7 %) of hexaphenylditin were isolated by elution chromatography. Yields of products are based on the total tin atoms of the diiodide and the diphenyltin consumed.

Reaction of methyldiphenyltin iodide with methyl iodide

Methyldiphenyltin iodide was prepared by refluxing methyltriphenyltin with iodine in chloroform, b.p. 115–116°/0.008 mm. (Found: C, 37.64; H, 3.16. $C_{13}H_{13}SnI$ calcd.: C, 37.74; H, 3.44%).

A mixture of 1.83 g (0.0044 mole) of methyldiphenyltin iodide, 2.36 g (0.017 mole) of methyl iodide and 3.0 ml of benzene was heated in a sealed glass bottle at 140° for 3 h. Methyl iodide and benzene were distilled and the reaction product was treated with 0.03 mole of n-butyl magnesium iodide (prepared from 5.5 g of n-butyl iodide) in ether and distilled *in vacuo* to give 1.42 g (0.0042 mole) of n-butylmethyldiphenyltin, b.p. 144–145°/3 mm, $n_D^{27} = 1.5620$, which was derived from the starting iodide. No other products were detected by gas chromatography.

Reaction of hexaphenylditin with methyl iodide

A mixture of 3.80 g (0.0054 mole) of hexaphenylditin, 3.36 g (0.024 mole) of methyl iodide and 3.0 ml of benzene was heated in a sealed glass bottle at 140° for 3 h. Recrystallization of the product from benzene gave 3.26 g (86%) of unchanged hexaphenylditin. The benzene was distilled from the filtrate and 0.28 g (6%) of triphenyltin iodide was obtained.

ACKNOWLEDGEMENT

We wish to thank Dr. TETURÔ SINGÛ of the Faculty of Pharmaceutical Sciences, Kyôto University, for his assistance in obtaining the NMR spectra and Professor H. NOZAKI of the Department of Industrial Chemistry, Kyôto University, for his helpful discussions.

SUMMARY

Treatment of diphenyltin, $(Ph_2Sn)_m$, with alkyl halide, RX, afforded Ph_2RSnX, Ph_3SnX, $PhRSnX_2$, PhR_2SnX and Ph_2SnX_2. The mode of formation of these compounds was studied.

The NMR spectra of the mixed tetra-substituted methyl and ethyltin compounds were studied systematically. Shielding constants for chemical shifts, and empirical parameters for coupling constants of the respective substituents were determined.

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