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

PREPARATION AND REACTIONS OF SOME SULFUR-SUBSTITUTED TETRAORGANOTIN COMPOUNDS

DONALD J. PETERSON
The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239 (U.S.A.)

(Received June 1st, 1970)

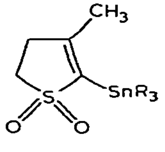
SUMMARY

Some sulfur-substituted organotin compounds, R_3SnCH_2X, where $X = -SCH_3$, $-SO_2C_4H_9$-n, $-SO_2C_6H_5$, $-S^+(CH_3)_2Z^-$, etc., have been synthesized and studied with regard to their solvolytic and "organometallic-like" behavior. Reactions of the organotin compounds with substrates known to be reactive toward classical organometallic compounds tend to place these materials by comparison on the lower end of the reactivity scale.

INTRODUCTION

One class of organometallic compounds that has received a limited amount of attention is that of carbon-functionally substituted organotin compounds. In particular, only a few reports[1,2] exist pertaining to α-substituted organotin compounds of the type, R_3SnCH_2X, where X is a functional group (excluding halide). The information which is available, however, clearly shows compounds of this type to be of interest with regard to potential synthetic utility and as model compounds for mechanistic study. With the intent of further elucidating the chemistry of α-substituted organotin compounds, the sulfur-substituted compounds (I)–(IX) have been prepared and subjected to reactions with (*a*) weak nucleophiles such as alcohols and amines to determine their solvolytic behavior, and (*b*) a variety of substrates that are known to undergo reactions with typical organometallic compounds.

R_3SnCH_2X $R = n\text{-}C_4H_9-$
$X = -SCH_3$ (I), $-SO_2R$ (II), $-SO_2N(CH_3)_2$ (III),
$-SO_2C_6H_5$ (IV), $-SO_2C_6H_4$-4-Cl (V), $-SO_2C_6H_4$-4-OCH_3 (VI),
$-\overset{+}{S}(CH_3)_2I^-$ (VII), $-\overset{+}{S}(CH_3)_2CH_3SO_4^-$ (VIII)



(IX)

The α-sulfur-substituted organotin compounds were chosen for study since it was expected that the "X" groups would impart gradations in reactivities of the compounds corresponding to the ability of "X" to stabilize a carbanion to which it was attached. Thus, regarding the labile carbon–tin bonds of these compounds in the sense $\geq Sn^+\ ^-CH_2X$, in the series sulfide, sulfone, sulfonium salt, it was anticipated that the leaving group ability of "$-CH_2X$" would progressively increase owing to increasing inductive and *d*-orbital resonance stabilization of the incipient carbanion.

RESULTS

Solvolytic behavior of R_3SnCH_2X

Incidental to other investigations, a few workers have reported observing non-catalyzed solvolysis reactions of compounds similar to those of this study, *e.g.*, the hydrolysis[3] of [(trimethylsilyl)methyl]diphenylphosphine oxide at 100°. While findings of this nature demonstrate the susceptibility of the $\geq M-CH_2X$ bond (M = Si, Sn, Ge) to nucleophilic displacement, no apparent attempt has been made to elucidate the details of these reactions.

In the present investigation three of the functionally-substituted organotin compounds (I)–(III) were reacted with n-butanol and piperidine, initially, under pseudo-first order conditions, *i.e.*, the nucleophiles were used in large excess (as solvent; reaction solutions 0.1 molar in organotin compound). The rates of reaction were determined by following the changes in concentration of starting organotin compounds by gas chromatographic analysis. In most runs, the reactions could be followed with reasonable accuracy to 60–80% completion.

The products of the reactions were either isolated in high yield, or demonstrated to have been formed in high yield by ^1H NMR spectral analysis or by gas chromatographic comparisons of the reaction mixtures to standard solutions of the appropriate compounds.

Not unexpectedly, the first compound of the series, (I), was found to be unreactive toward piperidine and butanol at 100°. Indeed, the sulfide was found to be essentially inert to n-C_4H_9OLi in butanol at the same temperature during 24 h.

The next obvious compound of this series, $R_3SnCH_2S(O)CH_3$, could not be prepared by oxidation of the corresponding sulfide, or from the reaction of tributyltin chloride with [(methylsulfinyl)methyl]lithium. It is of interest to note that the related silicon compound, $(CH_3)_3SiCH_2S(O)CH_3$, has been shown to be thermally labile and chemically quite reactive[4]. It is not unreasonable to ascribe our failure to synthesize [(methylsulfinyl)methyl]tributyltin as being due to it possessing a similar, and perhaps greater, instability.

In contrast to the (sulfinylmethyl)tin compound, the (sulfonylmethyl)tributyltin compounds were readily prepared from reactions of tributyltin chloride with the appropriate $XCH_2Li(MgY)$ (Y = halide).

The butanolysis of (II) was carried out over the temperature range of 54–100° [eqn. (1)]. The rate data so obtained gave a good Arrhenius plot (see Table 1 for reaction rates). For this reaction, ΔH^* and ΔS^* were calculated to be 18.4 kcal·mole^{-1} and −29.2 e.u., respectively.

$$(II) + ROH \rightarrow R_3SnOR + CH_3SO_2R \qquad (1)$$

The corresponding piperidinolysis of (II), which occurred at a rate approximately one order of magnitude faster than the butanolysis, was somewhat more

TABLE 1

RATE CONSTANTS FOR THE SOLVOLYSIS OF (II) AND (III)

Compound[a]	Nucleophile[b]	Temp. (°C)[c]	$10^5\,k$ (sec^{-1})[d]
(II)	n-C_4H_9OH	100	7.0
		85	2.8
		69	0.8
		54	0.2
	C_2H_5OH	69	1.2
	$C_5H_{10}NH$	100	55
		85	24
		77	9.2
		69	6.9
		60	2.5
		47.5	1.4
(III)	$C_5H_{10}NH$	100	40
	n-C_4H_9OH	100	1.5

[a] Exactly 0.001 mole of organotin compound was diluted to a volume of 10 ml with the appropriate solvent (nucleophile). [b] Solvents distilled under an argon atmosphere immediately before use. The amines were distilled from KOH pellets. [c] ±0.2°. [d] Rate constants = 2.3 × slope of line obtained from plot of log C_0/C_t *vs. t*.

difficult to reproduce. The reaction was quite subject to catalysis by minor contaminants. In particular, it was demonstrated that trace amounts of carbon dioxide markedly accelerated the rate of disappearance of (II). However, careful exclusion of CO_2 and examination of this reaction at six different temperatures over a range of 53° gave a reasonably reliable Arrhenius plot. From these data the activation parameters were calculated to be $\Delta H^* = 17.7$ kcal·mole^{-1} and $\Delta S^* = -26$ e.u.

A seemingly significant alteration in leaving group from RSO_2CH_2– (II) to $(CH_3)_2NSO_2CH_2$– (III) resulted in relatively minor changes in rates of butanolysis and piperidinolysis (Table 1). The rates of piperidinolysis of the two compounds were almost identical, while (II) solvolyzed ca. only five times faster than (III) in butanol at 100°. Directionally, the relative rates of reactions (II) and (III) are those to be expected from a consideration of the finding[5] that dimethyl sulfone is more acidic than *N,N*-dimethylmethanesulfonamide, *i.e.*, the stability of $CH_3SO_2CH_2^-$ exceeds that of $(CH_3)_2NSO_2CH_2^-$. However, the magnitude of the difference is surprisingly low.

Reactions of the [(arylsulfonyl)methyl]tributyltin compounds (IV)–(VI) with alcohols gave rise to spurious rate data. Several attempts to remove these irregularities in reaction rates by repurification of reactants failed.

An interesting variation in structure was realized with (IX) since a vinyl carbanion rather than an sp^3 hybridized carbanion is generated upon solvolysis. The (IX) solvolyzed in piperidine (100°) at a rate of 5.3×10^{-5} sec^{-1}, or, approximately one order of magnitude slower than (II). Since, in general, sp^2 carbanions are more stable than sp^3 carbanions, this result suggests that the tin atom of (IX) is less susceptible to attack by nucleophiles than (II) owing to steric hindrance.

The final compounds of this series, the sulfonium salts (VII) and (VIII), were readily prepared by reactions of (I) with methyl iodide and dimethyl sulfate, respectively. Although the potential nucleophilicities of the anions of these salts precluded meaningful information with regard to their solvolytic behavior, these compounds proved to be of considerable interest. Specifically, (VII) was found to be inherently unstable and decomposed to tributyltin iodide and methylenedimethylsulfurane [eqn. (2)]. Tributyltin bromide was isolated in 84% yield from a similar reaction of (I) with allyl bromide. Proof for the existence of the sulfur ylid as a product of the

$$I + CH_3I \rightarrow [R_3SnCH_2\overset{+}{S}(CH_3)_2I^-] \rightarrow R_3SnI + (CH_3)_2\overset{+}{S}CH_2^- \quad (2)$$

methylation reaction is discussed in the following section of this paper. By way of contrast, (VIII) was found to be quite stable and could be readily isolated. An indication of the stability of (VIII) was obtained by alkylating (I) with dimethyl sulfate in CD_3OD and following the rate of formation of $(CH_3)_2S^+CH_2D\ CH_3SO_4^-$ by ^1H NMR spectroscopy. At room temperature, a 0.1 molar solution of (VIII) had a half life of ca. two days.

"Organometallic-like" reactions

It was felt that some further insight into the lability of the carbon–tin bond could be obtained by placing the reactivities of R_3SnCH_2X compounds into perspective with the broad reactivity scale of the more classical organometallic compounds. For this purpose [(phenylsulfonyl)methyl]tributyltin (IV) was chosen as a model compound for study and was reacted with various substrates that are known to be reactive toward organometallic compounds. Reactions of (IV) with benzoyl chloride, decanoyl chloride, and chlorodiphenylphosphine, in the absence of solvent, afforded moderate yields of phenacylphenylsulfone, (1-phenylsulfonyl)undecanone-2, and [(phenylsulfonyl)methyl]diphenylphosphine, respectively. These products were accompanied by varying amounts of phenyl methyl sulfone. A temperature range of 130–170° was necessary to effect complete consumption of starting compounds within ca. 12 h (Table 2).

Surprisingly, a reaction of (IV) with benzoic anhydride gave tributyltin benzoate (94%) and phenyl methyl sulfone (40%) as the only isolable products. A ^1H NMR spectral analysis of the crude reaction mixture demonstrated the absence of the expected phenacyl phenyl sulfone. An 87% yield of phenyl methyl sulfone was obtained from the reaction of (IV) with octanal. Since the aldehyde was rigorously purified of octanoic acid before use, it can be concluded that, in this reaction, [(phenylsulfonyl)methyl]tributyltin functioned as a base rather than a nucleophile. The presumed enolate resisted characterization; however, interestingly, exposure of the

$$(IV) + n\text{-}C_7H_{15}CHO \rightarrow C_6H_5SO_2CH_3 + [C_6H_{13}CH{=}CHOSnBu_3] \quad (3)$$

reaction products to air resulted in a rapid formation of tributyltin octanoate.

[(Phenylsulfonyl)methyl]tributyltin was found to be unreactive toward carbon dioxide and oxygen at room temperature, while exposure of a thin layer of (IV) to air resulted in ca. 50% decomposition to phenyl methyl sulfone and tributyltin oxide within four days. These findings, when regarded in conjunction, are in accord with hydrolysis being responsible for the air sensitivity of (IV).

As mentioned above, [(dimethylsulfonio)methyl]tributyltin iodide spontaneously decomposed to give methylenedimethylsulfurane and tributyltin iodide. This reaction appeared to warrant further study since it provides a mild, non-base induced

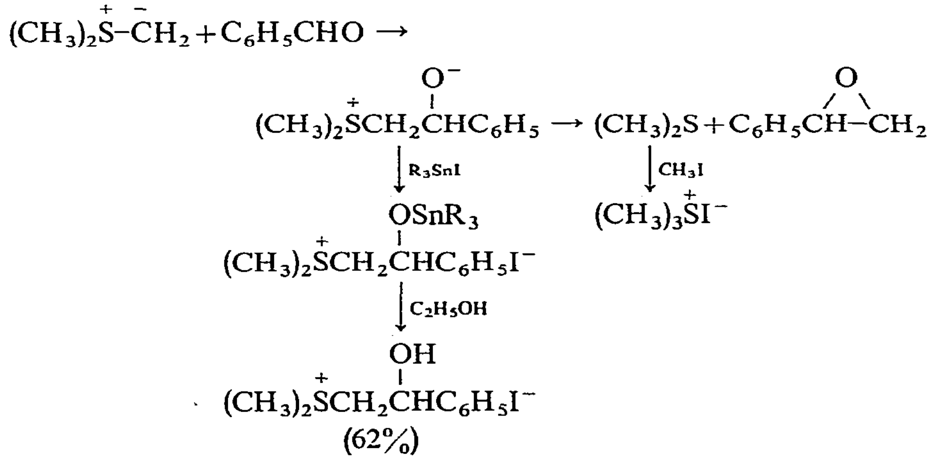
TABLE 2

REACTIONS OF R_3SnCH_2X

Organotin compound	Other reactant	Reaction temp. (°C)	Reaction time (h)	Products[a]		
				Compound	Yield (%)	M.p.
(III)	$C_6H_5C(O)Cl$	75	4	$C_6H_5C(O)N(CH_3)_2$	48	
				$(-SO_2CH_2-)_x$		
(IV)	$C_6H_5C(O)Cl$	145	17	$C_6H_5SO_2CH_2C(O)C_6H_5$	67	94–96[b]
				$C_6H_5SO_2CH_3$	33	
(VII)[c]	$C_6H_5C(O)Cl$	25	16	$CH_3SCH{=}C(C_6H_5)OC(O)C_6H_5$	60	74–76[d]
				$(CH_3)_3\overset{+}{S}I^-$	66	
(IV)	$n\text{-}C_9H_{19}C(O)Cl$	150	4	$C_6H_5SO_2CH_2C(O)C_9H_{19}$[e]	75	65–66
	$(C_6H_5)_2PCl$	110	17	$C_6H_5SO_2CH_2P(C_6H_5)_2$[f,g]	68	129–130
				$C_6H_5SO_2CH_3$	23	
	$n\text{-}C_7H_{15}CHO$	160–175	22	$C_6H_5SO_2CH_3$	87	
				$(C_4H_9)_3SnOC(O)C_7H_{15}$		54–55.5[h]
	$[C_6H_5C(O)]_2O$	160	47	$C_6H_5CO_2Sn(C_4H_9)_3$[i]	94	
				$C_6H_5SO_2CH_3$	40	
	Air	20	152	$[(C_4H_9)_3Sn]_2O$	95	
				$C_6H_5SO_2CH_3$	56	
[j]	O_2	20	8	No reaction		
	CO_2	20	72	No reaction		

[a] Tributyltin chloride was isolated in greater than 80% of theoretical value from first five entries of Table. [b] Lit.[11] m.p. 93–94. [c] From the reaction of (I) with methyl iodide. [d] Lit.[8] m.p. 75–76. [e] 2,4-Dinitrophenylhydrazone derivative; m.p. 110–111. (Found: C, 56.8; H, 6.6; N, 11.2. $C_{23}H_{30}N_4O_6S$ calcd.: C, 56.4; H, 6.15; N, 11.4%.) [f] Analyzed as the corresponding phosphine sulfide. (Found: C, 61.35; H, 4.75; S, 17.2. $C_{19}H_{17}O_2PS_2$ calcd.: C, 61.3; H, 4.57; S, 17.7%.) [g] ^1H NMR signal at τ 6.0 ($\rangle PCH_2SO_2$). [h] Lit.[12] m.p. 55–56. [i] See ref. 13. [j] In benzene.

method for the generation of sulfur ylids. Accordingly, in separate runs, methyl iodide was added to (I) in the presence of benzaldehyde and benzoyl chloride. From the aldehyde reaction, styrene oxide, trimethylsulfonium iodide, and (2-hydroxy-2-phenylethyl)dimethylsulfonium iodide (subsequent to treatment with ethanol) were isolated



$$(CH_3)_2\overset{+}{S}-\overset{-}{C}H_2 + C_6H_5CHO \rightarrow$$

$$(CH_3)_2\overset{+}{S}CH_2\overset{O^-}{C}HC_6H_5 \rightarrow (CH_3)_2S + C_6H_5CH\overset{O}{-}CH_2$$

$$\downarrow R_3SnI \qquad\qquad \downarrow CH_3I$$

$$(CH_3)_2\overset{+}{S}CH_2\overset{OSnR_3}{C}HC_6H_5I^- \qquad (CH_3)_3\overset{+}{S}I^-$$

$$\downarrow C_2H_5OH$$

$$(CH_3)_2\overset{+}{S}CH_2\overset{OH}{C}HC_6H_5I^-$$

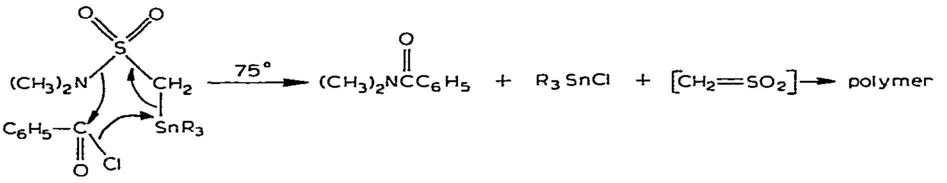
(62%)

(4)

[eqn. (4)]. The styrene oxide and trimethylsulfonium iodide undoubtedly were formed from the (known)[7] decomposition of the betaine intermediate. The tributyltin iodide which was present, however, significantly suppressed this reaction by stannylation of the reactive alkoxide. This method of generating the sulfur ylid therefore has the unique advantage of forming β-hydroxyethylsulfonium salts directly.

The reaction involving benzoyl chloride, (I), and methyl iodide gave trimethylsulfonium halides, tributyltin halides, and $CH_3SCH{=}C(C_6H_5)OC(O)C_6H_5$ as the major products. The tributyltin halide exerted little, if any, influence on the course of this reaction since the vinylbenzoate was realized from the reaction of benzoyl chloride with methylenedimethylsulfurane that had been generated by the standard method[8].

Interestingly, (III) did not react with benzoyl chloride to give the expected product, $(CH_3)_2NSO_2CH_2C(O)C_6H_5$. Instead, *N,N*-dimethylbenzamide and tributyltin chloride were formed as the major products along with a polymeric sulfur compound. These products are readily accounted for by a mechanism which involves the extrusion of sulfene from (III) [eqn. (5)].



(5)

The reactions of (III), (IV), and (VII) with various substrates demonstrate the synthetic utility of sulfur-substituted organotin compounds. Further, these reactions suggest that this series of substituted organotin compounds occupies a position at the lower end of the reactivity scale of organometallic compounds. Finally, it has been shown that, in reactions of (IV) with carboxylic acid derivatives, like the analogous reactions of organometallic compounds in general, proton abstractions can compete with additions to carbonyl groups.

EXPERIMENTAL

All reactions and manipulations involving organometallic compounds were performed under an atmosphere of oxygen-free argon. NMR spectra were obtained on Varian Associates HR-60 and HA-100 spectrometers.

Compounds (I)–(III) and (IX) were synthesized by reactions of the appropriate organolithium compound with tributyltin chloride in tetrahydrofuran. [(Methylthio)-methyl]lithium was prepared by a reported procedure[9], but with a 10% excess of dimethyl sulfide employed to insure complete consumption of the n-butyllithium. [(Butylsulfonyl)methyl]lithium, [(*N,N*-dimethylaminosulfonyl)methyl]lithium, and 5-lithio-2,3-dihydrothiophene-1,1-dioxide[10] were prepared by metalations of the corresponding sulfones with n-butyllithium in mixed hexane/THF solvent at −78°. Compounds (IV)–(VI) were prepared from reactions of the corresponding [(arylsulfonyl)methyl]magnesium bromide with tributyltin chloride in THF. The precursory magnesium compounds were obtained from room temperature reactions of methylmagnesium bromide with the arylsulfones in THF.

Subsequent to complete reactions of the sulfur-substituted organolithium compounds with tributyltin chloride, the reaction mixtures were hydrolyzed with aqueous ammonium chloride and worked up in the usual manner. All compounds were purified by distillation under reduced pressure to give yields ranging from ca. 50–80%. No attempt was made to optimize yields.

Compound (VIII) was prepared by the alkylation of (I) with dimethyl sulfate in methylene chloride.

The physical properties and analytical data for these compounds (I)–(IV) are compiled in Table 3. The ^1H NMR spectral determinations were run on samples dissolved in $CDCl_3$ and with tetramethylsilane as reference.

TABLE 3

SULFUR-SUBSTITUTED ORGANOTIN COMPOUNDS

Compound	B.p. (°C)/mm	Analysis, found (calcd.) (%)			^1H NMR Signals		
		C	H	S	τ[a]	J[b]	Assignment
(I)	106–107/0.07	48.1	9.2		7.9		$-SCH_3$
		(48.0)	(9.1)		8.1		$-SCH_2Sn\leq$
(II)	151–161/0.05	48.4	9.2		7.0		$-SO_2CH_2C\leq$
		(48.0)	(9.0)		7.4	40	$\geq SnCH_2SO_2-$
(III)	150–154/0.1	43.8	8.5	7.6	7.2		$-N(CH_3)_2$
		(43.7)	(8.5)	(7.8)	7.6	46	$\geq SnCH_2SO_2$
(IV)	172–180/0.07	51.4	7.9		7.3	33	$\geq SnCH_2SO_2$
		(51.3)	(7.7)				
(V)	185–190/0.07	47.3	7.0		7.3	32	$\geq SnCH_2SO_2$
		(47.5)	(6.9)				
(VI)	180–185/0.05	50.7	7.6		6.2		$-OCH_3$
		(50.5)	(7.6)		7.2	34	$\geq SnCH_2SO_2$
(VIII)					6.2		$CH_3SO_4^-$
					7.0		$(CH_3)_2\overset{+}{S}-$
					7.4	32	$\geq SnCH_2\overset{+}{S}$
(IX)	183/0.2	48.1	8.3		6.8		$-SO_2CH_2$
		(48.4)	(8.1)		7.15		$-SO_2CCH_2-$
					8.0		$>C{=}CCH_3$

[a] Centered at given τ. [b] All coupling constants J (Hz) given are for $CH_2-{}^{117/119}Sn$ interactions. The signals for the individual isotopes were not resolved.

All structure assignments were substantiated by the solvolysis reactions which gave the corresponding readily identifiable XSO_2CH_3.

Reactions of (I), (III), and (IV) with the carboxylic acid derivatives, chlorodiphenylphosphine, carbon dioxide, air, and oxygen are included in Table 2. For these runs, the reactants were heated at the given temperature for the given length of time under argon. The products were either isolated by distillation (liquids) or by filtration (solids).

Preparation of [(phenylsulfonyl)methyl]tributyltin

To a solution of 31.2 g (0.2 mole) of phenyl methyl sulfone in THF (130 ml) there was added 67 ml (0.2 mole) of 3 molar methylmagnesium chloride (in THF) which resulted in a slight warming and the evolution of a gas. Subsequent to ca 2 h of stirring at room temperature, the gas evolution had ceased and the reaction mixture was warmed to 45° for an additional 2 h to insure complete metalation. Tributyltin chloride (65 g, 0.2 mole) was added and the reaction mixture stirred overnight. Work-up of the product consisted of a hydrolysis with aqueous ammonium chloride, ether extraction from the water layer, and distillation under reduced pressure to give 73.1 g (82%) of [(phenylsulfonyl)methyl]tributyltin, b.p. 172–180° (0.07 mm) (see Table 3 for analytical data).

Preparation of [(N,N-dimethylaminosulfonyl)methyl]tributyltin

To a solution of 46.2 g (0.38 mole) of *N,N*-dimethylmethanesulfonamide in THF (200 ml) there was added dropwise 250 ml of 1.5 molar n-butyllithium (in hexane) while maintaining the temperature below −55°. Subsequent to 4 h of stirring at this temperature, the metalated sulfonamide was reacted with 122.5 g (0.38 mole) of tributyltin chloride. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The reaction mixture was then hydrolyzed with aqueous ammonium chloride, and the product was separated from impurities by two vacuum distillations to give 74 g (48%) of gas chromatographically pure material (see Table 3 for physical data). No attempt was made to recover any of the tin compound from less pure distillation fractions.

Reaction of [(methylthio)methyl]tributyltin with methyl iodide

(*a*). *In Butanol.* A solution 3.51 g (0.01 mole) of (I) and 4.3 g (0.03 mole) of methyl iodide in butanol (30 ml) was heated at 50° overnight. During this time (I) was completely consumed as evidenced by gas phase chromatographic analysis. Subsequent to chilling, the reaction mixture was filtered to give 1.92 g (94%) of trimethylsulfonium iodide, m.p. 210–212° (decompn). IR and ^{1}H NMR spectral analyses confirmed the structure assignment.

(*b*). *In the presence of benzaldehyde.* A solution of 3.51 g (0.01 mole) of (I), 2.84 g (0.02 mole) of methyl iodide, and 1.1 g (0.011 mole) of benzaldehyde in methylene chloride (30 ml) was heated at reflux (under argon). Subsequent to *ca.* 3 h, 97% of (I) had reacted. By comparison with a standard solution, the reaction mixture was shown to contain styrene oxide (9.3% yield) by GLC analysis. The reaction mixture was chilled and filtered to give 0.06 g (3 %) of trimethylsulfonium iodide, m.p. 205–210° (decompn.). The sulfonium salt was further characterized by IR and ^{1}H NMR spectral analyses.

The filtrate was concentrated on a rotary evaporator and then treated with 50 ml of absolute ethanol and allowed to stand overnight. The solid which settled out during this time was removed by filtration and identified as (β-hydroxyphenethyl)-dimethylsulfonium iodide[9], m.p. 137–138° (1.73 g, 56%).

A ^{1}H NMR spectral analysis of the mother liquor exhibited no prominent signals other than those for the $(C_4H_9)_3Sn$ group. No attempt was made to elucidate the structure(s) of the tin compound.

Reaction of [(methylthio)methyl]tributyltin with allyl bromide; isolation of tributyltin bromide

A solution of 17.5 g (0.05 mole) of (I) and 18.2 g (0.15 mole) of allyl bromide in 100 ml of methylene chloride was heated to reflux. The reaction, which was monitored by GLC, had occurred to the extent of 50% after 1 h, and was essentially complete within 4 h. The rate of formation of tributyltin bromide was ca. equal to the rate of disappearance of (I). The tributyltin bromide resulting from the reaction was isolated by distillation, b.p. 100–103°/0.2 mm (yield 15.4 g, 84%) and identified by bromine analysis (Found: Br, 21.6. $C_{12}H_{27}BrSn$ calcd.: Br, 21.6%.), ^1H NMR spectral analysis, and a comparison of the GLC retention time with that of authentic tributyltin bromide.

No attempt was made to work up the distillation residue.

ACKNOWLEDGEMENT

The author is grateful to Messrs. L. Dunham and M. Coleman for technical assistance in much of this work.

REFERENCES

1 J. G. Noltes, H. M. J. C. Creemers and G. J. M. van der Kerk, *J. Organometal. Chem.*, 11 (1968) 21.
2 G. J. M. van der Kerk, J. G. A. Luijten, J. G. Noltes and H. M. J. C. Creemers, *Chimia*, 23 (1969) 313, and references cited therein.
3 D. Seyferth and R. B. King, *Annual Surveys of Organometallic Chemistry*, Elsevier, New York, 1965, p. 132.
4 A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 46 (1968) 2115.
5 E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 87 (1965) 1345.
6 R. Alexander, C. Eaborn and T. G. Traylor, *J. Organometal. Chem.*, 21 (1970) P65.
7 A. W. Johnson, *Ylid Chemistry*, Academic Press, New York, 1966, p. 328.
8 A. W. Johnson and R. T. Amel, *Tetrahedron Lett.* 8 (1966) 819.
9 D. J. Peterson, *J. Org. Chem.*, 32 (1967) 1717.
10 R. A. Damico, unpublished results from this laboratory.
11 C. M. M. da Silva Correâ, A. S. Lindsay and W. A. Waters, *J. Chem. Soc., C*, (1968) 1872.
12 D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, (1962) 2050.
13 Po-Lin Cheng, *et al.*, *Hua Kung Hsueh Pao*, (1965) 169; *Chem. Abstr.*, 65 (1966) 16997.