

Substitution at Saturated Carbon. Part 24.¹ The Reactivity of the Benzyltin group towards Mercury(II) Salts in Methanol

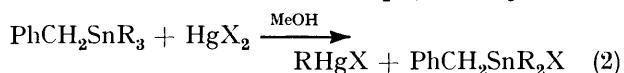
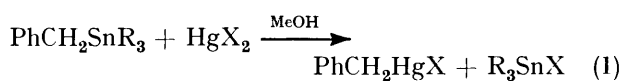
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In the reaction of the compounds $\text{PhCH}_2\text{SnR}_3$ with mercury(II) salts in methanol, only the benzyl group is cleaved from tin to form PhCH_2HgX when $\text{R} = \text{Bu}^n, \text{Pr}^n$ and Et . With $\text{PhCH}_2\text{SnMe}_3$, only the methyl group is removed to yield MeHgX . Rate constants are reported for the reaction of $\text{PhCH}_2\text{SnR}_3$ with mercury(II) chloride and acetate in methanol, and together with previous work yield the following sequence of reactivity of RSn groups towards mercury(II) chloride and acetate in methanol: $\text{R} = \text{Ph} (1.4 \times 10^5) > \text{Me} (430) > \text{PhCH}_2 (11) > \text{Et}(1) > \text{Pr}^n (0.19) > \text{Bu}^n (0.17)$.

THE action of electrophiles on alkyltin compounds has been studied in some detail, and for the electrophilic reagents iodine, bromine, and mercury(II) salts, the relative reactivity of most of the simple alkyl groups has now been established (see ref. 2). Surprisingly, the reactivity of the benzyltin group, by comparison with alkyltin groups, is not well known. It has been stated³ that the reactivity sequence of RSn bonds in electrophilic cleavages is $\text{R} = \text{Me} < \text{PhCH}_2 < \text{Ph}$, but in the cleavage of $\text{PhCH}_2\text{SnMe}_3$ by electrophilic reagents, sometimes the benzyl group is preferentially removed,^{4,6} sometimes the methyl group is preferentially removed,⁷⁻¹⁰ and sometimes the cleavages take place at comparable rates¹¹ (see Table 1). Because we had previously

first by careful product analyses and second by kinetic methods.

A mercury(II) salt, HgX_2 , could react with the benzyltrialkyltins either through reaction (1) or (2). In the case of the compounds $\text{PhCH}_2\text{SnR}_3$, where $\text{R} = \text{Bu}^n, \text{Pr}^n$, and Et , product analyses as described in the Experi-



mental section yield the pure crystalline compound PhCH_2HgCl in 90–98% yield based on equation (1), both for reaction with mercury(II) chloride and with mercury(II) acetate (in the latter case the acetate was converted to the chloride before isolation of the product). When the same product analytical method was applied to the reaction between $\text{PhCH}_2\text{SnMe}_3$ and mercury(II) chloride, no benzylmercury(II) at all was obtained, but only a small (and variable) yield of methylmercury(II) chloride. However, on following the reaction by n.m.r., using $[\text{}^2\text{H}_4]$ methanol as solvent, rapid formation of methylmercury(II) chloride and the other reaction product in equation (2), $\text{PhCH}_2\text{SnMe}_2\text{Cl}$, was observed; no PhCH_2HgCl was seen. On standing overnight, all the MeHgCl had disappeared and an n.m.r. signal due to Me_2Hg had appeared instead. It seems clear that a quite rapid reaction, equation (2; $\text{R} = \text{Me}, \text{X} = \text{Cl}$), leading only to MeHgCl as the organomercury(II) compound, is followed by a slower subsequent decomposition. This might explain the quite contrary result of Reutov *et al.*⁶ who found only PhCH_2HgCl as the organomercury(II) compound. These workers used a polarographic method to identify the RHgCl compound formed in equation (1) or (2) as either PhCH_2HgCl or MeHgCl . If, however, the subsequent decomposition product had the same E_3 value as PhCH_2HgCl , then an erroneous conclusion could have been reached. On the basis of our product analyses, there is no anomaly in the $\text{PhCH}_2\text{SnMe}_3$ reaction with mercury(II) chloride; in both methanol and DMSO, only the methyl group is removed.*

* Using $[\text{}^2\text{H}_6]$ DMSO as the solvent, we confirmed the conclusion of Reutov *et al.*¹⁰ conclusion that MeHgCl is the product in this solvent (see Table 1).

TABLE 1

Cleavage of $\text{PhCH}_2\text{SnMe}_3$ by electrophilic reagents

Reagent	Solvent	Group removed (%)	Ref.
SO_2	Methanol	PhCH_2 (100)	4
$\text{CF}_3\text{CO}_2\text{H}$	Benzene	PhCH_2 (56) *	11
		Me (44) *	
$\text{I}_2\text{-I}^-$	Methanol	Me (100)	7
$\text{I}_2\text{-I}^-$	DMSO	Me (100)	8
I_2	CCl_4	PhCH_2 (100)	5
$\text{Br}_2\text{-Br}^-$	DMSO	Me (100)	9
HgCl_2	Methanol	PhCH_2 (100)	6
HgCl_2	DMSO	Me (100)	10

* Not corrected for the statistical factor. When thus corrected, relative rate constants for removal of the groups from $\text{PhCH}_2\text{SnMe}_3$ are $\text{PhCH}_2 : \text{Me} = 3.8 : 1.0$.¹¹

studied² the action of mercury(II) salts on tetra-alkyltins, we chose also to investigate the electrophilic cleavage of benzyltin compounds by such salts in order to obtain a quantitative comparison of the reactivity of a benzyl group with simple alkyl groups. We also felt it useful to study this reaction in view of the surprising results of Reutov *et al.*^{6,10} on the cleavage of $\text{PhCH}_2\text{SnMe}_3$ by mercury(II) chloride. First, in dimethyl sulphoxide¹⁰ a methyl group is 100% removed whereas in methanol⁶ the benzyl group is 100% removed, and second the cleavage of the benzyl group in methanol takes place very rapidly, even more rapidly than a phenyl group, for example.⁶ We therefore prepared a series of $\text{PhCH}_2\text{-SnR}_3$ compounds, where $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n$, and Bu^n and studied the action of mercury(II) chloride and mercury(II) acetate in methanol on the tin compounds,

Having dealt with the anomaly over reaction products, we then studied the kinetics of substitution, using our previous spectrophotometric method.¹² In all cases but one, excellent second-order kinetic plots

TABLE 2

Second-order rate constants ($l \text{ mol}^{-1} \text{ min}^{-1}$) for the reaction of $\text{PhCH}_2\text{SnR}_3$ with HgCl_2 and $\text{Hg}(\text{OAc})_2$ in methanol at 298 K

R	HgCl_2 ^a	$\text{Hg}(\text{OAc})_2$ ^{a,b}
Bu ⁿ	0.460 ± 0.002	114 ± 5
Pr ⁿ	0.392 ± 0.003	135 ± 13
Et	0.646 ± 0.002	220 ± 16
Me	35.9 ± 0.7	20 000

^a Runs carried out in triplicate. Errors given are estimated standard deviations. ^b In the presence of 0.04M-acetic acid to suppress solvolysis.

were obtained; results are given in Table 2. The only difficulty occurred in the reaction of $\text{PhCH}_2\text{SnMe}_3$ with mercury(II) acetate, where the rate constant was so high that only an approximate value could be obtained. Rate constants for reaction (1; $\text{R} = \text{Bu}^n, \text{Pr}^n, \text{Et}$) can be compared with those for the corresponding R_4Sn compounds,¹³⁻¹⁵ statistically corrected, to yield a measure of the $\text{PhCH}_2 : \text{R}$ relative reactivity (Table 3). From these reactivities, sequences of the reactivity of RSn groups towards mercury(II) salts in methanol may be constructed (Table 4). We can also set up another such sequence using data¹⁶ on the $\text{RSnPr}_3\text{-Hg}(\text{OAc})_2$ reaction in methanol, assuming that cleavage of $\text{PhCH}_2\text{-SnR}_3$ compounds takes place at *ca.* 3.2 times the rate of cleavage of $\text{PhCH}_2\text{SnPr}_3$ (as previously found for

rapidly as the benzyl group, so that taking into account a statistical factor, it seems that a methyl group should preferentially be removed from $\text{PhCH}_2\text{SnMe}_3$ at *ca.* 120 times the rate of the benzyl group.* Our kinetic experiments therefore suggest that almost none of the benzyl group would be cleaved from $\text{PhCH}_2\text{SnMe}_3$ by mercury(II) salts in methanol, in complete agreement with our product studies. Comparison of the benzyl : alkyl reactivity in tin compounds with that found for a number of substitutions of alkyltransition-metal compounds can be obtained from results collected in

TABLE 3

Comparison of rate constants ($l \text{ mol}^{-1} \text{ min}^{-1}$) for cleavage of benzyl- and alkyl-tin bonds in methanol at 298 K

R	$\text{PhCH}_2\text{-SnR}_3$	R-SnR_3	$\text{PhCH}_2\text{-SnR}_3 : \text{R-SnR}_3$
(A) With mercury(II) chloride			
Bu ⁿ	0.460	$0.009\ 23$ ^a	49.8
Pr ⁿ	0.392	$0.009\ 43$ ^a	41.6
Et	0.646	0.050 ^a	12.9
Me		21.0 ^b	
(B) With mercury(II) acetate			
Bu ⁿ	114	2.16 ^c	52.8
Pr ⁿ	135	2.60 ^c	51.9
Et	220	12.8 ^c	17.2
Me		$2\ 910$ ^c	

^a Values from ref. 12. ^b Ref. 1. ^c From rate constants¹⁵ obtained at 303 K, corrected by the factor 51/61.4 found^{14,16} for Et_4Sn at 298 and 303 K.

Table 4. Although, for these substitutions by mercury(II) compounds, the reactivity sequence is always $\text{Me} \gg \text{benzyl}$, it seems that in the alkyltransition-metal series, the benzyl group is less reactive than in the alkyl-

TABLE 4

Alkyl group reactivity, relative to $\text{Et} = 1$, in some metal-for-metal exchange reactions

Substrate	Reagent	Solvent	Me	Benzyl	Et	Pr ⁿ	Bu ⁿ	Ref.
RSnR_3	HgCl_2	Methanol	420	10	1	0.19	0.18	a
RSnR_3	$\text{Hg}(\text{OAc})_2$	Methanol	230	12	1	0.20	0.17	a
RSnPr_3	$\text{Hg}(\text{OAc})_2$	Methanol	440	12	1	0.19	0.17	b
$[\text{RCr}(\text{H}_2\text{O})_5]^{2+}$	Hg^{2+}	Water	71	0.35	1	0.25		c
$[\text{RCr}(\text{H}_2\text{O})_5]^{2+}$	MeHg^+	Water	50	0.49	1	0.61		c
$[\text{RCoL}(\text{H}_2\text{O})]^{2+}$	$\text{Hg}(\text{OAc})_2$	Water	210	0.89	1	0.70	0.75	d
$[\text{RCoL}(\text{H}_2\text{O})]^{2+}$	$\text{Hg}(\text{ClO}_4)_2$	Water	330	0.43	1	0.32	0.34	d
$[\text{RCoL}'(\text{H}_2\text{O})]^{2+}$	$\text{Hg}(\text{OAc})_2$	Water	86	1.0	1	0.91	0.93	d
$[\text{RCoL}(\text{H}_2\text{O})]^{2+}$	Hg^{2+}	Water	270	0.66	1	0.50		e
$[\text{RFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$	HgCl_2	THF	6.4	0.02	1			f

^a From data in Table 3. ^b This work and from results in ref. 16, assuming that the rate of cleavage of R-SnR_3 is 3.2 times that of R-SnPr_3 as found¹⁶ for $\text{R} = \text{Et}$, and $\text{R} = \text{Pr}^n$. ^c Ref. 17. ^d V. E. Magnuson and J. H. Weber, *J. Organometallic Chem.*, 1974, **74**, 135; L is the ligand formed by condensation of butane-2,3-dione mono-oxime with ethylenediamine, and L' is the dimethylgloximate-ligand. ^e G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Organometallic Chem.*, 1974, **81**, 107; L is the 1,3-bis(diacetyl mono-oxime)propanato-ligand. The relative rate of cleavage of the Ph-Co bond is 650 ($\text{Et} = 1$). ^f Third-order rate constants used, from L. J. Dizikes and W. Wojcicki, *J. Amer. Chem. Soc.*, 1977, **99**, 5295. The relative rate of cleavage of the Ph-Fe bond is only 9.3 ($\text{Et} = 1$).

various alkyl groups¹⁶); this sequence is also in Table 4. Finally, we average the various RSn reactivities in Table 4 and include also the known PhSn reactivity to obtain the following sequence of reactivity of RSn bonds towards mercury(II) salts in methanol: Ph (1.4×10^5) $>$ Me (430) $>$ PhCH_2 (11) $>$ Et (1) $>$ Pr^n (0.19) $>$ Bu^n (0.17). The reactivity of a benzyltin group is some ten times that of an ethyl group and *ca.* 50 times that of the higher n-alkyl groups. However, the methyl group is cleaved from tin *ca.* 40 times as

tin case. This is not likely to be due to steric reasons, because for the chromium compounds¹⁷ listed in Table 4 steric effects of isopropyl and neopentyl groups are less than these found by us previously¹⁵ for alkyltin sub-

* At 298 K, rate constants for cleavage of a given Me-Sn bond are Me-SnMe_3 (2 900), Me-SnPr_3 (1 800), and $\text{Me-SnMe}_2\text{CH}_2\text{Ph}$ (*ca.* 6 700) for reaction with mercury(II) acetate,^{15,16} and Me-SnMe_3 (21.0) and $\text{Me-SnMe}_2\text{CH}_2\text{Ph}$ (12.0) for reaction with mercury(II) chloride¹ in methanol. These sequences show again that the leaving group has but little effect on the rate constant for cleavage of a given alkyl group.²

strates. However, it is difficult to comment on possible steric effects in benzyl-metal cleavages because of lack of knowledge of the stereochemistry of substitution at the carbon atom undergoing substitution. It is known that metal-for-metal exchanges can take place by both retention and inversion of configuration at carbon, and even when the stereochemical form is known for one particular alkyl group (*e.g.* Bu^tCHDCHD) in a given reaction, it is by no means certain that the same stereochemistry applies to reactions of other alkyl groups.

It is possible that reaction (1; R = Buⁿ, Prⁿ, and Et) takes place by a simple S_E2 substitution, although more complicated mechanisms, such as oxidative addition-elimination, and one-electron-transfer processes, are possible. We sought to check the latter by measuring the charge-transfer spectrum of the PhCH₂SnR₃-tetracyanoethylene complex at low temperature. In cases where a one-electron-transfer process has been suggested to apply,¹⁸ there is a good correlation between ΔG[‡] for reaction and a model process involving removal of an electron from the organometallic substrate, for example the vertical ionisation potential or the tetracyanoethylene (TCNE) charge-transfer band energies.¹⁸ However, as shown in Table 5, the ΔG[‡] value for reaction

TABLE 5

Comparison of ΔG[‡] for reactions (1) and (2) with the PhCH₂SnR₃-TCNE charge-transfer band energy

R	λ _{max.} ^{a/} nm	E ^b	ΔG [‡] ^c	
			HgCl ₂	Hg(OAc) ₂
Bu ⁿ	596	48.0	20.3	17.1
Pr ⁿ	594	48.1	20.4	17.0
Et	588	48.6	20.1	16.7
Me	572 ^d	50.0	17.8	14.0

^a Obtained using solutions in CH₂Cl₂ at low temperature (solid CO₂-ethanol). ^b In kcal mol⁻¹. ^c In kcal mol⁻¹ from rate constants in Table 2 after conversion to units of l mol⁻¹ s⁻¹. ^d Compare an estimated value of 571 by W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 7476, who observed that the PhCH₂SnMe₃-TCNE complex was unstable at room temperature.

with mercury(II) salts decreases as the charge-transfer energy increases and we therefore think that one-electron-transfer processes of the type suggested by Kochi *et al.*¹⁸ are unlikely to take place in reactions (1) and (2). At the moment, there is no evidence to suggest that reactions (1) and (2) are other than simple S_E2 metal-for-metal exchanges.

EXPERIMENTAL

The PhCH₂SnR₃ compounds were all prepared by the action of an ethereal solution of PhCH₂MgCl on the corresponding trialkyltin chlorides. After the usual work-up, the ethereal solution of the products was twice treated with ammonia to precipitate out any unchanged R₃SnCl, the ether removed, and the benzyltin compounds twice distilled under reduced pressure. In all cases, the n.m.r. spectra showed no impurities; the observed b.p.s are in Table 6. Methanol and the mercury(II) salts were as described before.^{12,14}

For the product analyses, a methanolic solution 0.05M in PhCH₂SnR₃ and 0.05M in the mercury(II) salt was stored

in the dark and then poured into an aqueous solution of 0.1M-sodium chloride. The mixture was extracted with chloroform and the extract washed with water and evaporated to small bulk, to yield a semi-solid residue of the required PhCH₂HgCl admixed with the liquid R₃SnCl compound. The liquid was dissolved by the addition of a small amount of hexane, and the residual solid was filtered off through a weighed, sintered-glass crucible, washed with hexane, and dried to constant weight. The n.m.r. of the dried solid showed only the spectrum due to

TABLE 6

Physical constants of the PhCH₂SnR₃ compounds and the PhCH₂HgCl reaction product ^a

R	PhCH ₂ SnR ₃ B.p. (°C)	Product from HgCl ₂		Product from Hg(OAc) ₂	
		M.p. (°C)	Yield (%)	M.p. (°C)	Yield (%)
Bu ⁿ	129—130/ 0.18 mmHg	103	92	106	93
Pr ⁿ	125—126/ 0.8 mmHg	105	90	105—106	98
Et	65—67/ 0.2 mmHg	104	92	106	95
Me	101—104/ 15 mmHg				

^a Literature m.p. of PhCH₂HgCl is 104 °C (L. G. Makarova and A. N. Nesmeyanov, 'The Organic Compounds of Mercury,' North Holland, Amsterdam, 1967).

benzylmercury(II) chloride (in the case of R = Buⁿ, Prⁿ, and Et); analytical details are in Table 6.*

In the case of PhCH₂SnMe₃, the above product analysis yielded variable, and small, quantities of methylmercury(II) chloride on very careful evaporation of the chloroform solution. The hexane treatment was omitted, and the n.m.r. spectrum of the crude solid showed the presence of MeHgCl together with PhCH₂SnMe₂Cl. A reaction between PhCH₂SnMe₃ and HgCl₂ was followed by n.m.r. using [²H₄]methanol as solvent. Rapid formation of MeHgCl and PhCH₂SnMe₂Cl was observed. The spectrum was unchanged after 2 h, but on leaving overnight the peak due to MeHgCl had disappeared and had been replaced by an upfield peak due to Me₂Hg. Because of the toxic properties of the latter compound, no further investigation was pursued. A similar product analysis using [²H₆]DMSO showed also that MeHgCl was the product; no PhCH₂HgCl was observed in the product n.m.r. spectrum.

Kinetic measurements were carried out exactly as described in detail before,¹²⁻¹⁶ with solutions thermostatted at 298.15 ± 0.01 K. In the case of reactions with HgCl₂, initial concentrations were 1.5 × 10⁻²M for PhCH₂SnR₃ and 1.0 × 10⁻²M for HgCl₂. For the acetate reactions, concentrations were reduced to 4.9 × 10⁻⁴M for PhCH₂SnR₃ and to 3.3 × 10⁻⁴M for Hg(OAc)₂, and experiments were run in the presence of 4.0 × 10⁻²M-acetic acid. With PhCH₂-SnMe₃ the reaction was much too fast to follow and we were able only to obtain a rough estimate of the rate constant (Table 2).

Charge-transfer spectra between PhCH₂SnR₃ compounds and TCNE were obtained in CH₂Cl₂ solutions using cells

* For the reaction of PhCH₂SnBu₃ with HgCl₂ in methanol, the n.m.r. spectrum of the chloroform extract was examined, and it was ascertained that this spectrum was identical to that of a synthetic mixture of PhCH₂HgCl and Bu₃SnCl in equimolar proportions in chloroform. We are indebted to M. D. Morris for carrying out this experiment.

surrounded by a solid CO₂-ethanol mixture. Values of λ_{max} obtained under these conditions are in Table 5. At room temperature the benzyltin compounds all reacted rapidly with TCNE in methylene chloride.

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