1192-03-6; 2-chloro-1,3,2-benzodioxaborole, 55718-76-8; 2-chloro-1,3,2-dioxaborinane, 1003-43-6; 2-chloro-1,3,2-tetramethyldioxaborolane, 67975-91-1; trimethylene borate, 52876-41-2; 2-methoxy-1,3,2-dioxaborolane, 1003-24-3; 2-methyl-1,3,2-dioxa-borolane, 37003-57-9; 2-methyl-1,3,2-benzodioxaborole, 78336-63-7; 2-methyl-1,3,2-dioxaborinane, 51901-48-5; 2-methyl-1,3,2-tetramethyldioxaborolane, 94242-85-0; calcium hydride, 7789-78-8; thionyl chloride, 7719-09-7; methyl chloride, 74-87-3.

Electrophilic Cleavages in $(CH_3)_3SnCH_2M(CH_3)_3$ (M = Sn, Ge, Si, C). 1. Product Distribution

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The extent to which Sn–CH_2 and/or Sn–CH_3 cleavage occurs in $(CH_3)_3SnCH_2M(CH_3)_3$ (M = Sn, Ge, Si) in reactions with several electrophiles has been determined. With iodine and with bromine in various solvents both sites are attacked with Sn–CH_2 cleavage favored for nonpolar solvents and for M = Sn. Protolysis leads to Sn–CH_2 cleavage only, and this site appears to be activated by the $(CH_3)_3M$ groups. On the other hand organometallic electrophiles exclusively attack the Sn–CH_3 groups and the $(CH_3)_3MCH_2$ groups are deactivating. With all reagents only the Sn–CH_3 groups are reactive in $(CH_3)_3SnCH_2C(CH_3)_3$. The complex mechanistic situation for halogenolysis can lead to variations in the relative reactivities of various sites during reaction and introduce serious errors into internal selectivity measurements.

Introduction

Substrates of the type $(CH_3)_3SnCH_2M(CH_3)_3$, where M = Sn, Ge, Si, and C, may undergo reactions with electrophiles to cleave the Sn–CH_3 and/or the Sn–CH_2 bonds. Comparison of the individual rates of these processes with one another and with the reference substrate $(CH_3)_4Sn$ provides information on the substituent effects of the $(CH_3)_3M$ and $(CH_3)_3MCH_2$ groups. In this paper we concentrate attention on the extent of reaction at these two sites and will deal with the rates of the processes, particularly halogenolysis for which there are a number of complications, subsequently.

A number of reactions of these related substrates have been described previously. The most reactive member of this set, M = Sn, when first prepared was reported[1] to be inert toward bromine at ambient temperatures, although reaction took place slowly in refluxing CCl_4 to yield $(CH_3)_2SnBr_2$ and other volatile products. Both Sn–CH_3 and Sn–CH_2 cleavage has clearly occurred but there is no indication of the preferred path. However, a recent report[2] notes that with bromine in a methanol/carbon tetrachloride mixture at –60 °C the major products are $(CH_3)_3SnBr$ and $(CH_3)_2SnBr_2$ implying predominant Sn–CH_2 cleavage. On the other hand, the reaction of $[(CH_3)_3SiCH_2]_2Sn(CH_3)_2$ with Br_2/CCl_4 gives a 65% yield of Sn–CH_3 cleavage product with a 31% yield of $(CH_3)_3SiCH_2Sn(CH_3)_2Br$, the result of Sn–$CH_2$ cleavage.[3] Furthermore, it is well-known that the solvent plays an important role in the differential reactivity of the alkyl groups in tetraalkylstannanes[4] (see below), and in a case related to the present studies, it is reported[5] that Br_2/CCl_4 opens the ring of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-

Table I. Halogenolysis of $(CH_3)_3SnCH_2M(CH_3)_3$—Product Composition

reagent/ solv	% reaction at CH_2[a]			
	M = C	Si	Ge	Sn
Br_2/DMF[b]	<<1	5	6	16
Br_2/CH_3OH	<<1	10	<<1	31
Br_2/CH_2Cl_2	<<1	10	7	10
Br_2/$CHCl_3$	<<1	13	6	13
Br_2/CCl_4	<<1	24	31	75
I_2/C_6H_5Cl	<<1	4	9	12.5
I_2/CH_3OH	<<1	8	10	24
I_2/CCl_4	<<1	10	12	54

[a] Mean of several reactions with ca. 0.1 M reactants analyzed by ^1H NMR. [b] Dimethylformamide.

distannacyclobutane whereas Br_2/CH_3OH can be employed to cleave one Sn–CH_3 bond.

Iodinolysis of $(CH_3)_3SnCH_2Si(CH_3)_3$ without solvent resulted[3] in a 79% yield of $(CH_3)_3SiCH_2I$. Presumably this was accompanied by $(CH_3)_3SnI$ although not mentioned. Reaction with I_2/$CHCl_3$ was used to convert $(CH_3)_3SnCH_2Sn(CH_3)_3$ to 2 equiv of $(CH_3)_3SnI$ and impure CH_2I_2 thus providing its structure proof.[6] These two results imply almost exclusive Sn–CH_2 cleavage.

Reaction of $(CH_3)_3SnCH_2Sn(CH_3)_3$ with 1 equiv of dry HCl has been reported[7] to yield chlorotrimethylstannane and tetramethylstannane in equal proportions, while excess acid reacts with the latter to form methane. Clearly the Sn–CH_2 site is once again preferentially attacked.

We have found[8] that substrates of the type $(CH_3)_3SnM(CH_3)_3$ may react at different sites with acids and with

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(4) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198.
(5) Seyferth, D.; Lefferts, J. L. *J. Organomet. Chem.* **1976**, *116*, 257.

(6) Kraus, C. A.; Neal, A. M. *J. Am. Chem. Soc.* **1930**, *52*, 695.
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(8) (a) McWilliam, D. C.; Wells, P. R. *J. Organomet. Chem.* **1975**, *85*, 165. (b) McWilliam, D. C.; Wells, P. R. *J. Organomet. Chem.* **1975**, *85*, 335, 347. (c) Arnold, D. P.; Cuthbertson, M. J.; Wells, P. R. *J. Organomet. Chem.* **1980**, *184*, 39. (d) Cuthbertson, M. J.; Hawker, D. W.; Laycock, B. G.; Wells, P. R. *J. Organomet. Chem.*, submitted for publication.

Table II. Halogenolysis of $(CH_3)_3SnCH_2M(CH_3)_3$—Internal Selectivity

	$S(R/CH_3) = 3(\% \ CH_2 \text{ reaction})/(\% \ CH_3 \text{ reaction})$					
reagent/solv	$R = CH_2Si(CH_3)_3$	$CH_2Ge(CH_3)_3$	$CH_2Sn(CH_3)_3$	$n\text{-}C_3H_7$	$n\text{-}C_4H_9$	$i\text{-}C_4H_9$
Br_2/DMF^a	0.16	0.19	0.57			
Br_2/CH_3OH	0.33	$\ll 0.03$	1.35			
Br_2/CH_2Cl_2	0.33	0.23	0.33			
$Br_2/CHCl_3$	0.45	0.19	0.45			
Br_2/CCl_4	0.95	1.35	9.00	$\underline{0.9}^b$	$\underline{0.8}^b$	$\underline{0.4}^b$
	$(0.7)^e$	$(0.9)^e$	$(\text{large})^e$			
I_2/C_6H_5Cl	0.13	0.30	0.43	$\underline{0.08}^c$	$\underline{0.07}^c$	
I_2/CH_3OH	0.26	0.33	0.95	$\underline{0.025}^c$ $\underline{0.04}^d$	$\underline{0.10}^d$	$\underline{0.007}^d$
I_2/CCl_4	0.33	0.41	3.52	$\underline{0.9}^c$	$\underline{0.9}^c$	$\underline{0.5}^c$

[a] Dimethylformamide. [b] Reference 10. [c] Reference 9. [d] Reference 11. [e] After correction for early part of reaction (see below).

organometallic electrophiles such as RHgX and R_3SnX. The situation for the $(CH_3)_3SnCH_2M(CH_3)_3$ substrates is clearly of interest and a number of reactions of this type are described below.

Results and Discussion

Halogenolysis. The results in terms of the percentage of product arising from $Sn-CH_2$ cleavage in reactions with bromine or with iodine in various solvents are given in Table I. These were carried out under "preparative" conditions with 1, or slightly less than 1, equiv of reagent at concentrations of ca. 0.1–0.2 M. In no case was any product observed arising from cleavages other than those at the $Sn-CH_2$ or $Sn-CH_3$ bonds, and none was expected in view of the much lower reactivity of the $(CH_3)_4M$ species for M = C, Si, or Ge. Further halogenolysis of the initially formed products was not a problem under these conditions except in the case of $(CH_3)_3SnCH_2Sn(CH_3)_3$. The second set of $Sn-CH_3$ groups in this substrate is sufficiently reactive for the appearance of $Br(CH_3)_2SnCH_2Sn(CH_3)_2Br$ to be significant and allowance was made for this in the product analysis leading to the results given in Table I. The corresponding reaction in iodinolysis is much slower.

The most outstanding feature of Table I is the absence of any detectable reaction of the $Sn-CH_2$ bond in $(CH_3)_3SnCH_2C(CH_3)_3$ and a careful examination of the ^1H NMR spectra of these reaction mixtures shows that a 1% yield of $(CH_3)_3SnX$ or $(CH_3)_3CCH_2X$ (X = Br or I) would be readily observable.

For the remaining substrates of this set the behavior pattern with respect to solvent variation is reminiscent of that reported by Gielen,[4] who finds that the relative reactivity of $(C_2H_5)_4Sn$ vs. $(CH_3)_4Sn$ changes from 0.12 (I_2/CH_3OH) and 0.4 (Br_2/DMF) to 6 (I_2/C_6H_5Cl), 12 (Br_2/C_6H_5Cl), and 95 (Br_2/CCl_4). Fukuzumi and Kochi[9] also report variations in selectivity with solvent of the iodinolysis of tetraalkylstannanes which show a reduced preference for $Sn-CH_3$ attack in the less polar solvents.

In the case of brominolysis we find that further reaction takes place with excess reagent, although in most cases prolonged reaction times are required. For CCl_4 solutions, where $Sn-CH_2$ reaction is most favorable in the original substrate, $(CH_3)_3CCH_2Sn(CH_3)_2Br$ yields ca. 55% products of $Sn-CH_2$ cleavage and ca. 45% of $(CH_3)_3CCH_2Sn(CH_3)_2Br_2$; $(CH_3)_3SiCH_2Sn(CH_3)_2Br$ gives 65% $(CH_3)_3SiCH_2Br/(CH_3)_2SnBr_2$ and 35% $(CH_3)_3SiCH_2Sn(CH_3)Br_2$, while $(CH_3)_3GeCH_2Sn(CH_3)_2Br$ yields only $(CH_3)_2SnBr_2$ and $(CH_3)_3GeCH_2Br$ with no detectable

$(CH_3)_3GeCH_2Sn(CH_3)Br_2$. As noted above, $(CH_3)_3SnCH_2Sn(CH_3)_2Br$ readily yields $Br(CH_3)_2SnCH_2Sn(CH_3)_2Br$. This accounts for ca. 80% of the further reaction of this product. The remaining ca. 20% arises from $Sn-CH_2$ cleavage to yield $Br(CH_3)_2SnCH_2Br$ and $(CH_3)_3SnBr$. No further iodinolysis of $(CH_3)_3MCH_2Sn(CH_3)_2I$ (M = C, Si, Ge) was observed to take place over several weeks, but for M = Sn excess iodine yields $I(CH_3)_2SnCH_2Sn(CH_3)_2I$.

With statistical correction for the number of sites available for reaction, the product composition data arising from intramolecular competitions can be expressed in terms of internal selectivities as given in Table II. For comparison some data are also given for the competition between methyl and other alkyl groups in the same reactions. As shown in Table I the neopentyl group is unable to compete with the methyl group in halogenolysis, i.e., $S(R/CH_3) \ll 0.03$, so that the closest model for the $CH_2M(CH_3)_3$ may be the $CH_2CH(CH_3)_2$ group. Unfortunately, few data are available on isobutylstannanes.

The overall pattern displayed in Table II suggests that two properties of the R' groups in $R'CH_2Sn(CH_3)_3$ determine the internal selectivities. One is a retarding steric effect for which, as anticipated, $(CH_3)_3C \gg (CH_3)_3Si > (CH_3)_3Ge > (CH_3)_3Sn$. This effect appears to be the dominant one for Br_2/DMF, i.e., the most polar system. The other is a rate enhancing effect, presumably electronic in origin, for which $(CH_3)_3Sn \gg (CH_3)_3Ge > (CH_3)_3Si$, and this is of greatest importance for the least polar solvent $(Br_2/CCl_4$ and $I_2/CCl_4)$. However, while one could certainly accommodate most of the data in Table II in terms of variable combinations of these two effects, there are some unusual features. It seems that CH_2Cl_2 and $CHCl_3$ for brominolyses and particularly C_6H_5Cl for iodinolysis must be classified as substantially "polar" solvents relative to CCl_4 and the position of CH_3OH is anomalous. In our view much has still to be clarified concerning the role of the solvent in halogenolysis of organometallics.

From the results of further reaction with Br_2/CCl_4 the $S(R/CH_3)$ values for brominolysis of $(CH_3)_2MCH_2Sn(CH_3)_2Br$ can be obtained and compared with the reactions of $(CH_3)_3MCH_2Sn(CH_3)_3$, thus

$CH_2C(CH_3)_3$	$CH_2Si(CH_3)_3$	$CH_2Ge(CH_3)_3$	$CH_2Sn(CH_3)_3$	$CH_2Sn(CH_3)_2Br$
$\ll 0.03^a$	0.95^a	1.35^a	9.0^b	0.75^a
2.4^b	3.7^b	$> 200^b$	large^b	$\cdots$

[a] In $RSn(CH_3)_3$. [b] In $RSn(CH_3)_2Br$.

The activating effect of the $Sn(CH_3)_3$ group is clearly lost by the introduction of the bromo substituent on the tin atom, and the $Sn(CH_3)_2Br$ group may be weakly deactivating. This accords with the presumed electronic effect arising from some electron-releasing mechanism operating on an electrophilic process. The slower, and

(9) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141.

hence more demanding, brominolysis of the $RSn(CH_3)_2Br$ substrates shows a much enhanced response to the electronic effect, and it is probable that $(CH_3)_3C > CH_3$ when the otherwise dominating steric effect is not important.

Preliminary kinetic studies on these substrates for reactions with I_2/C_6H_5Cl under first-order conditions (at least 10-fold excess substrate) resemble similar studies reported by Fuzukumi and Kochi,[9] and the initial drop in iodine absorbance, which these authors have shown arises from charge transfer complexation, is quite small for this solvent. However, with the two reactants in similar concentrations (ca. 0.05 M) kinetic data obtained by following substrate loss or product formation employing their ^1H NMR spectra are complex and not simply second order. There is an initial fast reaction not suppressed by added galvinoxyl and then a second-order phase to ca. 80% reaction approximately corresponding to the behavior expected from the above first-order reactions; and beyond ca. 80% the reaction is progressively retarded. This latter feature suggests inhibition by product which may arise from R_3SnI_3 formation and is currently under further examination. The initial phase could arise from processes of order higher than one in substrate or reagent. Indeed Fuzukumi and Kochi[9] have described one case in detail, $(C_2H_5)_4Sn/I_2/CH_2Cl_2$, for which the first-order rate constants obtained for various excess substrate concentrations depend upon both the first and second powers of these concentrations. This would correspond to two competing processes, i.e., $R_4Sn + I_2$ (or CT complex decomposition) and $R_4Sn + CT$ complex, and in the case studied the two reactions proceed at essentially equal rates for ca. 0.2 M tetraethylstannane. No other case was examined in detail so there is no reason to suppose that this feature is not more general. If there are two pathways for the formation of product and they have different dependencies on the substrate concentration, then it must be anticipated that the overall internal selectivities may be a function of substrate concentration even when this is constant for reactions run under first-order conditions. However, it is the common practice,[9-11] also followed by us, to determine rate constants with excess substrate and dilute reagent concentrations, but to determine internal selectivities under "preparative" conditions with roughly equal concentrations of reactants ca. 0.1–0.2 M. *These change drastically during reaction.*

In the case of $(CH_3)_3SiCH_2Sn(CH_3)_3$ in C_6H_5Cl the extent of $Sn-CH_2$ cleavage in iodinolysis is quite small (4%) and no variation during reaction could be identified. However in the case of $(CH_3)_3GeCH_2Sn(CH_3)_3$ (= S) all the $Sn-CH_2$ cleavage product observed, 8.7% for $[S]_0 = 0.065$ and $[I_2]_0 = 0.038$ M and 9.5% for $[S]_0 = 0.0056$ and $[I_2]_0 = 0.044$ M, is formed in the first 20 min of reaction which corresponds to an extent of reaction of ca. 45%. Thereafter only $Sn-CH_3$ cleavage takes place. For $(CH_3)_3SnCH_2Sn(CH_3)_3$ the primary products of both $Sn-CH_3$ (P) and $Sn-CH_2$ (P′) cleavage are observable as well as the product of further reaction, i.e., $I(CH_3)_2SnCH_2Sn(CH_3)_2I$ (Q), which allows a correction to be made ($P_{corr} = P + Q$). The ratio P'/P_{corr} remains essentially constant at 12.5/87.5 (mean of four experiments) despite the pronounced curvature of the second-order plots for this substrate. It seems that, unlike the case when M = Ge, the internal selectivities of the processes occurring in the case of M = Sn are not sufficiently different. This perhaps fortuitous situation does not apply to brominolysis as described below.
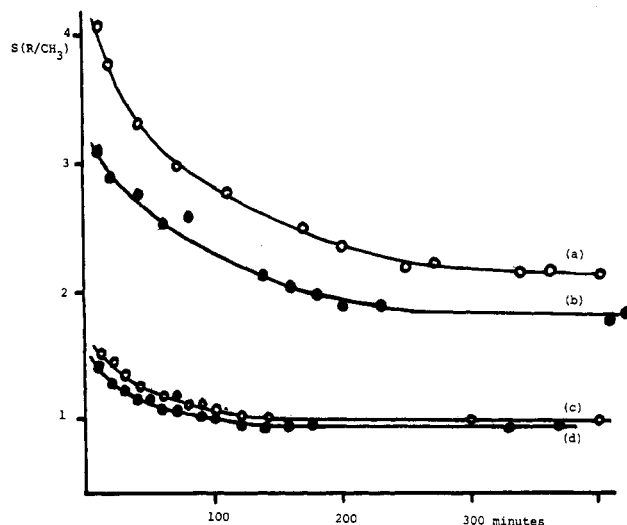

Figure 1. Variation of internal selectivity with time: (a) M = Ge, $[S]_0 = 0.06$, $[Br_2]_0 = 0.04$ M; (b) M = Ge, $[S]_0 = 0.075$, $[Br_2]_0 = 0.055$ M; (c) M = Si, $[S]_0 = 0.10$, $[Br_2]_0 = 0.10$ M; (d) M = Si, $[S]_0 = 0.15$, $[Br_2]_0 = 0.13$ M.

Brominolysis in CCl_4 solution gives the greatest proportion of $Sn-CH_2$ cleavage under "preparative" conditions (see Table I). Unfortunately, preliminary kinetic studies under first-order conditions show more complex behavior than found for the related results reported by Fuzukumi and Kochi.[10] There is evidence for charge-transfer complexation and its kinetic involvement, as well as both first- and second-order dependencies on bromine as found in many other studies of Br_2/CCl_4 reactions.[4,12,13] Not surprisingly kinetic studies by the NMR method with similar reactant concentrations (0.1–0.2 M) are also complex, and there is evidence of retardations by the products. Most significantly the extent of $Sn-CH_2$ and $Sn-CH_3$ cleavage varies quite markedly during the progress of these reactions as illustrated in Figure 1 for the cases of M = Si and Ge in $(CH_3)_3MCH_2Sn(CH_3)_3$. The values for $S(R/CH_3)$ for M = Si and Ge determined at completion of the reactions (see Table II) contain a contribution from the early part of the reaction which gives a high yield of $Sn-CH_2$ cleavage (P′). In the later, approximately second-order phase this process is less dominant. Throughout this second-order phase the ratios of the rates of product formation $d(P')/d(P)$ remains constant (see Figure 2a,b) and is 0.24 (±0.01) for M = Si corresponding to $S(R/CH_3) = 0.71$ (±0.05) and 0.31 (±0.07) for M = Ge corresponding to $S(R/CH_3) = 0.9$ (±0.3). After the initial period of the brominolysis of $(CH_3)_3SnCH_2Sn(CH_3)_3$ only $Sn-CH_2$ cleavage occurs and all the $Sn-CH_3$ cleavage product (P_{corr}) present at completion, corrected for further reaction (P → Q), has been formed in the first 10 min (see Figure 2c).

Modification of the entries in Table II for Br_2/CCl_4 has been made on the basis of the above identification of the "normal" reaction. Clearly a similar analysis for the reactions in other solvents would be informative, but this is only possible where the rates are slow enough for the NMR method to be applied in the early part of the reaction. It is evident that many compilations of internal selectivities may be seriously in error due to the occurrence of this behavior.

Protolysis. It is the generally held view that protolysis is an example of "simple" bimolecular electrophilic substitution in organometallics. Thus rates and internal se-

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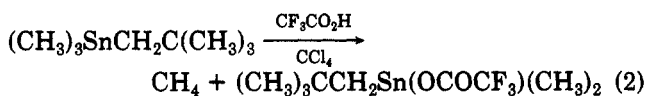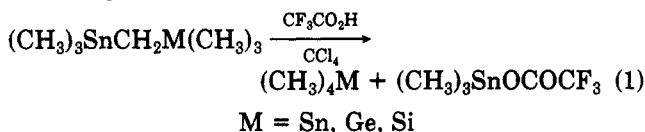(11) Boué, S.; Gielen, M.; Nasielski, J. *J. Organomet. Chem.* **1967**, *9*, 443.

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(13) Schmid, G. H.; Toyonaga, B. *J. Org. Chem.* **1984**, *49*, 761.
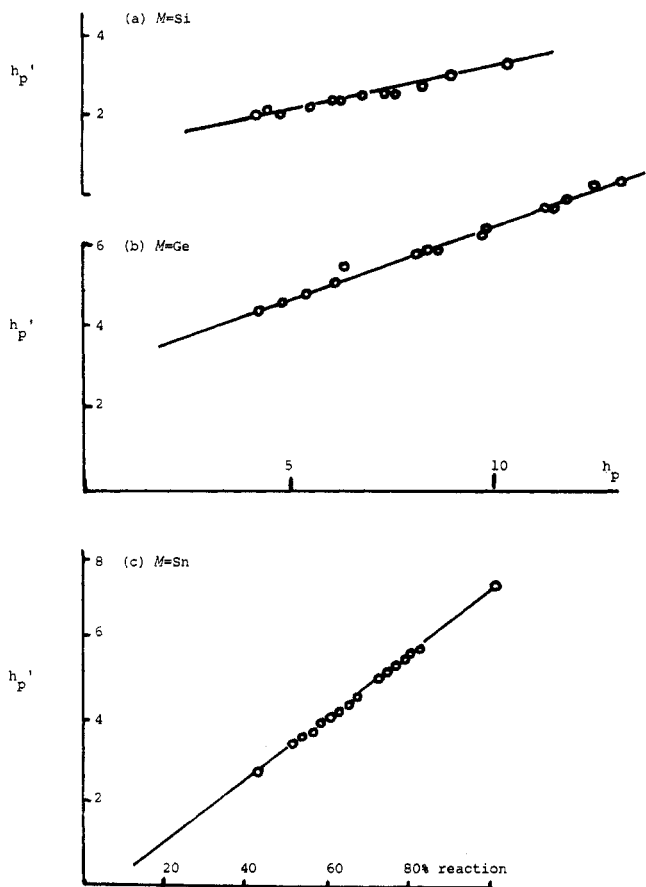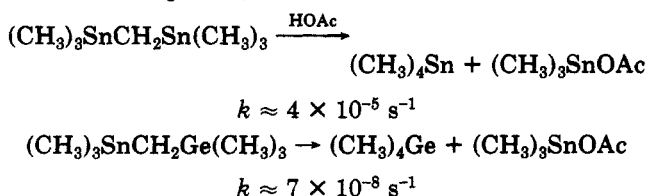
Figure 2. Comparison of yields (corrected peak heights, h) of Sn–CH$_2$ (P′) and Sn–CH$_3$ (P) products during reaction for brominolysis of (CH$_3$)$_3$MCH$_2$Sn(CH$_3$)$_3$ for (a) M = Si, [S]$_0$ = 0.13, and [Br$_2$]$_0$ = 0.12 M and (b) M = Ge, [S]$_0$ = 0.06, and [Br$_2$]$_0$ = 0.04 M and of h_p′ vs. extent of reaction for (c) M = Sn, [S]$_0$ = 0.036 and [Br$_2$]$_0$ = 0.024 M.

lectivities in such reactions should provide the norm with which other reactions may be compared. Trifluoroacetolysis of the substrates employed in the present studies is in all cases rapid and stoichiometrically simple. Exclusive Sn–CH$_2$ cleavage occurs for (CH$_3$)$_3$SnCH$_2$M(CH$_3$)$_3$ according to eq 1 for M = Sn, Ge, and Si but for the

$$(CH_3)_3SnCH_2M(CH_3)_3 \xrightarrow[CCl_4]{CF_3CO_2H}$$
$$(CH_3)_4M + (CH_3)_3SnOCOCF_3 \quad (1)$$

$$M = Sn, Ge, Si$$

$$(CH_3)_3SnCH_2C(CH_3)_3 \xrightarrow[CCl_4]{CF_3CO_2H}$$
$$CH_4 + (CH_3)_3CCH_2Sn(OCOCF_3)(CH_3)_2 \quad (2)$$

neopentyl derivative reaction occurs at Sn–CH$_3$ only (eq 2). Tetramethylstannane also reacts rapidly under these conditions (addition of aliquots of CF$_3$CO$_2$H to CCl$_4$ solutions of the substrate). However, since this species persists without observable further reaction during protolysis of the M = Sn substrate, then it is clearly uncompetitive and hence considerably less reactive.

Acetolysis of these substrates also occurs preferentially at the Sn–CH$_2$ bond, thus

$$(CH_3)_3SnCH_2Sn(CH_3)_3 \xrightarrow{HOAc}$$
$$(CH_3)_4Sn + (CH_3)_3SnOAc$$

$$k \approx 4 \times 10^{-5} \text{ s}^{-1}$$

$$(CH_3)_3SnCH_2Ge(CH_3)_3 \rightarrow (CH_3)_4Ge + (CH_3)_3SnOAc$$

$$k \approx 7 \times 10^{-8} \text{ s}^{-1}$$

but the reactions are quite slow and no acetolysis was detected after 2 months for M = Si and C nor for (CH$_3$)$_4$Sn. Dramatic activating effects are in evidence for the (CH$_3$)$_3$Ge group and especially the (CH$_3$)$_3$Sn group. Indeed the M = Sn substrate undergoes acetolysis faster than tetramethylplumbane (1.2 × 10^{-5} s^{-1}).[14] By inference from the trifluoroacetolysis results, the (CH$_3$)$_3$Si group also activates the Sn–CH$_2$ bond toward protolysis.

Organometallic Electrophiles. We have found differences between electrophiles such as (CH$_3$)$_3$PbX, (CH$_3$)$_3$SnX, and (CH$_3$)$_2$SnX$_2$ in methanol solution, which exclusively attack CH$_3$–Sn bond in hexamethyldistannane, on the one hand, and HgX$_2$ or CH$_3$HgX which seem to prefer to cleave the Sn–Sn bond. In the present context recent studies[2] have shown that (CH$_3$)$_2$SnCl$_2$ and SnCl$_4$ are suitable reagents for Sn–CH$_3$ cleavage in (CH$_3$)$_3$SnCH$_2$Sn(CH$_3$)$_3$. We find similar behavior for chlorotrimethylstannane, i.e., for M′ = Sn, thus

$$(CH_3)_3SnCH_2Sn(CH_3)_3 + (CH_3)_3M'Cl \rightarrow$$
$$(CH_3)_4M' + (CH_3)_3SnCH_2Sn(CH_3)_2Cl$$
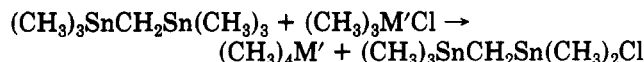
and for chlorotrimethylplumbane (M′ = Pb) although in the latter case the extent of reaction is limited to some 10–20% at equilibrium due to the greater reactivity of tetramethylplumbane toward the monochloro product.

However neither mercuric chloride nor methyl mercuric chloride show any evidence of Sn–CH$_2$ cleavage despite protolysis indicating this to be the activated site for electrophilic attack. Reactions all follow eq 3, and rate

$$(CH_3)_3MCH_2Sn(CH_3)_3 + RHgCl \rightarrow$$
$$(CH_3)_3MCH_2Sn(CH_3)_2Cl + CH_3HgR \quad (3)$$

$$M = Sn, Ge, Si, C; R = CH_3 \text{ or } Cl$$

measurements (by NMR method) give $3k$ = 1.3 × 10^{-3} M^{-1} s^{-1} (methanol, 28.5 °C) for M = Si with HgCl$_2$, cf. $4k$ = 1.55 M^{-1} s^{-1} for (CH$_3$)$_4$Sn (methanol, 25 °C),[15] and $3k$ = 5.1 × 10^{-5} M^{-1} s^{-1} (methanol, 28.5 °C) for M = Si with CH$_3$HgCl, cf. $4k$ = 1.8 × 10^{-4} M^{-1} s^{-1} for (CH$_3$)$_4$Sn and $3k$ = 3.5 × 10^{-5} M^{-1} s^{-1} for (CH$_3$)$_3$SnC(CH$_3$)$_3$ (methanol, 30 °C).[8b] It is thus clear that the Sn–CH$_2$ is not activated toward these "electrophiles" but rather that reaction occurs at the Sn–CH$_3$ site which, for the M = Si substrate at least, is substantially deactivated.

Conclusions

Our studies, which we must regard as incomplete, on the reactions of the substrates (CH$_3$)$_3$SnCH$_2$M(CH$_3$)$_3$ with a variety of "electrophiles" do not show a uniform behavior pattern. In protolysis, taken to be the simplest example of bimolecular electrophilic substitution, strong activation of the Sn–CH$_2$ in the order (CH$_3$)$_3$Sn >> (CH$_3$)$_3$Ge >> (CH$_3$)$_3$Si is observed to override any steric retardation although this looks to be important for M = C. Organometallic reagents on the other hand find the Sn–CH$_2$ bond much less reactive than the Sn–CH$_3$ bond and even here substantial retardation is found for M = Si. In neither iodinolysis nor in brominolysis is there such a clear-cut distinction between reaction sites nor, from preliminary kinetic studies, is there such a marked differentiation between the reactivities of the various substrates.

Experimental Section

General Comments. All preparative reactions were carried out under an atmosphere of purified nitrogen. Most solvents were

(14) Robinson, G. C. *J. Org. Chem.* **1963**, *28*, 843.
(15) Abraham, M. H.; Johnston, G. F. *J. Chem. Soc. A* **1970**, 193.

reagent grade materials that had been purified and dried by standard methods.[16] Chlorobenzene was A.R. grade, was further purified by distillation, and was stored in the dark. Carbon tetrachloride was AJAX "SPEC" grade.

^{1}H NMR spectra were generally recorded at 100 MHz on a JEOL PS-100 spectrometer in the CW mode. Some ^{1}H NMR spectra as well as ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded either on JEOL FX-100 (2.349 T) or Bruker CXP-300 (7.000 T) spectrometers in the FT mode. Full details of the NMR spectra are given elsewhere.[17]

Tetramethylstannane. This substrate was prepared by the method of Edgell and Ward[18] (stannic chloride and methylmagnesium iodide in di-n-butyl ether) in 81% yield with a boiling point of 77-79 °C (cf.[18] 76.6 °C) and freshly distilled before use.

(2,2-Dimethylpropyl)trimethylstannane. To 500 mL of anhydrous liquid ammonia condensed into a 1-L flange-topped flask under a nitrogen atmosphere and in a dry ice–acetone bath was added (16.25 g, 82 mmol) chlorotrimethylstannane[19] followed by sodium (3.75 g, 163 mmol) in finely divided pieces. After vigorous stirring for 1 h (12.0 g, 79 mmol) 1-bromo-2,2-dimethylpropane[20] was added dropwise. Following stirring for a further hour, the ammonia was evaporated under a strong stream of nitrogen. After workup with moist ether and water, the organic phase was titrated with an etherial solution of iodine and then washed with a solution of $Na_2S_2O_5$. Drying, removal of solvent, and fractional distillation under reduced pressure afforded 2.45 g (13% yield) of $(CH_3)_3SnCH_2C(CH_3)_3$ (bp 90-92 °C (98 mm)).

((Trimethylsilyl)methyl)trimethylstannane. This substrate was prepared by a procedure analogous to that employed for $(CH_3)_3SnCH_2C(CH_3)_3$. With use of chlorotrimethylstannane (10.5 g, 53 mmol) and Me_3SiCH_2Cl (5.5 g, 45 mmol) there resulted 5.4 g (48% yield) of $(CH_3)_3SnCH_2Si(CH_3)_3$ with a boiling point of 103-106 °C (121 mmHg), cf. 161 °C (140 mmHg).[22]

((Trimethylgermyl)methyl)trimethylstannane. Under a nitrogen atmosphere, the Grignard reagent derived from (C-$H_3)_3SnCH_2I$[23] (5.2 g, 17 mmol) and magnesium (0.45 g, 18.5 mmol)

in ether was prepared. After all the $(CH_3)_3SnCH_2I$ had been added, the reaction mixture was refluxed for 1 hour and then $(CH_3)_3GeBr$ (3.5 g, 17.7 mmol) in ether (5 mL) was added dropwise over a period of 45 min. After being refluxed for 1 h, the mixture was stirred overnight and then worked up using saturated NH_4Cl. Fractional distillation resulted in two principal fractions. The first fraction, collected at 74-78 °C (23 mmHg), was shown by multinuclear NMR and mass spectroscopic analysis to be the desired $(CH_3)_3SnCH_2Ge(CH_3)_3$ in 32% yield. The second fraction, with a boiling point range of 45-48 °C (1.5 mmHg) was similarly shown to be largely $(CH_3)_3SnCH_2CH_2Sn(CH_3)_3$. This latter product presumably arises from reaction of the Grignard reagent with $(CH_3)_3SnCH_2I$.

Bis(trimethylstannyl)methane. $(CH_3)_3SnCH_2Sn(CH_3)_3$ was prepared according to the method of Kaesz.[7] (Trimethylstannyl)sodium, prepared from chlorotrimethylstannane (14.3 g, 72 mmol) and sodium metal pieces (3.3 g, 144 mol) in liquid ammonia, was treated dropwise with dichloromethane (3.05 g, 36 mmol). Following the work-up procedure outlined for $(CH_3)_3$-$SnCH_2C(CH_3)_3$ above, 4.57 g (37% yield) of product was isolated having a boiling point of 114 °C (53 mm) (cf.[5,7] 58-60 °C (6 mm) and 199-201 °C (760 mm)).

Product Composition Studies. Reactions were carried out in 5-mm NMR tubes, wrapped in aluminum foil when not under examination, and were set up by adding a stock solution of the reagent to a known weight of the substrate. The composition of the reaction mixture at any time during reaction or at its completion was determined by peak height measurements in the ^{1}H NMR spectra. Details of the chemical shifts of the various sets of ^{1}H resonances of the substrates and their derivatives have been reported.[8,17] A sweep width of 270 Hz and a sweep rate of 2.2 Hz s^{-1} was generally used. Cyclohexane (in the stock solution of the reagent) was employed as a peak height reference in all spectra and the observed peak heights of other resonances in a particular sample were normalized to this reference. Corrections were then applied for (i) intensity missing from the observed resonance due to "satellites" arising from ^{13}C, ^{29}Si, or ^{117,119}Sn coupling, (ii) broadening, due to long range coupling,[17] and (iii) the number of protons contributing to a particular resonance. The various products were identified by multinuclear NMR spectroscopy and/or comparisons with the spectra of authentic compounds.

Registry No. $(CH_3)_3SnCH_2C(CH_3)_3$, 55204-72-3; $(CH_3)_3SnC$-$H_2Si(CH_3)_3$, 18297-50-2; $(CH_3)_3SnCH_2Ge(CH_3)_3$, 89748-43-6; $(CH_3)_3SnCH_2Sn(CH_3)_3$, 16812-43-4; Br_2, 7726-95-6; I_2, 7553-56-2; $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_3PbCl$, 1520-78-1; $HgCl_2$, 7487-94-7; $ClHgCH_3$, 115-09-3; CF_3CO_2H, 76-05-1; HOAc, 64-19-7; $BrCH_2$-$C(CH_3)_3$, 630-17-1; $(CH_3)_3SiCH_2Cl$, 2344-80-1; $(CH_3)_3SnCH_2I$, 23696-40-4; $(CH_3)_3GcBr$, 1066-37-1.

(16) Riddick, J. A.; Burger, W. B. "Techniques of Chemistry", 3rd ed.; Wiley-Interscience: 1970; Vol. II.

(17) Hawker, D. W.; Wells, P. R. *Org. Magn. Reson.* **1984**, *22*, 280.

(18) Edgell, W. F.; Ward, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 1169; **1955**, *77*, 6487.

(19) Formed in almost quantitative yield by 3 h of reflux of anhydrous $SnCl_4$ with 3 equiv and tetramethylstannane followed by distillation at 152-154 °C (760 mm).

(20) Prepared from the corresponding alcohol essentially as previously described in 67% yield with a boiling point of 105-106 °C (760 mm), cf. 104.8 °C (732 mm)).[21]

(21) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. S. *J. Am. Chem. Soc.* **1964**, *86*, 964.

(22) Schmidbauer, H. *Chem. Ber.* **1964**, *97*, 270.

(23) (Iodomethyl)trimethylstannane was prepared by a modification of the method described by Seyferth.[24] The product is very light sensitive.

(24) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1969**, *18*, 21. Seyferth, D. *J. Organomet. Chem.* **1971**, *30*, 151.