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PROTOLYSES OF $(CH_3)_3SnM(CH_3)_3$ (M = Sn, Ge, Si, C)

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Summary

Product and kinetic studies on the reactions of hydrogen chloride in methanol solution with the substrates $(CH_3)_3SnM(CH_3)_3$ (M = Sn; Ge and Si) show that both Sn–M and Sn–CH_3 cleavage reactions occur, at similar rates, and are followed by other reactions giving complex but explicable mixtures of products. Similar behaviour is observed for trifluoroacetolysis in carbon tetrachloride solution, and some intermediates are observable. Trifluoroacetolysis of $(CH_3)_3SnC(CH_3)_3$ results in exclusive Sn–CH_3 cleavage. The very slow apparent solvolysis in acetic acid solution is thought to involve reaction with dissolved oxygen.

Introduction

Results have been reported [1–5] for the reactions of a number of organometallic electrophiles in methanol with hexamethyldistannane, $(CH_3)_6Sn_2$, and with t-butyltrimethylstannane $(CH_3)_3SnC(CH_3)_3$, and rate comparisons made with tetramethylstannane, $(CH_3)_4Sn$. During studies on the related species trimethylsilyltrimethylstannane $(CH_3)_3SnSi(CH_3)_3$, and trimethylgermyltrimethylstannane, $(CH_3)_3SnGe(CH_3)_3$, described in the following paper [6], deviations were observed from the expected course of these reactions which could be attributed to reactions involving HCl generated in these systems. It thus became necessary to examine these disturbances in more detail so that appropriate allowances could be made. Furthermore comparative studies on this set of substrates for a markedly different type of electrophile, i.e. protolysis, are clearly of interest.

Shaw and Allred [7] have studied the reactions of trimethylgermyl- and trimethylsilyl-trimethylstannane with one, or somewhat less than one, equivalent of dry hydrogen chloride at 60°C in deuterated cyclohexane solution. For the former they report ^1H NMR evidence for the formation of $(CH_3)_3GeSn(CH_3)_2Cl$ (δ 0.48 and 0.57 ppm in ratio 3.0/2.0) and of small amounts of chlorotrimethylgermane and chlorotrimethylstannane, with mass spectral evidence for methane and hydrogen in the vapor over the sample. In contrast $(CH_3)_3SiSn(CH_3)_3$ is reported to yield

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chlorotrimethylsilane, chlorotrimethylstannane (by ^{1}H NMR), and an unidentified white precipitate of m.p. 108°C. The latter corresponds to dichlorodimethylstannane, m.p. 107°C, which has a low solubility in hydrocarbon solvents. It was also reported that $(CH_3)_3SiGe(CH_3)_3$ shows no indications of any reaction with hydrogen chloride at 70°C after 14 h. We have found similarly, and in common with many other workers, that hexamethyldigermane and hexamethyldisilane are quite stable towards acid.

The reaction of hexamethyldistannane with hydrogen chloride in methanol solution has been studied by Tagliavini, Belluco and Pilloni [8] who used solvolysis of acetyl chloride to generate the acid in situ. They report that the primary reaction gives hydrogen and chlorotrimethylstannane only, but that this reaction is accompanied by the chlorotrimethylstannane-catalysed decomposition of hexamethyldistannane to tetramethylstannane and yellow polymeric "dimethyltin". There is almost complete suppression of this second reaction when three equivalents of acetyl chloride are used.

Reactions of hexamethyldistannane with halogenated acetic acids, but not with acetic acid itself, have been reported by Birchall and Johnson [9] to give good yields of the $(CH_3)_4Sn_2X_2$ species, including the trifluoroacetoxy derivative.

Experimental

Materials

The methods of preparation, purification and storage of all the reagents and solvents employed in these studies have been previously described [5], with the exception of those given below.

Trimethylgermyl and trimethylsilyltrimethylstannane were prepared by the method of Schumann and Ronecker [10] with minor modifications. This method involves the reaction of trimethylstannyllithium (from chlorotrimethylstannane) in tetrahydrofuran with bromotrimethylgermane or chlorotrimethylsilane. The products obtained after distillation at reduced pressure, b.p. 83–86°C/80 mmHg and b.p. 78–81°C/90 mmHg respectively, were finally purified by preparative glc (Aerograph Autoprep 705; SE30 at 120°C; collection at −80°C).

Reactions with methanolic HCl

Typically 30–50 μl of 8.5 *M* aqueous hydrochloric acid was added to a methanol solution of the substrate of known concentration (ca. 0.2 *M*) and known volume (ca. 0.8 ml) containing cyclohexane (3 μl) as a reference in a capped NMR tube. The concentrations were corrected for the small volume change assuming no contraction or expansion. (N.B. The solvent is no longer anhydrous methanol, but contains some 2–4% v/v water). The ^{1}H NMR spectra were recorded before and after the addition of the acid and subsequently as reaction proceeded.

For kinetic studies involving an excess of hydrogen chloride, 150 μl of 8.8 *M* acid was added to 0.7 ml of ca. 0.05 *M* substrate, giving a solvent containing ca. 12% v/v water.

Competition experiments were carried out by adding a 5 μl portions of 8.8 *M* acid to a mixture of substrates in ca. 2/1 ratio such that the hydrogen chloride concentration did not exceed 2/3 of the lower substrate concentration.

Acetolysis reactions

Acetic acid, then the cyclohexane reference, were added to a pre-weighed NMR tube which was re-weighed at each stage then the substrate was added to produce a ca. 0.2 *M* solution. Reactions were so slow that the first ^{1}H NMR spectrum showed no reaction products. Reaction times of several days were required before significant product formation was observed.

Reactions with trifluoroacetic acid in carbon tetrachloride solution

Small aliquots (ca. 0.2 equivalents) of CF_3CO_2H were added to a solution of the substrate of known concentration (ca. 0.2 *M*) in CCl_4 containing cyclohexane as a reference, contained in an NMR tube, and the ^{1}H NMR spectra were recorded. Reactions were rapid and complete before the spectra were obtained. This procedure was repeated until most of the substrate had been consumed. (In the case of trimethylgermyltrimethylstannane the reaction was terminated at ca. 50% when product began to precipitate out).

Analysis of reaction mixtures

The composition of the reaction mixture at any time was determined from corrected peak height measurements of the various identified components, as previously described [5]. For kinetic studies the progress of the reaction was best followed by observation of the substrate resonances either as two separate measures or as their average. In the competition experiments, the complexity of the products meant that only the substrate resonances could be monitored.

Results

Reaction of HCl with $(CH_3)_3SiSn(CH_3)_3$

Figure 1 illustrates the ^{1}H NMR spectrum of the reaction mixture initially 0.19 *M* $(CH_3)_3SiSn(CH_3)_3$ and 0.50 *M* HCl in methanol after one day, and the observed resonances are indexed in Table 1.

The resonances of tetramethylstannane and hexamethyldisiloxane are coincident over a wide range of concentrations in methanol solution. At this stage in the reaction, however, no satellites arising from ^{117,119}Sn coupling are visible, so that the resonance labelled *J* must arise largely from the siloxane. There may be a small amount of tetramethylstannane present, and much later in the reaction very small satellites can, in fact, be seen.

From peak height measurements, with appropriate corrections, it can be calculated that 54% of the substrate has been consumed and the composition is:

$(CH_3)_3SnSi(CH_3)_3$	$8.7_6 \times 10^{-2}$ *M*	$\therefore 10.2_4 \times 10^{-2}$ *M* consumed
$(CH_3)_3SiCl$	$7.1_7 \times 10^{-2}$ *M*	Total Si products
$(CH_3)_6Si_2O$	$1.5_9 \times 10^{-2}$ *M*	$10.3_5 \times 10^{-2}$ *M*
$(CH_3)_3SnCl$	$4.9_4 \times 10^{-2}$ *M*	Total Sn products
$(CH_3)_2SnCl_2$	$5.2_0 \times 10^{-2}$ *M*	$10.1_4 \times 10^{-2}$ *M*
$(CH_3)_4Sn$	~ 0	

This corresponds to 49% reaction by path A and 51% by path B (see Scheme 1) assuming no loss of chlorotrimethylstannane or of dichlorodimethylstannane by reaction with the substrate. The former assumption is justified by the absence of

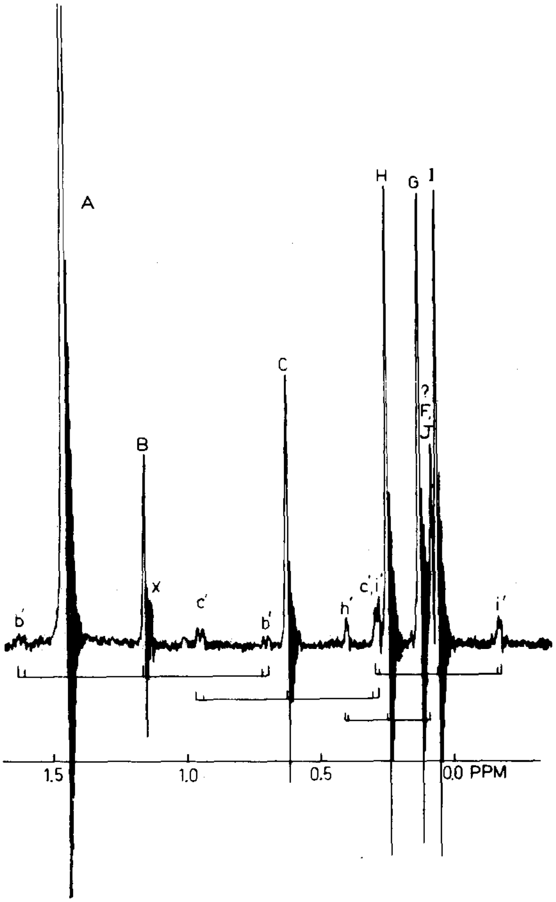


Fig. 1. ^{1}H NMR spectrum of reaction mixture: $(CH_3)_3SnSi(CH_3)_3$ (0.19 M)+HCl (0.50 M) after 1 day.

TABLE 1

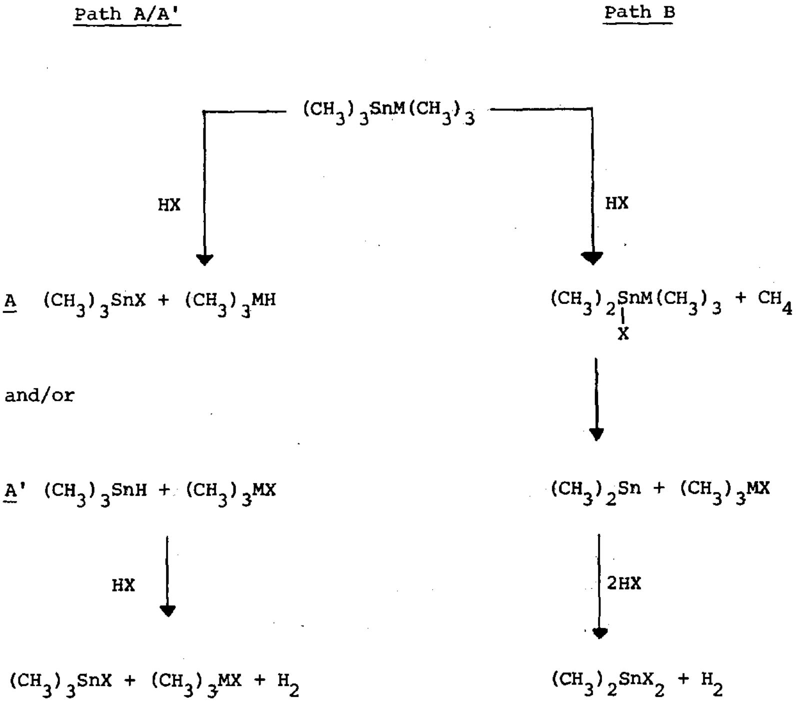
ASSIGNMENT OF RESONANCES IN FIG. 1, 2 AND 3 [a]

Peak	Chemical shift (ppm)	$J(^{119}Sn-H)$ (Hz)	Identity
A	1.45		cyclohexane
B	1.13	93	$(CH_3)_2SnCl_2$
C	0.60	68	$(CH_3)_3SnCl$
D	0.78	60 and 11	$(CH_3)_4Sn_2Cl_2$
E	0.21	49 and 16	$(CH_3)_6Sn_2$
F	0.06	55	$(CH_3)_4Sn$
G	(0.11)		$(CH_3)_3SiCl$ [b]
H	0.23	34	$(CH_3)_3SiSn(CH_3)_3$
I	0.04	47	$(CH_3)_3SnSi(CH_3)_3$
J	0.06		$(CH_3)_6Si_2O$
P	(0.69)		$(CH_3)_3GeCl$ [c]
R	0.33	27	$(CH_3)_3GeSn(CH_3)_3$
S	0.12	49	$(CH_3)_3SnGe(CH_3)_3$
T	0.21		$(CH_3)_3GeH$
X			spinning side-band of A

[a] The resonances labelled c' etc. are the satellite peaks arising from ^{117}Sn and $^{119}Sn-^1H$ coupling. [b] Variable average chemical shift of $(CH_3)_3SiCl/(CH_3)_3SiOCH_3$ equilibrium. [c] Variable average chemical shift of $(CH_3)_3GeCl/(CH_3)_3GeOCH_3$ equilibrium.

tetramethylstannane, but the latter is less secure because of the expected five-fold greater reactivity of $(CH_3)_2SnCl_2$ [5]. Indeed kinetic studies (see below) with hexamethyldistannane suggest that dichlorodimethylstannane may be some twenty times more reactive than hydrogen chloride. However dichlorodimethylstannane (0.5 *M* maximum) may be unable to compete with the excess of hydrogen chloride. (Even without allowance for the hydrolysis of chlorotrimethylsilane this concentration is estimated to remain at 0.25 *M* after 1 day). Any reaction of dichlorodimethylstannane will not affect its concentration since it is regenerated in a subsequent step (see Scheme 1), but chlorotrimethylstannane will be produced and the extent of reaction through path A will be slightly overestimated. (The small discrepancy between the total Si and Sn products could arise from an overestimation of $(CH_3)_6Si_2O$ due to the presence of $(CH_3)_4Sn$, but this discrepancy is barely outside the estimated uncertainty of ca. 1%).

SCHEME 1



$$(CH_3)_3SnM(CH_3)_3 + (CH_3)_3SnX \longrightarrow (CH_3)_4Sn + (CH_3)_2SnXM(CH_3)_3$$

$$(CH_3)_3SnM(CH_3)_3 + (CH_3)_2SnX_2 \longrightarrow (CH_3)_3SnX + (CH_3)_2SnXM(CH_3)_3$$

It is noteworthy that the resonance for dichlorodimethylstannane in this and the following reaction shows no indication of the line broadening observable in other reactions involving this species [5].

Allowing for an overall stoichiometry of 2.5 with respect to HCl, i.e. half-way between the values of 2 and 3 for paths A and B, respectively, an overall rate constant may be estimated as ca. $3 \times 10^{-5}\ M^{-1}\ s^{-1}$. Two kinetic runs were studied at stoichiometric ratios close to this value and evaluated by plots of $([S]+\delta)^{-1}$ vs. time, where $2\delta = \frac{1}{2.5}[HCl]_0 - [S]_0$. Several estimates of the path A/path B ratio were also obtained during these studies. The following results were obtained:

$[S]_0$	$[HCl]_0$	Second order rate constants *	Path A/Path B
$0.232\,M$	$0.604\,M$	$2.0_5 \times 10^{-5} M^{-1}s^{-1}$ (a) $1.8_5 \times 10^{-5}\ M^{-1}s^{-1}$ (b)	57/43
$0.266\,M$	$0.639\,M$	$1.6 \times 10^{-5} M^{-1}s^{-1}$(a) $1.4_5 \times 10^{-5} M^{-1}s^{-1}$ (b)	60/40

Reaction of HCl with $(CH_3)_3GeSn(CH_3)_3$

The ^1H NMR spectrum of the reaction mixture formed from $0.24\ M$ $(CH_3)_3GeSn(CH_3)_3$ and $0.29\ M$ HCl in methanol after 50 h is shown in Fig. 2, and indexed in Table 1. No resonances that could be assigned to $(CH_3)_3GeSn(CH_3)_2Cl$ were observed, but these may be obscured by resonances P and C.

The chemical shift of the resonance assigned to $(CH_3)_3GeCl$ varies slightly during the course of the reaction due to equilibrium 1, which is discussed more fully

$$(CH_3)_3GeCl + CH_3OH \rightleftharpoons (CH_3)_3GeOCH_3 + HCl \qquad (1)$$

elsewhere [11]. In the present system this solvolysis ensures that sufficient hydrogen chloride is provided for all the purposes that it is required.

Analysis of the reaction mixture by corrected peak height measurements shows that ca. 70% of the substrate has reacted and that the composition is:

$(CH_3)_3SnGe(CH_3)_3$	$0.06_5\ M$	$\therefore 0.17_5\ M$ consumed
"$(CH_3)_3GeCl$"	$0.13_5\ M$	Total Ge products $0.18_3\ M$
$(CH_3)_3GeH$	$0.04_8\ M$	
$(CH_3)_3SnCl$	$0.10_3\ M$	Total Sn products $0.17_1\ M$
$(CH_3)_2SnCl_2$	$0.04_6\ M$	
$(CH_3)_4Sn$	$0.02_2\ M$	
$(CH_3)_4Sn_2Cl_2$	trace	

The quantities of dichlorodimethylstannane and tetramethylstannane produced allow estimates to be made of the amount of substrate consumed by path B and by reaction with chlorotrimethylstannane. This leaves $0.13\ M$ substrate consumed by paths A and A′. Thus ca. 85% reaction has proceeded via paths A and A′, while path B accounts for ca. 15% reaction. It is of course again possible that some of the substrate has reacted with dichlorodimethylstannane, but assuming that this process occurs at twice the rate of the chlorotrimethylstannane reaction (a 5-fold greater reactivity is expected but the compound is at a $2\frac{1}{2}$-fold lower concentration) modifies the analysis to the extent that ca. 80% is by paths A and A′. The

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* By following variation in (a) the CH_3-Sn or (b) the CH_3-Si signals of the substrate.

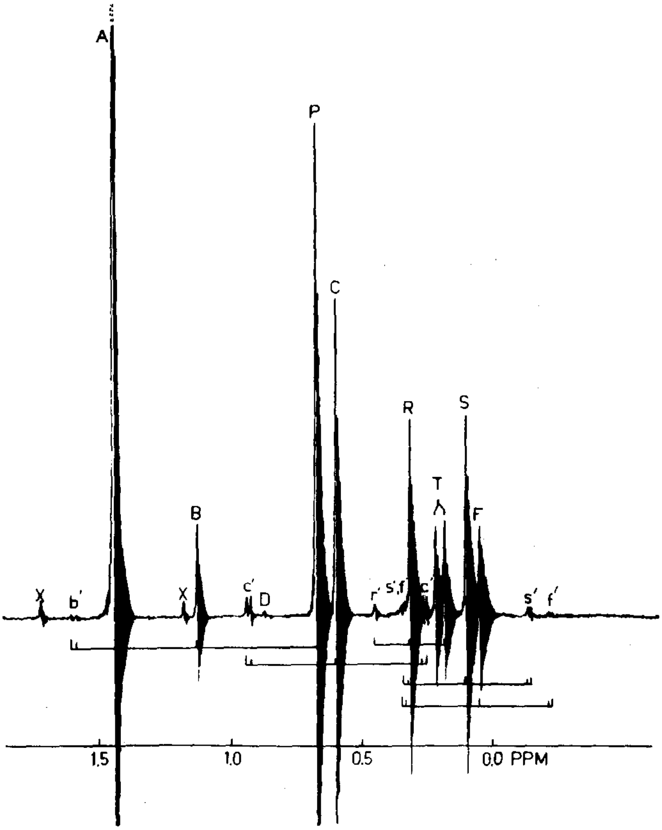


Fig. 2. ^{1}H NMR spectrum of reaction mixture: $(CH_3)_3SnGe(CH_3)_3$ (0.24 *M*)+HCl (0.29 *M*) after 50 h.

progressive analysis of this system is illustrated in Table 2, which shows that the concentration changes not employed in the analysis are correctly predicted, with the exception of the consumption of HCl. However hydrolysis of chlorotrimethylger-

TABLE 2

ANALYSIS OF REACTION PRODUCTS FROM $(CH_3)_3SnGe(CH_3)_3 + HCl$

	t 0	*t* 50 h	Change observed	a[a]	b	c	d	Total change calculated
HCl	0.29	0	−0.29	−0.04	−0.07	−0.05	−0.16	−0.32
$(CH_3)_3SnGe(CH_3)_3$	0.24	0.06_5	-0.17_5	−0.02	-0.02_5	−0.05	−0.08	-0.17_5
$(CH_3)_3SnCl$	0	0.10_5	$+0.10_5$	−0.02	.	+0.05	+0.08	+0.11
$(CH_3)_2SnCl_2$	0	0.04_5	$+0.04_5$	+0.02	$+0.02_5$	.	.	$+0.04_5$
$(CH_3)_4Sn_2Cl_2$	0	trace	+ trace	.	.	.	.	0
$(CH_3)_4Sn$	0	0.02	+0.02	+0.02	.	.	.	+0.02
"$(CH_3)_3GeCl$"	0	0.13_5	$+0.13_5$	+0.02	$+0.02_5$	.	+0.08	$+0.13_5$
$(CH_3)_3GeH$	0	0.05	+0.05	.		+0.05	.	+0.05

[a] Change in composition due to substrate reaction with (a) $(CH_3)_3SnCl$; (b) HCl by path B; (c) HCl by path A; (d) HCl by path A′.

mane to the extent of some 20% would provide the required additional reagent.

If trimethylgermane survives completely in this system, then the yield of this product compared with the total yield of Ge-products via paths A and A′ indicates that path A is responsible for ca. 35% of the Sn–Ge cleavage process. This is, of course, a minimum value.

Kinetic studies were carried out with a large excess of HCl over substrate (S) and the data evaluated by plots of ln[S] vs. time with [S] determined as the average from observation of the Sn-CH_3 and Ge-CH_3 signals to give the following results:

$[S]_0$	$[HCl]_0$	second order rate constant	Path A/Path B
0.054 *M*	1.52 *M*	$9.35 \times 10^{-6} M^{-1} s^{-1}$	34.5/65.5
0.061 *M*	1.52 *M*	$9.23 \times 10^{-6} M^{-1} s^{-1}$	34.5/65.6

Under the conditions of these kinetic studies only very small amounts of trimethylgermane are observed, presumably due to its consumption by reaction with excess acid. The solvent for these studies is substantially more aqueous than that for the analysis above.

Competition studies were carried out between $(CH_3)_3SiSn(CH_3)_3$ (I) and $(CH_3)_3GeSn(CH_3)_3$ (II) and a deficiency of HCl in ca. 1% aqueous methanol. Three experiments gave $k_I/k_{II} = 1.5(\pm 0.3)$, confirming the ratio $1.7 \times 10^{-5}/9.3 \times 10^{-6}$ obtained in the above kinetic investigations. Trimethylgermane was an observed product under these conditions.

Reaction of HCl with $(CH_3)_6Sn_2$

During the early stages of the reaction of hexamethyldistannane (0.20 *M*) with excess HCl (0.615 *M*) the only observable product is chlorotrimethylstannane, arising from reaction by path A alone, although the analyses of the system at 30 and 60 min (see Table 3) would be unlikely to reveal a small methyl group loss by path B nor a very low concentration of dichlorodimethylstannane. Further analyses of the system at 24 and 48 h are given in Table 3.

Allowance can be made with the data at 24 and 48 h for the reaction of the substrate with chlorotrimethylstannane which is the source of tetramethylstannane

TABLE 3

ANALYSES FOR SYSTEM WITH $[(CH_3)_6Sn_2]_0 = 0.215$ *M*; $[HCl]_0 = 0.615$ *M*

	30 min	60 min	24 h	48 h
$[(CH_3)_6Sn_2]_t$	0.20_0 *M*	0.17_9 *M*	0.09_8 *M*	0.03_2 *M*
$[(CH_3)_3SnCl]_t$	0.06_3	0.07_2	0.17_7	0.26_7
$[(CH_3)_2SnCl_2]_t$	.	.	0.03_7	0.08_0
$[(CH_3)_4Sn]_t$	.	.	0.01_7	0.01_9
Treatment by Path B				
$[(CH_3)_6Sn_2]$	0.0 [a]	0.0 [a]	0.02_2 [b]	0.06_1 [b]
Treatment by Path A				
$[(CH_3)_6Sn_2]$	0.01_5 [a]	0.03_6 [a]	0.07_9 [c]	0.10_3 [c]
Formed by Path A				
$[(CH_3)_3SnCl]$	0.03_5 [a]	0.07_2 [a]	0.15_6 [d]	0.20_6 [d]

[a] No allowance made for unobserved Path B products. [b] From $[(CH_3)_2SnCl_2]_t$ with allowance for other source of this product. [c] After allowance for Path B and reaction with $(CH_3)_3SnCl$. [d] After allowance for product via Path B.

and an equivalent amount of dichlorodimethylstannane. This yields measures of the extent of reaction proceeding by path B and hence estimates of path A. As Table 3 shows, there is good agreement between the chlorotrimethylstannane calculated to be so produced and twice the hexamethyldistannane estimated to be consumed by this path.

From the extent of reaction at 30 and 60 min approximate first order rate constants can be calculated. Assuming an essentially constant [HCl] ~ 0.58 M these give a second order rate constant of ca. 8×10^{-5} $M^{-1}s^{-1}$. The analyses for 24 and 48 h indicate ratios for path A/path B of 79/21 and 63/37, respectively. But kinetic studies under these conditions are difficult since the rate constants for $(CH_3)_6Sn_2$/$(CH_3)_2SnCl_2$ and /$(CH_3)_3SnCl$ are 4.8×10^{-4} and 1.0×10^{-4} $M^{-1}s^{-1}$ respectively [5].

A kinetic run with $[S]_0$ 0.51 M and $[HCl]_0$ 1.52 M in ca. 12% aqueous methanol gave a second order rate constant of $9.0_5 \times 10^{-5}$ $M^{-1}s^{-1}$ and the average of several estimates of the extent of reaction by path B was 18(±1)%, (i.e a ratio of 82/18). Competition between $(CH_3)_6Sn_2$ (III) and $(CH_3)_3SiSn(CH_3)_3$ (I) in ca. 1% aqueous methanol gave $k_{III}/k_I = 3.05 \pm 0.5$ indicating that $k_{III} \sim 5 \times 10^{-5}$ $M^{-1}s^{-1}$.

Addition of HCl to $(CH_3)_6Sn_2/(CH_3)_3SnCl$ system

In none of the above reactions was any precipitate (nor yellow colouration of the solution) due to "polymeric dimethyltin" observed although this is a characteristic feature of the hexamethyldistannane/chlorotrimethylstannane reaction and has been ascribed to reactions of the intermediate, dimethylstannylene [1,4,5]. Whenever dichlorodimethylstannane is observed in the present case its resonance is not broadened, in contrast to the situation when it undergoes rapid reversible reaction with dimethylstannylene [5]. Nevertheless dimethylstannylene is still postulated for the HCl reaction systems as an intermediate arising from dissociation of chloropentamethyldistannane and related species (path B). The key reaction in Scheme 1 is the rapid consumption of dimethylstannylene by reaction with HCl, and the subsequent reaction is of interest.

A mixture of $(CH_3)_6Sn_2$ (0.28 M) and $(CH_3)_3SnCl$ (0.56 M) in methanol was allowed to react for 70 h at which stage the catalysed decomposition of the hexamethyldistannane had proceeded to the stage shown by the ^1H NMR spectrum shown in Fig. 3a with the resonances labelled as in Table 1. The solution had assumed the faint yellow colour characteristic of the "dimethyl polymer" formed in this system but precipitation had not yet occurred. One drop of 8.5 M aqueous HCl was added and this immediately discharged the yellow colour. The ^1H NMR spectrum was otherwise unchanged at first except for the appearance of a sharp peak for dichlorodimethylstannane. Subsequently a little 1,2-dichlorotetramethyldistannane also appears and the spectrum after 10 min. is illustrated in Fig. 3b.

The analyses of the system are as follows:

	(a)	(b)
$(CH_3)_6Sn_2$	0.17 M	0.15 M 0.02 M decrease
$(CH_3)_3SnCl$	0.56 M	0.60 M 0.04 M increase
$(CH_3)_2SnCl_2$	0	0.12 M
$(CH_3)_4Sn$	0.11 M	0.11 M
$(CH_3)_4Sn_2Cl_2$	0	trace

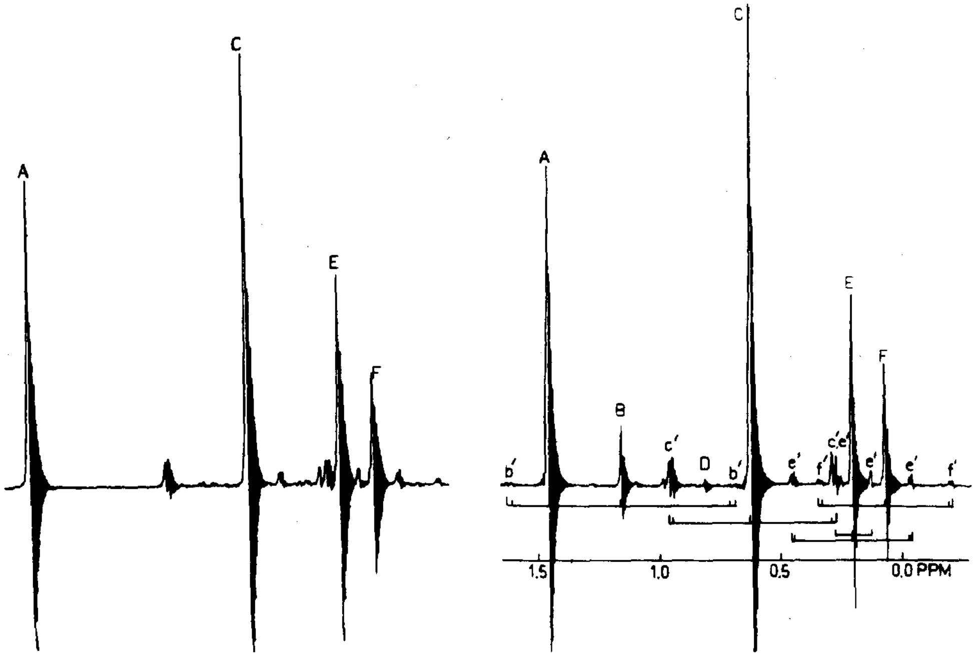


Fig. 3. ^{1}H NMR spectrum of reaction mixture: $(CH_3)_6Sn_2$ (0.28 *M*)+$(CH_3)_3SnCl$ (0.56 *M*) after 70 h (a) before (b) 10 min after addition of HCl.

The quantity of dichlorodimethylstannane produced corresponds almost exactly to material present in the system that would have arisen in the preceding reaction from dimethylstannylene and which would ultimately have appeared as precipitated "dimethyltin polymer".

During 10 min there is a small extent of reaction involving conversion of hexamethyldistannane into trimethylchlorostannane, presumably due to the action of the acid, but without detectable production of tetramethylstannane.

Acetolysis reactions

In all cases acetolysis is extremely slow and proceeds at essentially the same rate for $(CH_3)_6Sn_2$ (ca. 34% reaction in 21 days), $(CH_3)_3SnGe(CH_3)_3$ (ca. 29% reaction in 20 days), and $(CH_3)_3SnSi(CH_3)_3$ (ca. 39% reaction in 21 days), at which stage products, i.e. diacetoxydimethylstannane and tetramethylstannane, begin to appear arising from reactions of the substrates with acetoxytrimethylstannane. There is an initial 5–10% reaction in the first two days, then, as revealed by analyses at various times during the 15 to 30 days of reaction, there is a first order acetolysis, which for all three substrates is in the rate range $2\text{–}3 \times 10^{-7}$ s^{-1}. The acetolysis reaction in each case corresponds to:

$$(CH_3)_3SnM(CH_3)_3 \rightarrow (CH_3)_3SnOCOCH_3 + (CH_3)_3MOCOCH_3$$

Treatment of t-butyltrimethylstannane and of tetramethylstannane with glacial acetic acid failed to produce any observable reaction over an extended period of several weeks.

TABLE 4

^1H NMR SPECTRAL DATA FOR ACETOLYSES AND TRIFLUOROACETOLYSES [a]

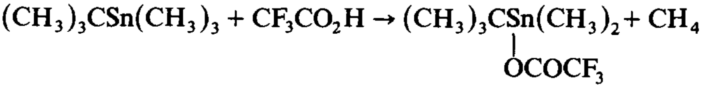
Species	Acetic acid solutions [b]	CCl_4 solutions [c]
F $(CH_3)_4Sn$	0.07 (53.5)	0.05 (52)
E $(CH_3)_6Sn_2$	0.22 (47.5 and 16)	0.20 (48 and 16)
$(CH_3)_3Sn$		0.01 (48)
$C(CH_3)_3$		1.06 (64)
I $(CH_3)_3Sn$	0.06 (45)	0.05 (45)
H $Si(CH_3)_3$	0.32 (28)	0.35 (27)
S $(CH_3)_3Sn$	0.12 (48.5)	0.11 (47)
R $Ge(CH_3)_3$	0.32 (26)	0.31 (24.5)
C $(CH_3)_3SnX$	0.53_5 (62)	0.69 (60)
B $(CH_3)_2SnX_2$	0.95 (?)	1.15 (?)
D $(CH_3)_4Sn_2X_2$	0.65(39 and 11.5)	0.88 (59 and 13)
Z $(CH_3)_3Sn$		0.42 (? and 27)
Y $Sn(CH_3)_2X$		0.74 (? and 6)
$(CH_3)_3C$		1.27 (89)
$Sn(CH_3)_2X$		0.63 (49)
O $(CH_3)_3Ge$		0.53 (39)
N $Sn(CH_3)_2X$		0.67 (42)
P $(CH_3)_3GeX$	0.57	0.72
G $(CH_3)_3SiX$	0.13	0.41
J $(CH_3)_6Si_2O$	0.07	0.10
CH_4		0.22

[a] Chemical shifts (ppm) relative to TMS and, in parentheses, $^1H-^{119}Sn$ coupling constants (Hz). [b] $X = OCOCH_3$. [c] $X = OCOCF_3$.

The characteristic ^1H chemical shifts for the various species observed in the acetolysis and trifluoroacetolysis studies are given in Table 4.

Reactions with trifluoroacetic acid in CCl_4 solution

The reaction of trifluoroacetic acid with t-butyltrimethylstannane in CCl_4 solution proceeds quite rapidly and generates a single set of products arising from:



$$(CH_3)_3CSn(CH_3)_3 + CF_3CO_2H \rightarrow (CH_3)_3C\underset{\displaystyle OCOCF_3}{\underset{|}{Sn}}(CH_3)_2 + CH_4$$

The organometallic product has ^{13}C NMR: δ -4.44 ($^1J(^{13}C-^{119,117}Sn)$ 297.3, 283.8 Hz), $Sn(CH_3)_2$; δ 28.85 ($^2J(^{13}C-^{119,117}Sn)$ ~ 0.0), $C(CH_3)_3$; δ 33.43 ($J(^{13}C-^{119,117}Sn)$ 473.6, 432.9 Hz), $C(CH_3)_3$; δ 115.20 ($^1J(^{13}C-^{19}F)$ 286.3 Hz), CF_3 and δ 161.05 ($^2J(^{13}C-^{19}F)$ 41.1 Hz), $C{=}O$. ^{119}Sn NMR δ -100.1 relative to $(CH_3)_3CSn(CH_3)_3$, i.e. δ -81.6 relative to $(CH_3)_4Sn$. (The ^1H NMR spectral details are given in Table 4).

A complex mixture of products is obtained from the other $(CH_3)_3SnM(CH_3)_3$ substrates and these are illustrated in Figs. 4, 5 and 6. Various analyses of these mixtures are given in Table 5. It is evident that both path A and path B products are

(Continued on p. 20)

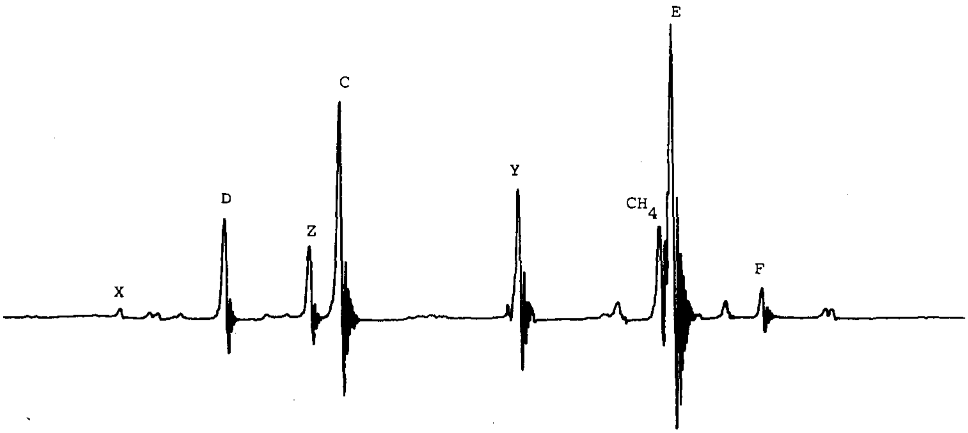


Fig. 4. ^1H NMR spectrum of $(CH_3)_6Sn_2 + CF_3CO_2H/CCl_4$ system No. 3.

TABLE 5

ANALYSES OF PRODUCTS OF SUCCESSIVE CF_3CO_2H ADDITIONS (IN CCl_4)

	1	2	3	4	5
(a) $(CH_3)_6Sn_2 = S$					
$([S]_0 - [S]/[S]_0$	0.14	0.39	0.66	0.90	
$[(CH_3)_3SnX]/[S]_0$	0.17	0.31	0.33	0.53	
$[(CH_3)_5Sn_2X]/[S]_0$	0.05	0.17	0.25	0.23	
$[(CH_3)_4Sn_2X]/[S]_0$	~ 0	0.04	0.18	0.37	
$[(CH_3)_4Sn]/[S]_0$	~ 0	< 0.01	0.04	0.08	
Corrected extent [a] of reaction	0.14	0.39	0.62	0.82	
Corrected path A [b]	(0.08_5)	0.15_5	0.18_5	0.30_5	
Corrected path B [c]	0.05	0.21	0.39	0.52	
% Path B[d]		64	71	69	(68 ± 3)
(b) $(CH_3)_3GeSn(CH_3)_3 = S$					
$([S]_0 - [S])/[S]_0$	0.03_5	0.09_5	0.17	0.35	0.61
$[(CH_3)_3SnX]/[S]_0$	0.03_5	0.06_5	0.07	0.09	0.12_5
$[(CH_3)_3GeX]/[S]_0$	0.04	0.06	0.06_5	0.09	0.19
$[(CH_3)_5SnGeX]/[S]_0$	~ 0.00_5	0.04	0.11	0.27	0.45
$[(CH_3)_40$	0	0	0.01	0.02_5	
Corrected path A [e]	(0.04)	0.06	0.07	0.09	0.17
Corrected path B [f]	0.00_5	0.04	0.11	0.26	0.42
% Path B [d]	–	(58)	78	83.5	76.5(80 ± 3)
(c) $(CH_3)_3SiSn(CH_3)_3 = S$					
$[(S]_0 - [S])/[S]_0$	0.08_5	0.32	0.55	0.79	
$[(CH_3)_3SnX]/[S]_0$	0.09	0.19_5	0.29	0.34_5	
$[(CH_3)_4Sn_2X_2]/[S]_0$	0	0.02_5	0.06	0.09_5	
$[(CH_3)_2SnX_2]/[S]_0$	0	0.02	0.03	0.03_5	
$[(CH_3)_3SiX]/[S]_0$	0.08	0.21?	?	?	
% Path B [d]		53	56	63	

[a] Corrected for reaction of substrate with $(CH_3)_3SnX$, i.e. $(CH_3)_4Sn$ yield. [b] Half the yield of $(CH_3)_3SnX$ after allowance for substrate/$(CH_3)_3SnX$ reaction. [c] Yield of $(CH_3)_5Sn_2X$ and $(CH_3)_4Sn_2X_2$ after allowance for substrate/$(CH_3)_3SnX$ reaction. [d] After substraction of products formed by aliquot 1. [e] Mean of yields of $(CH_3)_3GeX$ and $(CH_3)_3SnX$ with allowance for substrate/$(CH_3)_3SnX$ reaction. [f] Yield of $(CH_3)_5SnGeX$ after allowance for substrate/$(CH_3)_3SnX$ reaction.

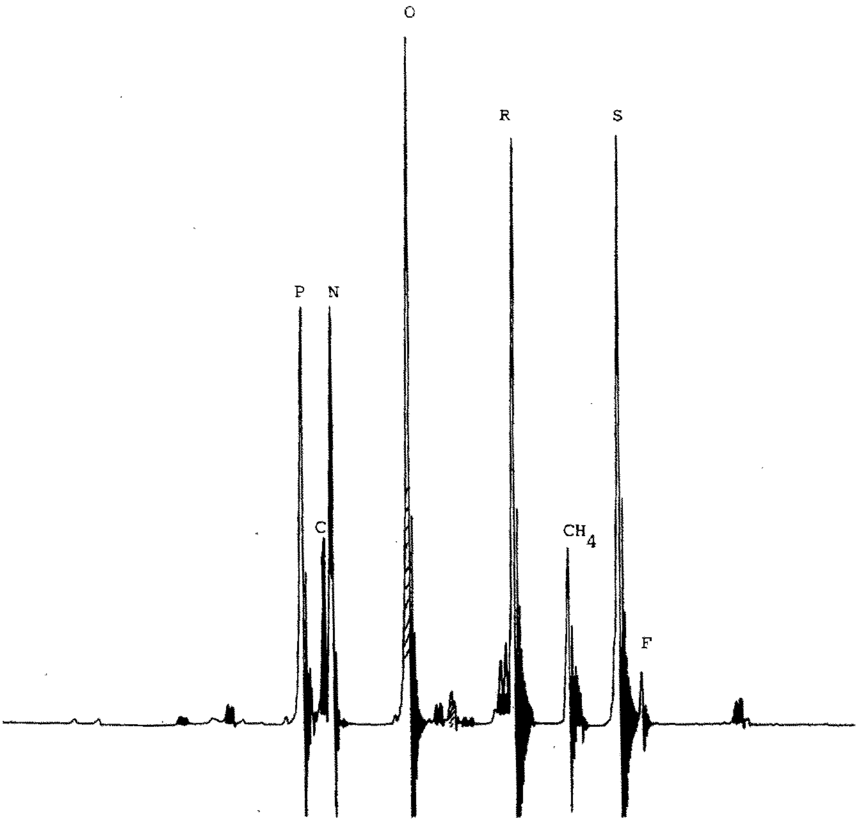


Fig. 5. ^{1}H NMR spectrum of $(CH_3)_3SnGe(CH_3)_3 + CF_3CO_2H/CCl_4$ system No. 5.

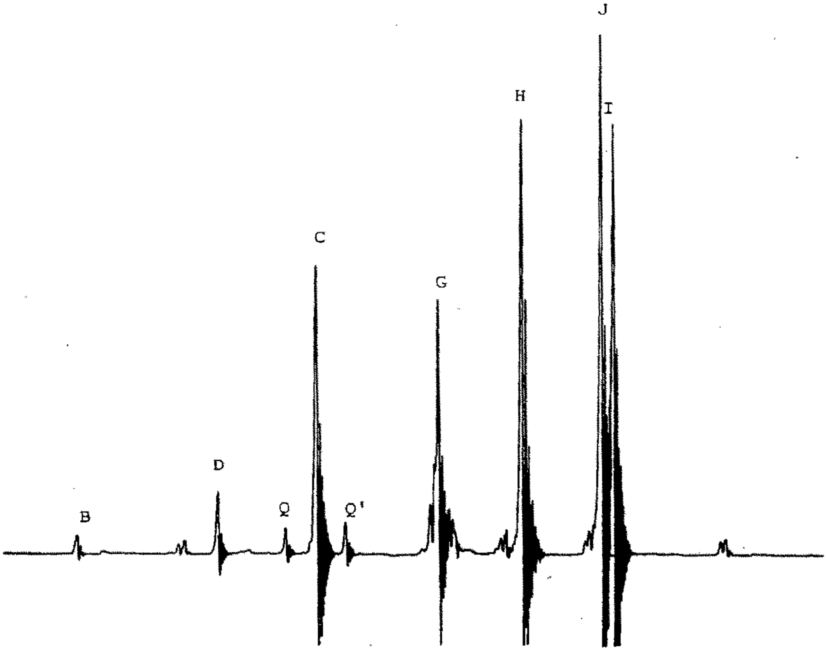


Fig. 6. ^{1}H NMR spectrum of $(CH_3)_3SnSi(CH_3)_3 + CF_3CO_2H/CCl_4$ system No. 3.

obtained, and that in the time between the additions of trifluoroacetic acid decompositions via dimethylstannylene and reactions between the substrate and $(CH_3)_3SnOCOCF_3$ may have occurred. In making allowances for these reactions, so that the extent of reaction by paths A and B may be estimated it is presumed that the only source of $(CH_3)_4Sn_2(OCOCF_3)_2$ when $(CH_3)_2Sn(OCOCF_3)_2$ is absent is the trifluoroacetolysis of $(CH_3)_5Sn_2OCOCF_3$, and that it arises otherwise solely from dimethylstannylene or its equivalent.

It is noteworthy that $(CH_3)_5Sn_2OCOCF_3$ survives sufficiently for it to be observed by ^1H NMR spectroscopy as a substantial component of the reaction mixture from $(CH_3)_6Sn_2$. We assign to this trifluoroacetate the two resonances labelled Y and Z in Fig. 4 at δ 0.42 and 0.74 in 3/2 ratio). It was completely decomposed, however, to $(CH_3)_3SnOCOCF_3$ and "polymeric dimethyltin" during attempts to recover it from this mixture, and did not survive long enough for satisfactory ^{13}C or ^{119}Sn NMR spectroscopy.

The major product of the trifluoroacetolysis of trimethylgermyltrimethylstannane is $(CH_3)_3GeSn(CH_3)_2OCOCF_3$, identified by its ^1H NMR spectrum (Fig. 5 and Table 5), and this is accompanied by small amounts of products from the various other reactions. Beyond the stage shown as item no. 5 (60% reaction), material begins to crystallise from the solution. This is composed mainly of the monotrifluoroacetoxy derivative, but is decomposed by attempts at further purification.

In the case of trimethylsilyltrimethylstannane there are several small resonances observed (Q and Q′ in Fig. 6) in addition to those identified, measured and listed in Table 5. The anticipated product of path B could not be identified, but the overall composition data suggests ca. 40% of the reaction may have followed this route. While we presume this product to have decomposed via dimethylstannylene, the analyses of the system show that there are substantial amounts of silicon and tin not accounted for by the identified species. In particular, the complexity in the region of the $(CH_3)_3SiOCOCF_3$ resonance (see Fig. 6) indicates the presence of other unknown species, and prevents a proper analysis for $(CH_3)_3Si$ derivatives.

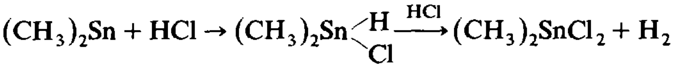
Discussion

There are evidently two sites for attack by HCl on $(CH_3)_3SnM(CH_3)_3$, namely the $Sn-CH_3$ and the Sn–M bonds, and the difference in reactivities is not large. The case of M = C is, of course, an extreme one, involving Sn–C bond cleavage at both sites, and with a large number of electrophiles exclusive $Sn-CH_3$ reaction is reported [11].

A generalized scheme for the reactions in these systems can be suggested (Scheme 1) which involves two primary processes. In path A the Sn–M bond is broken, to yield $(CH_3)_3SnCl$, presumably by electrophilic attack at M expelling the good trimethylstannyl leaving group, probably with nucleophilic assistance. Electrophilic attack at C breaks a CH_3-Sn bond in path B. An additional path (A′) could be postulated, yielding $(CH_3)_3SnH$ and $(CH_3)_3MCl$, but these would ultimately yield the same products as path A due to acidolysis of the hydride, and this would make paths A and A′ indistinguishable. It is only in the case of the substrate with M = Ge that some of the hydride product survives, because it is "quite remarkably stable to mineral acids in contrast to both organo-silanes and -stannanes" [12]. Nevertheless this result serves to demonstrate that at least some reaction follows path A in one case, and makes path A′ redundant. Moreover, since trimethylgermane is only observed in systems where the acid concentration is low, it is most likely that path A represents the total Sn–Ge cleavage process in this case, even though we have chosen to analyse the data in terms of both paths A and A′. Probably it is the presence of a suitable leaving group which makes the $(CH_3)_3SnM(CH_3)_3$ substrates reactive, whereas $(CH_3)_3GeSi(CH_3)_3$, $(CH_3)_6Ge_2$ and $(CH_3)_6Si_2$ are inert. An additional path (B′) in which methyl groups are removed from Ge or Si can be rejected on the grounds of insufficient reactivity.

Gaseous products are formed in these reactions, but were not observed in the NMR spectra. Hydrogen is anticipated to show up at δ 4.2 ppm but this spectral region is obscured by the solvent. Methane at δ 0.16 ppm might well be observable in the spectra, but Levi [13] reports that at 25°C one atmosphere pressure of methane over methanol only gives a mole fraction of 7.1×10^{-4} in solution, i.e. 1.5×10^{-2} *M*. This would give a signal indistinguishable from the background noise in the spectra shown in Fig. 1 and 2. However methane is clearly identified in the products of trifluoroacetolysis.

The first intermediate formed in path B, $(CH_3)_3MSn(CH_3)_2Cl$, was not observed in our experiments, although Shaw and Allred [7] report its presence for M = Ge and we have observed the same species in related reactions of $(CH_3)_3GeSn(CH_3)_3$ [6]. We consider that such intermediates readily dissociate to yield dimethylstannylene, as is the case for the elusive $(CH_3)_5Sn_2Cl$, and that the reverse insertion reaction is prevented by rapid reaction of dimethylstannylene with hydrogen chloride, possibly by the sequence 2.



$$(CH_3)_2Sn + HCl \rightarrow (CH_3)_2Sn\begin{matrix} H \\ Cl \end{matrix} \xrightarrow{HCl} (CH_3)_2SnCl_2 + H_2 \qquad (2)$$

Our evidence for this comes from the effect of adding HCl to the $(CH_3)_6Sn_2 + (CH_3)_3SnCl$ system. Chlorotrimethylstannane catalyses the decomposition of hexamethyldistannane to tetramethylstannane and yellow polymeric "dimethyltin". We have established that this polymer is formed by successive insertions of dimethylstannylene into Sn–Cl bonds [4], and further that, despite dimethylstannylene itself being unobservable, in the $(CH_3)_6Sn_2 + (CH_3)_2SnCl_2$ system the prototype insertion is evident [5] from the line broadening of the ^{1}H NMR resonances of dimethyldichlorostannane and 1,2-dichlorotetramethyldistannane caused by reaction 3.

$$(CH_3)_2SnCl_2 + (CH_3)_2Sn \rightleftharpoons (CH_3)_4Sn_2Cl_2 \qquad (3)$$

The immediate result of the HCl addition is the formation of a quantity of dichlorodimethylstannane equivalent to the tetramethylstannane already produced, and hence derived from all the products of dimethylstannylene currently in the system. The equilibria involving these insertion products are rapidly shifted as dimethylstannylene is removed. (Whenever there are dimethylstannylene precursors present with dichlorodimethylstannane reaction 3 takes place, and line broadening is observed). However in the presence of HCl the dimethylstannylene concentration is reduced, so that reaction 3 is no longer fast enough, and in the present series of experiments the dichlorodimethylstannane resonance was always sharp.

Our estimates of the reactivity of these substrates towards hydrogen chloride are somewhat imprecise due to the complexities of the systems, but suggest that for

M = Sn, Ge and Si they do not differ from one another by more than a factor of 10. Attack via path A is faster in general than attack via path B, as judged by the statistically corrected rate constants given in Table 6. The rate constants for Sn–CH_3 cleavage seem to be essentially the same for all three substrates, but Sn–Ge cleavage appears to be significantly slower than Sn–Sn or Sn–Si cleavage.

Although comparative rate data have been obtained for the HCl reactions, our principal aim was simply to identify the possible complications arising in reactions where $(CH_3)_3GeCl$ and $(CH_3)_3SiCl$ were produced and would be solvolysed. These complications arise in an essentially water-free solution rather than the partially aqueous media of the present studies. It may be noted that the "anomalously" high path A/path B ratio for $(CH_3)_3GeSn(CH_3)_3$ in the least aqueous system accords well with our interpretation of this as a side reaction in other cases [6].

The reactions of these substrates with acetic acid are extremely slow and hence very sensitive to trace reagents and catalytic impurities. While the exclusive Sn–M cleavage observed and the absence of Sn–CH_3 cleavage for related substrates might seem to be appropriate to a highly discriminating reagent, the general similarity of the observed rates argues against this view. The kinetic studies suggest that there is an initial somewhat faster reaction before the first order acetolysis sets in. It is quite likely that the initial phase involves reaction with dissolved oxygen, and that the subsequent measured rate is that of oxygen dissolution from the vapour space above the sample.

The trifluoroacetolysis studies were undertaken mainly in the hope that there might be identifiable intermediates. This is certainly the case for M = Ge, and $(CH_3)_3GeSn(CH_3)_2OCOCF_3$ is the dominant reaction product, but we have yet to devise a satisfactory method for its isolation. The corresponding species for M = Sn appears as a low concentration intermediate, but the corresponding M = Si product could not be identified, although it may be present in small amounts.

The extent to which paths A and B are followed in trifluoroacetolysis are given in Table 5 and consistent results could only be obtained by comparing substrate loss and product formation after the first addition had been made. As in the case of acetolysis this first stage gives considerable Sn–M cleavage and thus appears to contain at least some "clean-up" reaction, possibly involving dissolved oxygen although very much more rapid than in acetolysis. Thereafter $(CH_3)_6Sn_2$ reacts with 68(±3)% Sn–CH_3 cleavage, and a second cleavage of this type will give a substantial yield of $(CH_3)_4Sn_2(OCOCF_3)_2$ under conditions of excess of acid as observed by Birchall and Johnson [9]. A second cleavage for $(CH_3)_3GeSn(CH_3)_2OCOCF_3$ will be quite slow, and this product could also be obtained in good yield since path B

TABLE 6

STATISTICALLY CORRECTED RATE CONSTANTS FOR HCl REACTIONS

	A. Sn–M cleavage [a]	B. Sn–CH_3 cleavage [a]
$(CH_3)_3SiSn(CH_3)_3$	a. $1.0(\pm.1)\times10^{-5}\ M^{-1}s^{-1}$	a. $2.4(\pm.4)\times10^{-6}\ M^{-1}s^{-1}$
$(CH_3)_3GeSn(CH_3)_3$	b. $3.2(\pm.1)\times10^{-6}\ M^{-1}s^{-1}$	b. $2.0(\pm.1)\times10^{-6}\ M^{-1}s^{-1}$
$(CH_3)_6Sn_2$	a. $2.4(\pm.5)\times10^{-5}\ M^{-1}s^{-1}$ b. $3.7(\pm.4)\times10^{-5}\ M^{-1}s^{-1}$	a. $3.2(\pm.9)\times10^{-6}\ M^{-1}s^{-1}$ b. $2.7(\pm.3)\times10^{-6}\ M^{-1}s^{-1}$

[a] (a) Solvent ca. 5% aq. methanol, (b) Solvent ca. 12% aq. methanol.

constitutes 80(± 3)% of the overall reaction. In contrast, we estimate from its observable decomposition products that path B, yielding $(CH_3)_3SiSn(CH_3)_2OC$-OCF_3, proceeds to an extent of only some 30%.

Acknowledgements

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