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Articles

Oxidation of Organotins (R_4Sn, $RSnMe_3$, and R_3SnSnR_3) by the Thianthrene Cation Radical

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Reactions of thianthrene cation radical perchlorate ($\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$) with R_4Sn, R = methyl (Me), ethyl (Et), *n*-butyl (Bu), phenyl (Ph), and vinyl, in acetonitrile took place cleanly in the stoichiometric ratio $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-/\mathrm{R_4Sn}$ 2:1. Oxidative cleavage of R_4Sn occurred into R_3Sn^{3+}, that was assayed as R_3SnCl, and the radical $R^\bullet$. The latter was primarily trapped as the 5-R-thianthreniumyl perchlorate (**1a–e**), although abstraction of hydrogen atom from the solvent was significant in the cases of phenyl and vinyl radicals. Reactions of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ with $RSnMe_3$, R = allyl, vinyl, Ph, Et, isopropyl (*i*-Pr), and *tert*-butyl (*t*-Bu), occurred with the same stoichiometry. Exclusive loss of the *i*-Pr, *t*-Bu, and allyl groups occurred. The allyl radical was trapped by $\mathrm{Th}^{\bullet+}$ as 5-allylthianthreniumyl perchlorate (**1f**). The *i*-$\mathrm{Pr}^\bullet$ radicals were mostly and the *t*-$\mathrm{Bu}^\bullet$ completely oxidized by $\mathrm{Th}^{\bullet+}$ to the respective cations. Some *i*-$\mathrm{Pr}^\bullet$ were trapped by $\mathrm{Th}^{\bullet+}$ as ring-substituted thianthrenes. Loss of vinyl, phenyl, and ethyl radicals was competitive with loss of methyl radical from the corresponding $\mathrm{RSnMe_3}^{\bullet+}$, and ratios (R/Me) of loss were measured from the composition of the products that were formed. From reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ with R_6Sn_2 (R = Me and Ph) R_3Sn^+ was formed exclusively; that is, the R_6Sn_2 underwent two-electron oxidation.

Recently, we reported the reaction of symmetrical and unsymmetrical dialkylmercurials (R_2Hg and RHgMe) with thianthrene cation radical perchlorate ($\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$).[3] It was shown, particularly with the use of RHgMe, that reaction begins with single-electron transfer (SET). Thereby, an organometal cation radical (either $\mathrm{R_2Hg}^{\bullet+}$ or $\mathrm{RHgMe}^{\bullet+}$) is formed fleetingly, decomposing into fragments, for example RHg^+ and $R^\bullet$, from which the final products are derived.

We report now an analogous study on the reaction of tetrasubstituted tins, R_4Sn, in which R = methyl (Me), ethyl (Et), *n*-butyl (Bu), phenyl (Ph), and vinyl, and a series of trimethyltins, $RSnMe_3$, in which R = allyl, vinyl, Ph, Et, isopropyl (*i*-Pr), and *tert*-butyl (*t*-Bu). The objective of the study was again to find if reaction would be initiated by SET oxidation or by electrophilic cleavage of a carbon–tin bond. The basis for the distinction between the two pathways has been established by Kochi and coworkers[4-7] with selectivities in departure of groups from organometals in both inner- and outersphere electron-transfer reactions. For example, among unsymmetrical ethylmethyltins the selectivity Et/Me was about 11 for innersphere and about 26 for outersphere oxidations. In contrast, the selectivity Et/Me for electrophilic reactions with, for example, ethylmethylleads ranged from 0.018 to 0.11. Thus, the preferential loss of the group that is both larger and better able to stabilize radical character was diagnostic of an SET initiation. This characteristic was seen with even greater emphasis in reactions of, for example *i*-$PrSnMe_3$ and *t*-$BuSnMe_3$ with tris(1,10-phenanthroline)iron(III) perchlorate $\mathrm{Fe(phen)_3(ClO_4^-)_3}$, when exclusive loss of the *i*-Pr and *t*-Bu groups occurred.

We set out first to establish the broader nature of the reactions with $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ by working with the series R_4Sn, shown above. Next we turned to the series of $RSnMe_3$. In that series we anticipated, if SET were operative, the exclusive loss of the group R = allyl, *i*-Pr, and *t*-Bu, and possible competitive losses of Me and R groups when R = Et, Ph, and vinyl. Based on our experiences in reactions of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ with the diorganomercurials[3] and Grignard reagents,[8] it was further anticipated that, depending on its structure, the radical $R^\bullet$ would either add to or be oxidized by $\mathrm{Th}^{\bullet+}$.

Last, in order to probe the reactivity of $R_3Sn^\bullet$, reactions of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ with $Ph_3SnSnPh_3$ and $Me_3SnSnMe_3$ were studied.

Results

Reactions of R_4Sn with $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$. Reactions with Me_4Sn, Et_4Sn, and Bu_4Sn took place rapidly on dropwise addition of the organotin by microsyringe to a solution/suspension of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ in acetonitrile. The additions were, in effect, titrations until the purple/pink color of the $\mathrm{Th}^{\bullet+}$ disappeared. Reactions were complete at a ratio of $\mathrm{Th}^{\bullet+}/\mathrm{R_4Sn}$ of 2:1. Reactions with Ph_4Sn and $\mathrm{(vinyl)_4Sn}$ were slower, and therefore a mixture of the reactants in the 2:1 ratio was stirred until the color of $\mathrm{Th}^{\bullet+}$ had faded. Each reaction took place cleanly according to eq 1. That

$$\mathrm{R_4Sn + Th^{\bullet+} \rightarrow R_3Sn^+ + Th + R^\bullet} \qquad (1)$$

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[3] Lochynski, S.; Shine, H. J.; Soroka, M.; Venkatachalam, T. K. *J. Org. Chem.* **1990**, *55*, 2702.

[4] Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

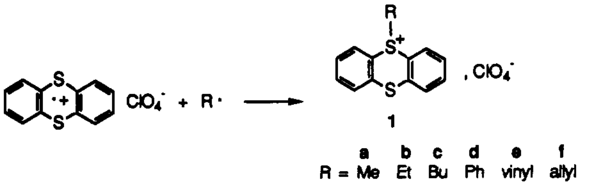
[5] Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

[6] Rollick, W. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.

[7] Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

[8] Boduszek, B.; Shine, H. J.; Venkatachalam, T. K. *J. Org. Chem.* **1989**, *54*, 1616.

0022-3263/91/1956-0914$02.50/0



1

(2)

(3)

$$R^{\bullet} + Th^{\bullet+} \rightarrow R^{+} + Th \quad (4)$$

$$R^{+} + CH_3CN \rightarrow \xrightarrow{H_2O} RNHCOCH_3 \quad (5)$$

is, according to that equation, 75% of the R groups in R_4Sn should appear as R_3Sn^+. This was found to be essentially the case, in that the R_3Sn^+, which was trapped in workup and assayed as R_3SnCl, was obtained in yields of 72.4–74.3% (Table I).

The fate of radical $R^{\bullet}$ was primarily to be trapped by $Th^{\bullet+}$. For the greater part this led to the formation and isolation of 5-R-thianthreniumyl perchlorates (**1a**–**e**), eq 2. That is, the liberated $R^{\bullet}$ was trapped as **1** to the extents of 86.8 and 86% for R = Me and vinyl, and of 61.2, 68.0, and 69.2% for R = Bu, Et, and Ph. Because $Th^{\bullet+}$ is a highly delocalized radical ion, trapping of $R^{\bullet}$ can occur at ring positions (eq 3) as well as at one of the sulfur atoms. This was seen in some cases in the formation of 1- and 2-substituted thianthrenes (1- and 2-RTh) and some disubstituted thianthrenes (R_2Th). This led to the total trapping of $R^{\bullet}$ by $Th^{\bullet+}$ to the extents of 89, 88, and 77% for R = Me, Et, and Bu. As described earlier,[3,8] the assignments of 1-RTh and 2-RTh were made on the basis of relative yields (Table I) and the distribution of spin densities in $Th^{\bullet+}$. The way of forming R_2Th has been set out earlier, too.[3] Significant amounts of RH (benzene, ethene) were obtained from R = Ph and vinyl, and small amounts of alkene from R = Et and Bu. Oxidation of $R^{\bullet}$ to R^+ by $Th^{\bullet+}$ and trapping of R^+ by solvent (eqs 4 and 5) were detected only in one case (R = Bu). An accounting of all reactant units ($Th^{\bullet+}$, R, and Sn) is given in Table III.

Table I lists MeCl, EtCl, and BuCl. These, however, were not primary products, but were formed in workup by reaction of the corresponding **1** with added chloride ion. They cannot be considered as primary products for in that case the total amount of group R in products would exceed the amount available in the R_4Sn. Each **1** was isolated in a separate workup procedure, and its yield, listed in Table I, corresponds approximately with the amount of RCl that was assayed.

Reactions of $RSnMe_3$ with $Th^{\bullet+}ClO_4^-$. Each member of the series $RSnMe_3$ was prepared by reaction of commercial Me_3SnCl with a Grignard reagent, RMgCl, or RMgBr. The Me_3SnCl was found by GC and GC–MS to contain an impurity, Me_2SnCl_2, and this led in the Grignard reaction in two cases (R = *i*-Pr and *t*-Bu) to the formation of some R_2SnMe_2 that we failed to remove from the $RSnMe_3$ by distillation. The presence of R_2SnMe_2 in the $RSnMe_3$ has a bearing (see later) on the assessment of group cleavages from $RSnMe_3$, as measured by the formation of Me_3SnCl and RMe_2SnCl. In Table II, therefore, which lists the amounts of reactant $RSnMe_3$, the effective amounts of *t*-$BuSnMe_3$ (run 7) and *i*-$PrSnMe_3$ (run 8) are listed in parentheses.

Reactions of $RSnMe_3$ (R = *i*-Pr, *t*-Bu, and allyl) gave quantitative loss of the R group, as measured by the amount of Me_3Sn^+ that was formed (eqs 6 and 7) and trapped in workup as Me_3SnCl. Among these three cases,

$$RSnMe_3 + Th^{\bullet+} \rightarrow RSnMe_3^{\bullet+} + Th \quad (6)$$

$$RSnMe_3^{\bullet+} \rightarrow R^{\bullet} + Me_3Sn^{+} \quad (7)$$

$$RSnMe_3^{\bullet+} \rightarrow Me^{\bullet} + Me_2RSn^{+} \quad (8)$$

only in that of R = allyl was the $R^{\bullet}$ radical trapped as a sulfonium salt (i.e., **1f**), and to the extent of nearly 64% of the available allyl radicals. However, 16% of the isopropyl radicals from *i*-$PrSnMe_3$ (and *i*-Pr_2SnMe_2) was trapped by $Th^{\bullet+}$ in the form of 1- and 2-RTh and R_2Th. No evidence was found for the formation of either 5-isopropyl- or 5-*tert*-butylthiantheniumyl perchlorate.

Only 86% of $PhSnMe_3$, 74% of vinyl$SnMe_3$ and 90% of $EtSnMe_3$ was converted into Me_3Sn^+. Loss of a methyl group from these unsymmetrical compounds (eq 8) also occurred, as shown not only by the formation of RMe_2SnCl, but also by that of the sulfonium salt, **1a**. Consequently, two sulfonium salts were obtained in each case: **1a** and **1d** from $PhSnMe_3$, **1a** and **1e** from vinyl$SnMe_3$, and **1a** and **1b** from $EtSnMe_3$. Each of these pairs of salts could not, of course, balance the sum of Me_3SnCl and RMe_2SnCl because R groups were converted into other products beside **1d**, **1e**, and **1b**.

Table II lists five of the products RMe_2SnCl. These must have been formed in the workup procedure from the corresponding ion, RMe_2Sn^+. We feel confident that in the cases of R = *i*-Pr and *t*-Bu the ion RMe_2Sn^+ was formed by the loss of R group from the R_2SnMe_2 that was present as an impurity in our preparation of $RSnMe_3$ and was detectable by GC and GC–MS. In contrast, we feel equally confident that in the cases of R = Ph, vinyl, and Et, the ion RMe_2Sn^+ was formed by loss of Me group from $RSnMe_3$. The reason for this distinction is that in these cases not only was the $RSnMe_3$ found by GC and GC–MS to be free of R_2SnMe_2 but also the Me group was trapped by $Th^{\bullet+}$ as **1a** and small amounts of 2-MeTh.

Unfortunately, authentic, individual compounds RMe_2SnCl were not available for use as quantitative GC standards. The amounts of RMe_2SnCl are listed in Table II arbitrarily, therefore, and in two ways. In the cases of R = *i*-Pr and *t*-Bu the amounts of RMe_2SnCl are derived from the amount of R_2SnMe_2 that was calculated from GC and ^{1}H NMR measurements to be present in the $RSnMe_3$. In each of the cases of R = Ph, vinyl, and Et, the amount of RMe_2SnCl is that which, with the assayed amount of Me_3SnCl, exactly balances the initial amount of $RSnMe_3$ that was used. In this way, the recovery of tin products is set arbitrarily as 100%. That this choice of amount of RMe_2SnCl is not far from correct is shown, in fact, by the accounting balance in groups (R and Me) that is obtained when all products, including the arbitrarily assigned amounts of RMe_2SnCl, are summed. The totals are given in Table III.

Table II shows that when R = *t*-Bu, all of the liberated R groups were converted into isobutene and other derivatives of the *tert*-butyl cation, namely *t*-BuCl, *t*-BuOH, and *t*-BuNHAc. Similarly, most (77%) of the liberated *i*-Pr groups appeared as propene, *i*-PrCl, and *i*-PrNHAc; the remainder (16%) appearing, as noted earlier, as derivatives of Th.

Table II lists also allyl chloride (run 9), which might, analogously, be thought to have been formed by the trapping of the allyl cation in the workup procedure. However, this cannot be correct, for if it were, the total of allyl units from all products would be 0.496 mmol and would far exceed the number (0.309 mmol) that was

Table I. Products of Reaction of R_4Sn with $\text{Th}^{\bullet+}\text{ClO}_4^-$ in Acetonitrile

		reactants, mmol		products, mmol and %[b]										
run	R	R_4Sn	$\text{Th}^{\bullet+}$[a]	RH	R(−H)	RCl[c]	RNHAc	R_3SnCl[d]	Th[e]	ThO[e]	1-RTh	2-RTh	R_2Th	1
1	Me	0.234	0.469	tr		0.194		0.226	0.254			0.005		0.203[f]
						20.7[d]		72.4				0.6[d]		21.7[d]
									54.2			1.1[e]		43.3[e]
2	Et	0.516	1.032		0.008	0.254		0.508	0.552	0.053	0.02	0.075	0.004	0.350[g]
					0.4	12.3[d]		73.8			1.0[d]	3.6[d]	0.4[d,e]	17.0[d]
									50.6	5.1	1.9[e]	7.3[e]		33.9[e]
3	Bu	0.561	1.124	tr	0.03	0.398	0.017	0.558	0.658	0.045	0.023	0.051	0.008	0.343[h]
					1.3	17.7[d]	0.8	74.6			1.0[d]	2.2[d]	0.7[d,e]	15.3[d]
									58.5	4.0	2.0[e]	4.5[e]		30.5[e]
4	Ph	0.434	0.866	0.128				0.429	0.518	0.049				0.300[i]
				7.4[d]				74.1						17.3[d]
									59.8	5.6				34.6[e]
5	Vi[j]	0.505	1.006	0.135				0.499	0.584	0.053				0.364[k]
				6.7[d]				74.1						18.0[d]
									58.0	5.3				32.2[e]

[a] $\text{Th}^{\bullet+}\text{ClO}_4^-$. [b] Percent data are listed under mmol entries. [c] Formed not as a primary product but from reaction of **1** with 4 M LiCl during workup. [d] Yield based on the amount of R group in R_4Sn. [e] Yield based on $\text{Th}^{\bullet+}\text{ClO}_4^-$. [f] **1a**. [g] **1b**. [h] **1c**. [i] **1d**. [j] Vinyl. [k] **1e**.

available. Instead, allyl chloride was formed in the workup procedure by reaction of the sulfonium salt (**1f**) with chloride ion. The validity of this conclusion is supported by the concordance in the amount of allyl chloride (0.202 mmol) that was assayed and of **1f** (0.197 mmol) that was isolated separately. The same conclusion is to be made about the inclusion of MeCl and EtCl (run 11) among the products of reaction of $EtSnMe_3$; that is, that these halides were derived from **1a** and **1b**.

Table II lists mixtures of **1a** and **1d**, **1a** and **1e**, and **1a** and **1b**. The amount of each product in each pair was obtained by integration of appropriate signals in the ^1H NMR spectrum of the mixture (see the Experimental Section). In the case of the mixture of **1a** and **1e**, confirmation of the composition derived from integration, namely 26% of **1a** and 74% of **1e**, was obtained from following the reaction of the mixture in $CDCl_3/CD_3CN$ with added aqueous 4 M LiCl. The ^1H NMR signals of **1a** slowly disappeared and were replaced by those of MeCl and Th. Integration of the Th signals and of the vinyl signals of unchanged **1e** showed that the original ratio of **1a**/**1e** must have been 26.8:73.2.

Reactions of R_3SnSnR_3 with $\text{Th}^{\bullet+}\text{ClO}_4^-$. By addition of liquid $Me_3SnSnMe_3$ to $\text{Th}^{\bullet+}\text{ClO}_4^-$ in the titrimetric way, reaction occurred quickly and was complete at the usual 2:1 ratio of reactants. Reaction of a mixture of $\text{Th}^{\bullet+}\text{ClO}_4^-$ and solid $Ph_3SnSnPh_3$ in the 2:1 ratio, suspended in MeCN, was also made fast by sonification. No products other than Th, a small amount of ThO, and R_3SnCl (after workup) were obtained.

Discussion

Reactions of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with R_4Sn. The results listed in Table I are fully consistent with oxidative scission of each tetralkyl tin (R_4Sn), eq 1. Thereby, the trialkyltin cation (R_3Sn^+) was formed and was recovered substantially quantitatively as R_3SnCl. A substantially quantitative account of the concomitantly formed radical ($R^\bullet$) was also obtained. In the case of $R^\bullet = Me^\bullet, Et^\bullet$, and $Bu^\bullet$, little other than the trapping products **1**, 1-RTh, 2-RTh, and R_2Th was obtained. From $R^\bullet = Ph^\bullet$ and vinyl$^\bullet$, **1** was again the dominant product. In these cases, none of the ring-substituted thianthrenes was formed, a result that was experienced also earlier in reactions of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with PhLi and PhMgCl.[8] On the other hand, approximately 7% of phenyl radicals was converted into benzene, and of vinyl radicals into ethene by (assumed) hydrogen atom abstraction from the solvent. Our results with Me_4Sn are analogous to those obtained by Rollick and Kochi in reaction of Me_4Sn with Fe(phenanthroline)$_3$ $(PF_6)_3$. That is, in that reaction, substantially quantitative formation of Me_3Sn^+ occurred, accompanied by trapping (91%) of $Me^\bullet$ as 4-methylphenanthroline.[6] Our results are analogous also to those reported recently from reactions of R_2Hg with $\text{Th}^{\bullet+}\text{ClO}_4^-$ in acetonitrile, in that the cation (RHg^+), corresponding with the present R_3Sn^+, was obtained in substantially quantitative yields (R = Me, Et, and Bu), along with trapping of $R^\bullet$ by $\text{Th}^{\bullet+}$. Only small amounts of hydrocarbon products (about 2%) from reactions of $R^\bullet$ ($Et^\bullet$ and $Bu^\bullet$) were obtained in those reactions, too. At that time, the reaction of **1b** and **1c** with 4 M LiCl was shown to lead to the corresponding RCl. That conversion was experienced in the present work with **1a**–**c** and is recorded in Table I. There, the yields of MeCl, EtCl, and BuCl are seen to be similar to the isolated yields of the corresponding **1**. It is to be noted that, as would be expected of a presumed S_N2 displacement, reaction of **1d** (R = Ph) and **1e** (R = vinyl) with LiCl did not take place.

Reactions of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with $RSnMe_3$. It is evident from Table II that when R = *i*-Pr, *t*-Bu, and allyl, exclusive loss of radical $R^\bullet$ from $RSnMe_3^{\bullet+}$ occurs. No evidence was obtained at all for the loss of the methyl radical. As noted earlier, the listing of RMe_2SnCl (R = *i*-Pr and *t*-Bu) in Table II is derived also from the exclusive loss of $R^\bullet$ from the impurity, $R_2SnMe_2^{\bullet+}$. Exclusive loss of these groups is in accord with the greater stabilization of radical $R^\bullet$ as compared with the methyl radical. Distinction occurred between allyl and the *i*-Pr and *t*-Bu radicals in the follow up reactions. Most (71%) of the allyl radicals added to $\text{Th}^{\bullet+}$, particularly at the sulfur atom as **1f**. On the other hand no addition of the *t*-Bu radical occurred, the exclusive fate being oxidation to and reactions of the *t*-Bu cation. A small amount of addition of the *i*-Pr radical occurred, but as ring-substituted thianthrenes and not as a sulfonium salt. This is in spite of the fact that the highest spin density in $\text{Th}^{\bullet+}$ is on the sulfur atoms[9] and suggests that the problem with addition of an *i*-Pr radical at a sulfur atom in $\text{Th}^{\bullet+}$ is a steric one.

Reactions of $RSnMe_3$ with R = Ph, vinyl, and Et resulted in competitive loss of both R and Me groups. A measure of the relative extents of group loss should be given most readily by the amounts of Me_3SnCl and RMe_2SnCl listed in Table II. However, this would be an

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(9) Shine, H. J. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; p 529.

Table II. Products of Reaction of $RSnMe_3$ with $Th^{\bullet+}ClO_4^-$ in Acetonitrile

		reactants, mmol		products, mmol and %[a]														
run	R	$RSnMe_3$	$Th^{\bullet+}ClO_4^-$	RH[c]	R–R	R(–H)	RCl	ROH	RNHAc	Me_3SnCl[d]	RMe_2SnCl	Th	ThO	1-RTh	2-RTh	R_2Th	1	
6	Ph	0.297	0.593	0.115 38.7						0.256 86.2	(0.041)[b] 13.8[c] 9.2[d]	0.325 54.8	0.036 6.1		*e*		0.144[f] 48.5[c] 24.3[h]	0.052[g] 5.8[d] 8.8[h]
7	*t*-Bu	0.246[i] (0.214)	0.492			0.035 12.6[k]	0.030 10.8[k]	0.079 28.4[k]	0.042 15.1[k]	0.212 99.1	0.032[j] 11.5[k]	0.452 91.9	0.020 4.1					
8	*i*-Pr	0.501[l] (0.452)	0.983			0.040 7.3[k]	0.235 42.7[k]		0.113 20.5[k]	0.445 98.5	0.049[j] 8.9[k]	0.859 87.4	0.024 2.4	0.014 2.5[k] 1.4[h]	0.052 9.5[k] 5.3[h]	0.004 1.5[k] 0.4[h]		
9	allyl	0.309	0.586	0.052 16.8	0.011 7.1		0.202[c,m] 65.4			0.308 99.7		0.362 61.8		0.004 1.3[c] 0.7[h]	0.019 6.1[c] 3.2[h]	tr	0.197[n] 63.8[c] 33.6[h]	
10	vinyl	0.506	1.00	0.117 23.1	0.0034 1.3					0.374 73.8	(0.132)[b] 26.1[c] 17.4[d]	0.569 56.9	0.07 7.0		*o*		0.258[p] 51.0[c] 25.8[h]	0.089[g] 5.9[d] 8.9[h]
11	Et	0.753	1.503	0.0022 0.29		0.0037 0.49	*q*			0.676 89.8	(0.077)[b] 10.2[c] 6.8[d]	0.743 49.4		0.029[r] 3.86[c] 1.93[h]	0.083 11.0[c] 5.5[h]	0.0014 0.37[c] 0.09[h]	0.526[s] 69.9[c] 35.0[h]	0.074[g] 3.3[d] 4.9[h]

[a] Percent data are listed under the mmol entries. [b] This is abitrarily chosen to balance the amount of $RSnMe_3$ that was not converted into Me_3SnCl. [c] Percent yield is based on R in $RSnMe_3$. [d] Percent yield is based on Me groups in $RSnMe_3$. [e] 2-MeTh, 0.002 mmol. [f] **1d**. [g] **1a**. [h] Based on $Th^{\bullet+}ClO_4^-$. [i] The $RSnMe_3$ contained R_2SnMe_2 as shown by GC and GC–MS. The effective initial amount of $RSnMe_3$ is assumed to have been 0.246–0.032 mmol. [j] Derived from R_2SnMe_2. [k] Yield is based on total amount of R group in $RSnMe_3$ and R_2SnMe_2. [l] Impurity R_2SnMe_2 shown by GC–MS to be present in $RSnMe_3$. Effective amount of $RSnMe_3$ is assumed to have been 0.501–0.049 mmol. [m] From reaction of **1e** with LiCl. [n] **1f**. [o] 2-MeTh (0.010 mmol, 0.7%,[d] 1.0%[h]). [p] **1e**. [q] EtCl and MeCl were obtained from reactions of **1b** and **1a** with LiCl; see the Experimental Section. [r] 2-MeTh (0.006 mmol) was also obtained. [s] **1b**.

Table III. Accounting (%) of Reactant Groups in Reactions of R_4Sn, $RSnMe_3$, and R_6Sn_2 with $Th^{\bullet+}ClO_4^-$[a]

run	Th units from $Th^{\bullet+}ClO_4^-$	R units from R_4Sn or R_6Sn_2	Me units from $RSnMe_3$	R units from $RSnMe_3$	Sn
1	98.6	94.7			96.6
2	98.8	96.2			98.4
3	99.5	95.9			99.5
4	100	98.8			98.8
5	99.5	98.8			98.8
6	94.0		101	101	100[b]
7	96.0		99.1	81.3[c,d]	99.1
8	96.9		98.5	92.9[c]	98.6
9	99.3		99.7	88.0	99.7
10	99.5		97.8	102	100[b]
11	96.9		100	96.1	100[b]
12	99.7	100			98.3
13	99.1	95.3			95.3

[a] The table sums yields of all products containing a Th group, all products containing an R group derived from R_4Sn, R_3SnSnR_3, and $RSnMe_3$, all products containing a Me group derived from $RSnMe_3$, and all products containing Sn derived from a tin reactant. [b] Fixed at 100% from summing Me_3SnCl and arbitrarily assigned RMe_2SnCl.' [c] In this case, R groups from the impurity R_2SnMe_2 (see Table II) are included among the total available R. [d] Includes *t*-BuOO*t*-Bu (0.004 mmol).

invalid measure because, as explained earlier, the amounts of RMe_2SnCl have been arbitrarily assigned. Instead, a measure of the tendency of $RSnMe_3^{\bullet+}$ to lose R• and one Me•, that is the ratio R/Me, can be properly obtained from summation of assayed products containing R and Me groups, listed in Table II. This ratio, adjusted for the statistical advantage of three Me groups in $RSnMe_3^{\bullet+}$, is Ph/Me = 14.4, vinyl/Me = 11.6, and Et/Me = 24.2. The last result is closely similar to that (26 and 27) obtained by Kochi and co-workers from outersphere oxidations of $EtSnMe_3$ and Et_2SnMe_2 by $Fe(phen)_3(ClO_4^-)_3$.[5,7] The selectivity of ethyl over methyl radical is understandable on the well-accepted basis of the greater stabilization of the ethyl radical. The selectivity to be expected between methyl and phenyl or between methyl and vinyl is not so readily evident, however. An impression of the relative stabilizations among these radicals can be obtained from the bond dissociation energies $D(CH_3–H)$, $D(CH_2{=}CH–H)$, and $D(C_6H_5–H)$. These have been tabulated as 104, 108, and 110 kcal/mol, respectively.[10] The most recent experimental and theoretical determinations of $D(CH_2{=}CH–H)$ are, in fact, 109.7 ± 0.8[11] and 109.5 kcal/mol,[12] respectively. In spite of some controversy with earlier literature over these data,[11,12] there is no doubt that $D(CH_3–H)$ is lower than that of ethene and benzene. On this basis one would expect methyl to be formed more easily than vinyl or phenyl radical. This, in fact, seems to be the case for the phenyl radical in the gas-phase decompositions of azomethane and azobenzene.[10] Analogous data are not available for the vinyl analogue, but we assume that comparison would again favor azomethane. Insofar as the competitive loss of a radical from $RSnMe_3^{\bullet+}$ is concerned, mass spectrometry data provide guidance. Loss of R• prevails over loss of methyl radical when R is an alkyl group. Thus for R = Et, *i*-Pr, and *t*-Bu the relative abundances of ions Me_3Sn^+ and RMe_2Sn^+ were 100/32,

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(10) See: Wentrup, C. *Reactive Molecules*; J. Wiley and Sons: New York, 1984; Chapter 2, for these findings and a discussion of radical stabilities.

(11) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750. This paper also quotes $D(CH_3–H)$ as 103.24 kcal/mol.

(12) Wu, C. J.; Carter, E. A. *J. Am. Chem. Soc.* **1990**, *12*, 5893. This paper lists earlier experimental and theoretical results, too.

100/15, and 100/3.9, respectively. On this basis it was pointed out that fragmentation of $RSnMe_3^{\bullet+}$ is controlled by the relative stabilities of the radicals (i.e., $R^\bullet$ and $Me^\bullet$).[13] In contrast, mass spectrometric data for a number of $ArSnMe_3$ showed that loss of methyl from $ArSnMe_3^{\bullet+}$ was dominant. That is, the major ion intensity in each mass spectrum was of $ArMe_2Sn^+$. Loss of the aryl group was a minor occurrence, and when R = Ph, the ratio of abundances of $PhMe_2Sn^+$ and Me_3Sn^+ was 59/0.6.[14] The situation, then, is that in the decomposition of $RSnMe_3^{\bullet+}$, with R = phenyl and vinyl, we should expect the loss of methyl radical rather than $R^\bullet$. Our results are to the contrary and suggest that in the decomposition of $RSnMe_3^{\bullet+}$ in solution the relative stability of $R^\bullet$ and methyl radical is not the only deciding factor on selectivity. In the case of R = phenyl and vinyl it seems that decomposition (i.e., greater loss of $R^\bullet$) occurs so as to maximize the formation of Me_3Sn^+ as compared with RMe_2Sn^+. We do not have a firm explanation for these results. They may mean that in solution decomposition occurs so as to give the smaller and more easily solvated ion, Me_3Sn^+. The latter factor would, of course, parallel that of radical stability in the decomposition of alkyl$SnMe_3^{\bullet+}$.

Trapping of Radicals by $Th^{\bullet+}$. Once a radical has been formed from $R_4Sn^{\bullet+}$ and $RSnMe_3^{\bullet+}$ it has the options of being "trapped" by $Th^{\bullet+}$, being oxidized by $Th^{\bullet+}$, or reacting with the solvent. Qualitatively our results with methyl, ethyl, isopropyl, and *tert*-butyl radicals parallel those reported by Rollick and Kochi for reactions of radicals with $Fe(phen)_3^{3+}$ in acetonitrile;[6] that is, large amounts of trapping of $Me^\bullet$ and $Et^\bullet$, a small amount of trapping of *i*-$Pr^\bullet$, and virtually none of *t*-$Bu^\bullet$, the fates of the last two radicals being mainly oxidation. We are surprised in our finding that allyl radicals (from allyl$SnMe_3^{\bullet+}$) that were not trapped by $Th^{\bullet+}$ were not oxidized, but instead either reacted with solvent (17%) or dimerized (7%).[15] Kochi and co-workers did not work with allyl$SnMe_3$ but have reported that reaction of analogous benzyl$SnMe_3$ with $Fe(phen)_3^{3+}$ in acetonitrile led mainly (97%) to oxidation of the benzyl radical and formation of benzylNHAc; very little addition to oxidant or reaction with solvent occurred. We have not used benzyl$SnMe_3$, and our attempts to study the reaction of $(allyl)_4Sn$ with $Th^{\bullet+}ClO_4^-$ were abandoned. Reaction occurred at a ratio $Th^{\bullet+}/(allyl)_4Sn$ approaching 4:1 and we were unable to account satisfactorily for the products that were formed.

It is interesting to compare the competition of being trapped by $Th^{\bullet+}$ with other available reactions for the not-so-easily oxidizable phenyl and vinyl radicals. These radicals were liberated from both $R_4Sn^{\bullet+}$ and $RSnMe_3^{\bullet+}$, so that comparison of trapping and formation of RH can be made for the radicals produced from each source. Trapping of these two radicals amounted only to the formation of **1d** (R = Ph) and **1e** (R = vinyl) because ring substitution did not occur. The data in Tables I and II show that the ratio **1d**/C_6H_6 was 2.3 from Ph_4Sn and 1.3 from $PhSnMe_3$. The ratio **1e**/ethene was 2.7 from $(vinyl)_4Sn$ and 2.2 from vinyl$SnMe_3$. The results have a reasonable degree of internal consistency and reflect the relatively high reactivity of these vinylic-type radicals toward hydrogen atom abstraction.

In connection with our results with allyl$SnMe_3$, Maruyama and Matano reported recently that, in acetonitrile, acylquinones oxidized this stannane to the allyl radical and Me_3Sn^+. Allyl$SnBu_3$ behaved similarly. Thereafter, the allyl radical was trapped by the anion radical of the acylquinone.[16]

Reactions of R_6Sn_2. Compounds with metal–metal bonds of the type R_3MMR_3 are currently of interest as two-electron reductants. For example, the 10-methylacridinium ion (MA^+) is reduced by $Me_3SnSnMe_3$ (and other metal analogues) to the $MA^\bullet$ radical, which dimerizes. Thereby, 2 mol of Me_3Sn^+ are formed, the significance of which is that the first-formed $Me_3Sn^\bullet$ (eq 10) is oxidized by MA^+ (eq 11) rather than being coupled with $MA^\bullet$ or a second mole of MA^+.[17] Analogously, reactions of $Fe(phen)_3(ClO_4)_3$ with a number of R_6Sn_2 led to the reduction of Fe^{3+} and total formation of R_3Sn^+.[18] On the other hand, reaction of Bu_6Sn_2 with tetracyanoethylene (TCNE) and of Me_6Sn_2 with 9,10-phenanthraquinone (PQ) led to the addition of $Bu_3Sn^\bullet$ to TCNE[19] and of $Me_3Sn^\bullet$ to PQ.[20]

$$Me_3SnSnMe_3 + MA^+ \rightarrow Me_3SnSnMe_3^{\bullet+} + MA^\bullet \quad (9)$$

$$Me_3SnSnMe_3^{\bullet+} \rightarrow Me_3Sn^+ + Me_3Sn^\bullet \quad (10)$$

$$Me_3Sn^\bullet + MA^+ \rightarrow Me_3Sn^+ + MA^\bullet \quad (11)$$

$$2MA^\bullet \rightarrow (MA)_2 \quad (12)$$

We were interested to find if $Th^{\bullet+}$ would oxidize hexasubstituted ditins and, if so, if a radical $R_3Sn^\bullet$ could be coupled with rather than oxidized by $Th^{\bullet+}$. One-electron oxidation was anticipated on the basis of the relative redox couples (vs NHE) $Th/Th^{\bullet+}$ (1.54 V[3]) and $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ (1.212 V[5]) and on the work of Peloso.[11] We have found that not only was oxidation by $Th^{\bullet+}$ facile but that it went to completion with the formation of 2 mol of R_3Sn^+ (R = Ph and Me). Thus, these $R_3Sn^\bullet$ radicals are analogous to *t*-$Bu^\bullet$ radical in reaction with $Th^{\bullet+}$.

Experimental Section

Gas chromatography (GC) analyses were made on a Varian gas chromatograph, Model 3700, attached to a Spectra-Physics integrator, Model 4290. Three columns were used: A, 13 ft, $^1/_8$ in., stainless steel (ss) packed with 20% BEEA on Chrom-PAW 60–80 mesh, attached to a similar 8-in. guard column, for hydrocarbons and alkyl chlorides; B, 6 ft, $^1/_8$ in. ss, packed with 10% Carbowax on Chrom-WHP, 80–100 mesh, attached to a similar 6-in. guard column, for reasonably volatile products such as alcohols; C, 1.5 ft, $^1/_8$ in. ss, packed with 5% OV-101 on Chrom-WHP, 100–120 mesh, for tin compounds, thianthrene, and its derivatives. The columns were used either isothermally or with programmed heating as necessary. Cyclohexane was used as an internal standard for analyses on columns A and B, while naphthalene was used with C. Concentration factors (CF) were measured against these standards for each component (except where noted) of a mixture of products immediately before analysis. CF of RTh and R_2Th were assumed to be the same as that of Th. Mass spectra were measured on a Hewlett-Packard instrument, Model 5995, either in the GC–MS or selected-ion-monitoring (SIM) mode. ^1H NMR spectra were recorded with an IBM-Bruker 200-MHz instrument. Chemical shifts (δ) are with respect to TMS, and coupling constants (*J*) are in hertz.

Acetonitrile (MeCN, Eastman 488) was distilled over P_2O_5 and stored under argon. Dichloromethane (CH_2Cl_2, Omnisolve) was

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[13] Boué, S.; Gielen, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1968**, *77*, 43.

[14] Gielen, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1968**, *77*, 5.

[15] Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861 have shown recently that alkyl radicals ($R^\bullet$) add to the allyl group of allyl$SnMe_3$ forming $RCH_2CH{=}CH_2$ and $Me_3Sn^\bullet$. This reaction could be a source of the dimer in reactions of allyl$SnMe_3$ with $Th^{\bullet+}$. In that case, oxidation of $Me_3Sn^\bullet$ to Me_3Sn^+ by $Th^{\bullet+}$ would follow and the overall stoichiometry would be unaffected.

[16] Maruyama, K.; Matano, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3877.

[17] Fukuzumi, S.; Kitano, T. *J. Am. Chem. Soc.* **1990**, *112*, 3246.

[18] Peloso, A. *J. Organomet. Chem.* **1974**, *67*, 423.

[19] Krusic, P. J.; Stoklosa, H.; Manzer, L. E.; Meakin, P. *J. Am. Chem. Soc.* **1975**, *97*, 667.

[20] Kochi, J. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 509.

used as obtained. Alkyl- and phenylmagnesium halides, 1.0 or 2.0 M in tetrahydrofuran (THF), were from Aldrich Chemical Co. Hydrocarbon gases, to serve as standards for GC analyses were from Matheson, Coleman and Bell. Me_4Sn and $(vinyl)_4Sn$ were from Aldrich, while other R_4Sn (R = Ph, Bu, and ET) were from Alfa Products (Johnson Matthey). R_6Sn_2 (R = Ph, Me) were from Strem Chemicals. Thianthrene (Th) was from Fluka AG and was purified by column chromatography on silica gel with petroleum ether before crystallization from acetone; mp 155–156 °C. Almost all other chemicals for preparative and analytical (GC) work were from Aldrich.

Unsymmetrical trimethyltins ($RSnMe_3$, R = Ph, *t*-Bu, *i*-Pr, allyl, vinyl, and Et) were prepared according to the procedure of Abel and Rowley[21] by addition of an equimolar amount or small excess (10%) of either RMgCl or RMgBr (vinyl) in THF to a solution of Me_3SnCl in ether. The quality of the Me_3SnCl was found by GC and GC–MS to vary with the lot. The lot from which $vinylSnMe_3$ and $EtSnMe_3$ were prepared was free of Me_2SnCl_2; that from which $allylSnMe_3$ was prepared contained 0.7% (GC) of Me_2SnCl_2 which led to the formation of a small amount of $allyl_2SnMe_2$ in the $allylSnMe_3$. The impurity was removed by distillation. The Me_3SnCl from which the remaining $RSnMe_3$ (R = Ph, *i*-Pr, and *t*-Bu) were prepared was found, after its use, by both GC and ^1H NMR spectroscopy, to contain 7.3% of Me_2SnCl_2, which led to the formation of substantial amounts of R_2SnMe_2. Ph_2SnMe_2 was removed from the $PhSnMe_3$ by distillation, but distillation failed to remove all of the $i\text{-}Pr_2SnMe_2$ and $(t\text{-}Bu)_2SnMe_2$ from the corresponding $RSnMe_3$. The impurities were detectable in the GC and ^1H NMR spectra of these $RSnMe_3$. Products were distilled at atmospheric pressure and had boiling point (R = Ph,[22] allyl,[22,23] vinyl,[22,23] Et,[22] and *i*-Pr,[24]), melting point (*t*-Bu[24]), and ^1H NMR spectra[25] in agreement with those in the literature. The ^1H NMR spectra of $RSnMe_3$ (R = allyl and vinyl) could not be found in the literature. However, our NMR data for group R were in agreement with analogous data for R_4Sn.[26] Bu_3SnCl was from Aldrich. Et_3SnCl was prepared by reaction of Et_4Sn with acetyl chloride–aluminum chloride and had bp 95–96 °C (15 Torr).[22] $(Vinyl)_3SnCl$ was prepared by reaction of $(vinyl)_4Sn$ with $SnCl_4$ and had bp 57–58 °C (6 Torr)[27] and a satisfactory ^1H NMR spectrum. *N-tert*-Butylacetamide (*t*-BuNHAc) was prepared from *t*-BuOH by the Ritter reaction[28] and had mp 94–96 °C. *N*-Isopropylacetamide (*i*-PrNHAc) was prepared by acetylating $i\text{-}PrNH_2$[29] and had bp 105–106 °C (17 Torr). $Th^{\bullet+}ClO_4^-$ was prepared as described earlier.[30] *This salt is potentially explosive* and should be treated carefully. Only small amounts should be prepared and used soon after preparation. Fritted-disk filters and metal spatulas should be avoided.

Reaction of Bu_4Sn with $Th^{\bullet+}ClO_4^-$. In a 25-mL volumetric flask sealed with a septum were placed 355 mg (1.12 mmol) of $Th^{\bullet+}ClO_4^-$ and 10 mL of MeCN. The flask was purged with argon, and to it was added dropwise through the septum with a tared microsyringe through Bu_4Sn (195 mg, 0.561 mmol) to cause the purple color of $Th^{\bullet+}$ to disappear completely. A colorless precipitate (Th) formed that redissolved on making the volume up to 25 mL with MeCN. A 5-mL aliquot of this solution was transferred by syringe to another flask to which was added 0.02 mL of 4 M aqueous lithium chloride solution. This MeCN solution was used for assay of 1-butene and butyl chloride (BuCl) on column B. Results are listed in Table I.

The remaining 20 mL of the MeCN solution was evaporated to dryness. The residue was dissolved in 15 mL of CH_2Cl_2, and the solution was shaken with 1% aqueous LiCl and dried over $MgSO_4$. To the dried solution was added 20 mL of dry ether, causing the precipitation of white solid which soon turned into an oil. The mixture was evaporated again, and the residue was dissolved in 5 mL of CH_2Cl_2. Precipitation with ether again gave an oil that crystallized on rubbing. Filtration and washing with ether gave 102 mg of 5-butylthianthreniumyl perchlorate (**1c**), mp 116–119 °C. This corresponded with a yield of 128 mg (0.343 mmol) of **1c**. The filtrate after removal of **1c** was used for assay on column C of all other products listed in Table I. These products were identified by use of authentic compounds except for 1-butyl-, 2-butyl-, and dibutylthianthrene (1-BuTh, 2-BuTh, and Bu_2Th), which were characterized by GC–MS. The BuCl assayed on column A is regarded as having been formed during workup by reaction of **1c** with 4 M LiCl in the 5-mL aliquot of reaction mixture. **1c** had a satisfactory ^1H NMR spectrum.

Reaction of Et_4Sn with $Th^{\bullet+}ClO_4^-$. Reaction was carried out as with Bu_4Sn, with 326 mg (1.03 mmol) of $Th^{\bullet+}ClO_4^-$ and 121 mg (0.516 mmol) of Et_4Sn. The sulfonium salt (**1b**) precipitated as a solid and had mp 114–117 °C [lit.[3] mp (from reaction of $Th^{\bullet+}ClO_4^-$ with Et_2Hg) 117–121 °C].

Reaction of Me_4Sn with $Th^{\bullet+}ClO_4^-$. Reaction was carried out as described with Bu_4Sn. Only one peak other than the internal standard (C_6H_{12}) was seen with the BEEA column. This was assumed to be MeCl and in the absence of an authentic sample its CF was assumed to be half that of EtCl. The result is given in Table I and is fortuitously close to the amount of **1a** isolated separately. Continued workup gave crude 5-methylthianthreniumyl perchlorate (**1a**) in a total yield of 67 mg (0.203 mmol), mp 186–188 °C. (lit.[31] mp 192–194 °C). Other products were assayed on column C and are listed in Table I.

Reaction of Ph_4Sn with $Th^{\bullet+}ClO_4^-$. Because it is not very soluble in MeCN, 185 mg (0.434 mmol) of solid Ph_4Sn and 274 mg (0.866 mmol) of $Th^{\bullet+}ClO_4^-$ were placed in the septum-capped, 25-mL volumetric flask. To this was added 15 mL of MeCN in the usual way, and the mixture was stirred for 72 h, by which time the purple color of $Th^{\bullet+}$ had faded to pink. The remaining procdure was as described for reaction of Bu_4Sn. Precipitation gave 118 mg (0.300 mmol) of 5-phenylthianthreniumyl perchlorate (**1d**), mp 253–257 °C (lit.[31] mp 259–261 °C). All other products are listed in Table I.

Reaction of $(Vinyl)_4Sn$ with $Th^{\bullet+}ClO_4^-$. The $(vinyl)_4Sn$ was shown by GC to contain no impurity. Reaction was carried out in a capped 25-mL volumetric flask between 318 mg (1.006 mmol) of $Th^{\bullet+}ClO_4^-$ and 120 mg (0.527 mmol) of $(vinyl)_4Sn$ in 15 mL of MeCN and was complete after 27 h of stirring. The reaction volume was then made up to 25 mL with MeCN. Workup of a 5-mL aliquot in the usual way with 0.05 mL of 4 M LiCl and GC assay on column C showed that (for the total volume, 25 mL) 0.022 mmol of $(vinyl)_4Sn$ remained. Assays of $(vinyl)_3SnCl$ (0.499 mmol, 99.2%), Th (0.548 mmol, 54.5%), and ThO (0.045 mmol, 4.5%) were made and based on the amount of $(vinyl)_4Sn$ (0.505 mmol) that had reacted. A 15-mL aliquot of the reaction solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and from the solution a gray solid (**1e**) was precipitated with ether and weighed 74.9 mg after overnight drying in air. This represents a total yield of 125 mg (0.364 mmol, 18.0% of vinyl groups) of **1e**. The crude **1e** had mp 112–114 °C. **1e** had a satisfactory ^1H NMR spectrum. The filtrate from precipitate of **1e** was treated with 0.5 mL of 4 M LiCl and assayed on column C for $(vinyl)_4Sn$ (0.023 mmol), $(vinyl)_3SnCl$ (0.479 mmol, 95.2%), Th (0.584 mmol, 58.0%), and ThO (0.053 mmol, 5.3%).

The 5 mL of reaction solution that remained in the 25-mL flask was shaken with 4 M LiCl, and to the mixture was added the cyclohexane standard by syringe. Assay on column A gave 0.135 mmol (6.7% of vinyl groups) of ethene. All results are listed in Table I.

Reactions of $RSnMe_3$ with $Th^{\bullet+}ClO_4^-$. The procedure adopted was essentially as described for the reactions of R_4Sn.

Reaction with $t\text{-}BuSnMe_3$, which occurred immediately on dropwise addition to the $Th^{\bullet+}ClO_4^-$ suspension, failed to give a

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[21] Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199.

[22] Ingham, R.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.

[23] Seyferth, D.; Stone, F. A. G. *J. Am. Chem. Soc.* **1957**, *79*, 515.

[24] Boué, S.; Gielen, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1967**, *76*, 559.

[25] Gielen, M.; De Clercq, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1969**, *78*, 237.

[26] Blears, D. J.; Danyluk, S. S.; Cawley, S. *J. Organomet. Chem.* **1966**, *6*, 284.

[27] Rosenberg, S. D.; Gibbons, A. J., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 2138.

[28] Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045. Benson, F.; Ritter, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 4128.

[29] Gillis, B. T. *J. Org. Chem.* **1959**, *24*, 1027. Wyness, K. G. *J. Chem. Soc.* **1958**, 2934.

[30] Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. Note the warning on explosiveness therein.

[31] Bandlish, B. K.; Porter, W. R.; Shine, H. J. *J. Phys. Chem.* **1978**, *82*, 1168.

sulfonium perchlorate (**1g**) when precipitation with ether was tried in the usual way. GC and GC–MS analysis showed that both Me_3SnCl and t-$BuMe_2SnCl$ had been formed, and the latter (Table II) has been attributed to reaction of $(t\text{-}Bu)_2SnMe_2$ originally present as an impurity in the t-$BuSnMe_3$. GC analysis on column B showed also that a small amount of di-*tert*-butyl peroxide had been formed.

Reaction of i-$PrSnMe_3$ was similarly rapid and also failed to give a sulfonium perchlorate (**1h**). Similarly, also, some i-$PrMe_2SnCl$ was formed (Table II) and is attributed to the reaction of the $(i\text{-}Pr)_2SnMe_2$ present in the i-$PrSnMe_3$.

Reaction of $allylSnMe_3$ occurred immediately on its dropwise addition to the $Th^{\bullet+}ClO_4^-$. Workup gave the products listed in Table II. Precipitation gave 70.6 mg (0.197 mmol) of 5-allylthianthreniumyl perchlorate (**1e**), mp 111–112 °C (lit.[3] mp 110–112 °C).

Reaction of $PhSnMe_3$. Formation of Both 1a and 1d. When $PhSnMe_3$ was used, the precipitated sulfonium perchlorate (73.8 mg total) had mp 198–200 °C. ^1H NMR spectroscopy showed that it was a mixture of the 5-methyl- and 5-phenylthiantheniumyl perchlorates, **1a** and **1d**. Integration of the methyl signal (3 H, δ 3.219) of **1a** and of the ortho protons (2 H, δ 7.109) of the phenyl group of **1d** showed that the ratio **1a**/**1d** was 23.5:76.5. These data are expressed separately in Table II, namely 56.5 mg (0.144 mmol) of **1d** and 17.3 mg (0.052 mmol) of **1a**. The formation of both **1a** and **1d** was supported by the formation after workup and subsequent GC measurements of $PhMe_2SnCl$ (for **1a**) and Me_3SnCl (for **1d**), Table II.

Reaction of $VinylSnMe_3$. Formation of Both 1a and 1e. To 316 mg (1.00 mmol) of $Th^{\bullet+}ClO_4^-$ under CH_3CN in a 25-mL volumetric flask was added in the usual way 3.28 mL (containing 0.506 mmol) of a standard solution of $vinylSnMe_3$ in CH_3CN. Reaction was complete after 14 h of stirring. Treatment of a 5-mL aliquot with 0.05 mL of 4 M LiCl and GC analysis on columns A and C gave ethene, 1,3-butadiene, Me_3SnCl, and $vinylMe_2SnCl$ in the quantities listed (for the total volume) in Table II. Workup of a 15-mL aliquot and precipitation of sulfonium salt with ether gave 50.7 mg of product, representing a total of 118 mg. ^1H NMR spectroscopy in $CDCl_3/CD_3CN$ showed that this solid was a mixture of **1a** and **1e**. Integration of the methyl signal (3 H, δ 3.21) of **1a** and of the vinyl signals (each of 1 H, between δ 5.99 and 6.73) showed that the mixture contained 74% of **1e** and 26% of **1a**. These data are expressed in mmol in Table II. GC and GC–MS assay of the filtrate from precipitation of the sulfonium salts gave Th, 2-MeTh, and ThO in the amounts listed in Table II.

To a solution of the mixture of **1a** and **1e** in $CDCl_3/CD_3CN$ in an NMR tube was added a small amount of 4 M LiCl. The methyl signal (δ 3.21) of **1a** diminished slowly and was replaced by a new singlet at δ 3.03, assumed to be for CH_3Cl. At the same time the NMR spectrum of thianthrene (Th) appeared as two symmetrical multiplets between δ 7.25 and 7.50. The disappearance of **1a** was complete in 15 days. The signals for **1e** remained unchanged during this time. Integrations of the three vinyl signals (each 1 H) and Th signals (8 H) were in the ratio 1.01:1.03:1.00:2.95. This meant that the ratio of concentrations of **1e**/Th (and hence of **1e**/**1a**) was 73.2/26.8. The integrated signal for (assumed) CH_3Cl was low in intensity (0.32 H), a result attributed to the fact that the NMR tube was capped but not sealed, allowing for the escape of volatile CH_3Cl during the 15-day period.

Reaction of $EtSnMe_3$. The $ETSnMe_3$ after distillation (bp 101–102 °C; lit.[22] bp 105 °C) was found by GC to contain 0.34% of an unidentified impurity. Reaction was carried out by adding neat $EtSnMe_3$ dropwise from a tared syringe to a stirred solution/suspension of 475 mg (1.053 mmol) of $Th^{\bullet+}ClO_4^-$ in 15 mL of MeCN until the color of $Th^{\bullet+}$ has disappeared and was complete after 145.3 mg (0.753 mmol) had been added. The volume was made up to 25 mL with MeCN. A 5-mL aliquot was treated with 0.05 mL of 4 M LiCl. Analysis on column C gave Me_3SnCl, Th, 2-MeTh, 1-EtTh, 2-EtTh, and Et_2Th as listed in Table II. The identities of these products were based on GC–MS data and GC retention times from the same products in other experiments. GC analysis on column C gave also $EtMe_2SnCl$ in an amount assumed to be the maximum possible, namely 0.077 mmol (10.2% of the $EtSnMe_3$ that was used).

Workup of a 15-mL aliquot of reaction solution gave 124 mg of a mixture (^1H NMR) of **1a** and **1b**, with mp 116–121 °C, namely close to that (117–121 °C[3]) of **1b**. This corresponded with a total yield (25 mL) of 206 mg. Integration of the triplet (δ 1.322) of the ethyl group of **1b** and of the singlet (δ 3.212) of the methyl group of **1a** showed that the ratio **1a**/**1b** was 11.9/88.1. This result corresponded, then, with the formation of 0.526 mmol (69.9%) of **1b** and 0.074 mmol (9.8%) of **1a**, based on the amount of $EtSnMe_3$ that was used. The filtrate from the precipitation was analyzed for free Th on column C and gave a total yield of 0.743 mmol (49.4%).

The remaining 5 mL of reaction solution was treated with 0.05 mL of 4 M LiCl and was analyzed on column A and gave (for 25 mL of solution) ethane (0.0022 mmol, 0.29%), ethene (0.0037 mmol, 0.49%), MeCl (0.069 mmol, 3.1%, based on an assumed CF of 0.150), and EtCl (0.520 mmol, 69.1%). The origin of the MeCl and EtCl is assumed to have been the reaction of **1a** and **1b** with LiCl.

Reactions with Me_6Sn_2 and Ph_6Sn_2. Addition of neat, liquid Me_6Sn_2 dropwise by microsyringe to a flask containing 162 mg (0.513 mmol) of $Th^{\bullet+}ClO_4^-$ and 15 mL of MeCN (run 12) was complete after 77 mg (0.235 mmol) had been added. Workup in the usual way gave only Me_3SnCl (0.448 mmol, 95.3%), Th (0.503 mmol, 98.1%), and ThO (0.005 mmol, 1.0%). No evidence for the formation of a 5-thianthreniumyl perchlorate was found.

Because Ph_6Sn_2 is a solid and not very soluble in MeCN, reaction (run 13) was carried out with a mixture of 170 mg (0.243 mmol) of Ph_6Sn_2 and 154 mg (0.486 mmol) of $Th^{\bullet+}ClO_4^-$ suspended in 15 mL of MeCN. However, reaction was brought to completion within 5 min by placing the volumetric flask in a sonic bath. Workup then gave 0.478 mmol (98.3%) of Ph_3SnCl, 0.477 mmol (98.1%) of Th, 0.008 mmol (1.6%) of ThO, and 0.025 mmol (1.7%) of benzene. No evidence for the formation of a 5-thianthreniumyl perchlorate was found.

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