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Direct Fluorination of Tetramethyltin. Synthesis of Trifluoromethyltin Compounds

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Trifluoromethyltin compounds have been synthesized by controlled, low-temperature fluorination of tetramethyltin. The partially fluorinated tetramethyltin compounds were identified by methyl exchange between dimethylcadmium and the fluorine-containing methyltin fluorides produced in the reaction. The following fluorine-containing compounds were identified: $Sn(CH_3)_3(CH_2F)$, $Sn(CH_3)_3(CHF_2)$, $Sn(CH_3)_2(CH_2F)_2$, $Sn(CH_3)_3(CF_3)$, and $Sn(CH_3)_2(CF_3)_2$.

Introduction

Tin–carbon bond cleavage usually occurs in the reaction of the halogens with tetramethyltin. The degree of cleavage is in the order of Cl > Br > I.[1] Side-chain chlorination on halomethyltin compounds does not occur due to extensive cleavage of tin–carbon bonds during chlorination, in contrast to the chlorination observed with halomethylsilanes.[2] Because of the extreme reactivity of fluorine and facile bond cleavage by chlorine, the reaction of fluorine with tetramethyltin has not been previously investigated.

We report here our initial work on the direct fluorination of tetramethyltin. Previously we have shown that it is possible to preserve both metal–carbon and metalloid–carbon bonds during direct fluorination. We were successful in the direct fluorination of dimethylmercury to give bis(trifluoromethyl)mercury.[3] Direct fluorination of tetramethylsilane has allowed the isolation of many partially fluorinated tetramethylsilanes.[3,4] By very carefully choosing fluorination conditions we have been able to synthesize tetrakis(trifluoromethyl)germanium, $Ge(CF_3)_4$, in 63.5% yield.[5] Thus, continued interest in investigating the limits of direct fluorination in group 4A has led to tetramethyltin. (Successful direct fluorination of neopentane was accomplished in this laboratory previously.[6])

The reaction of fluorine with tetramethyltin leads to several fluorine-containing methyltin fluorides. By methyl exchange with dimethylcadmium, we were able to isolate the following compounds: $Sn(CH_3)_4$, $Sn(CH_3)_3(CH_2F)$, $Sn(CH_3)_3(CHF_2)$, $Sn(CH_3)_2(CH_2F)_2$, $Sn(CH_3)_3(CF_3)$, and $Sn(CH_3)_2(CF_3)_2$.

Experimental Section

Tetramethyltin and dimethyltin difluoride, both from Alfa Inorganics, were used without further purification.

Physical Measurements. Infrared spectra of gases were obtained in gas cells with KBr windows and of solids as KBr pellets using a Beckman IR20A spectrophotometer. Mass spectra were obtained in the gas phase with an Hitachi Perkin-Elmer RMU-6 mass spectrometer. Proton and fluorine NMR spectra were obtained using an Hitachi Perkin-Elmer R20B NMR spectrometer, operating at 60.0 and 56.47 MHz, respectively. Chemical shifts and coupling constants were measured with a Takeda-Riken TR-3824x frequency counter in conjunction with the R20B instrument.

Apparatus. Fluorinations were done in a cryogenic-zone reactor previously described.[7] The compounds, after methyl exchange, were separated on a Bendix 2300 gas chromatograph, equipped with an automatic temperature controller and a thermal conductivity detector. A 10% fluorosilicon QF-1-0065 on Chromosorb P column was used.

Reaction 1. A 0.95-mL (1.25 g, 6.98×10^{-3} mol) sample of $Sn(CH_3)_4$ was syringed into the reactor through a Swagelok T-assembly with only zone 2 at −78 °C and a helium flow of 100 cm^3/min. After several hours, fluorination began with a fluorine flow of 1.0 cm^3/min and a helium flow of 60 cm^3/min. After 163 h, the fluorine flow was terminated. After being purged with helium for 8 h, the reactor was allowed to warm to room temperature. After being purged with helium for 34 h, the contents in the liquid-nitrogen trap were fractionated into −131 and −196 °C fractions. The −196 °C fraction contained mainly CF_4, CF_3H, CF_2H_2, and CH_3F. Very little material was in the −131 °C fraction. The ^{19}F NMR spectrum of the −131 °C fraction in benzene showed no peaks of interest.

Reaction 2. A 0.65-mL sample of $Sn(CH_3)_4$ was syringed as above into the reactor with a helium flow of 100 cm^3/min with zone 4 at −78 °C. After 1 h of purging with helium, zones 1, 2, 3, and 4 were all cooled to −78 °C. The following fluorination conditions were used with zones 1, 2, 3, and 4 held at −78 °C.

F_2 flow, cm^3/min	He flow, cm^3/min	Time, h
1.0	60	44
1.0	30	13
2.0	30	30
2.0	15	45
0.0	30	12
0.0	30	16 (room temp)

Separation of the volatile materials showed mainly CF_4 and CF_3H in the −196 °C fraction. Very little material was in the −131 °C trap. The ^{19}F NMR spectrum showed a singlet at approximately 50 ppm upfield from TFA, indicating the possible presence of a Sn–F-type compound.

Reaction 3. A 0.875-mL sample of $Sn(CH_3)_4$ was syringed into the reactor with a 100 cm^3/min helium flow and with zone 2 cooled to −110 °C. After 1 h of purging with helium, a fluorine flow of 1 cm^3/min to a helium flow of 60 cm^3/min was used for 240 h. Fluorine was purged from the reactor for 8 h after which the reactor was allowed to warm to room temperature. The reactor was purged with helium for 3 days to carry out in the vapor stream any material of low volatility.

The contents of the liquid-nitrogen trap were separated into −131 and −196 °C fractions. The −196 °C fraction contained CF_4, CF_3H, and CF_2H_2. Very little material stopped in the −131 °C trap. The ^1H and ^{19}F NMR spectra showed patterns attributable to CF_2H- and CFH_2-type groups. Of interest were peaks in the proton NMR around τ 10, indicative of methyl groups on a metal. Insufficient quantity of material made it impossible to identify the compounds which might have been present.

Reaction 4. Due to the small amount of volatile materials present, we decided to take a look at the material left in the reactor from reactions 1–3 which at first we believed to be only tin fluorides. The following two experiments were done using the off-white powder scraped out of the reactor and off the copper turnings.

(a) To approximately $^1/_2$ mL of the powder was added 0.28 mL of $Cd(CH_3)_2$ in a vacuum system. Upon contact at room temperature, the material turned gray, and the volatile materials were subsequently removed.

Infrared spectra of the volatile materials showed no $Cd(CH_3)_2$. An NMR spectrum was taken of the mixture, whereby two resonances at −34.1 and −31.6 ppm from TFA were observed. Also present in the spectrum were what was believed to be tin-117 and -119 satellites. (This material was kept and its disposition will be discussed after reaction 4c.)

(b) To another portion of the off-white powder was added 0.30 mL of $Cd(CH_3)_2$, again in a vacuum system. Analogous results were observed as in (a), except the two resonances were in different ratios. (The disposition of this material will be discussed after reaction 4c.)

(c) To $^1/_2$ mL of $Sn(CH_3)_2F_2$ was added 0.25 mL of $Cd(CH_3)_2$. The resultant infrared and NMR spectra showed the sample to be only $Sn(CH_3)_4$. There was no $Cd(CH_3)_2$ present.

The (a) and (b) samples, prepared by the reaction of the powder with $Cd(CH_3)_2$, were then separated by chromatography. Each of

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Table I. Proton NMR Spectra for Polyfluorotetramethyltin Compounds[a]

Compd	CH_3	$J_{^{117/119}SnH}$	CH_2F^b	J_{HF}	$CHF_2{}^c$	J_{HF}
$Sn(CH_3)_4$	0.047	53.1				
$Sn(CH_2F)(CH_3)_3{}^d$	−0.037	53.9/56.0	4.75	48.0		
$Sn(CH_2F)_2(CH_3)_2$	0.10	55.9	4.93	47.9		
$Sn(CHF_2)(CH_3)_3{}^e$	−0.028	56.7			6.08	45.8
$Sn(CF_3)(CH_3)_3$	0.09	57.7/60.0				
$Sn(CF_3)_2(CH_3)_2$	0.39	64.1/66.4				

[a] All samples run as neat liquids. ^1H shifts in ppm and downfield from TMS (external). *J* in Hz. [b] Doublet. [c] Triplet. [d] Reference 8: CH_3 (−0.015), CH_2F (4.85), $J_{HF} = 48$. [e] Reference 9: CH_3 (+0.18), $J_{^{117/119}SnH} = 53.5/57.5$, CHF_2 (6.25), $J_{HF} = 45.5$.

Table II. Fluorine NMR Spectra for Polyfluorotetramethyltin Compounds[a]

Compd	CF_3	$J_{^{117/119}SnF}$	$CHF_2{}^b$	J_{HF}	CH_2F^c	J_{HF}
$Sn(CH_3)_4$						
$Sn(CH_2F)(CH_3)_3$					190.73	48.0
$Sn(CH_2F)_2(CH_3)_2$					190.85	47.3
$Sn(CHF_2)(CH_3)_3{}^d$			48.15	46.0		
$Sn(CF_3)(CH_3)_3$	-29.14^e	263.2/276.2				
$Sn(CF_3)_2(CH_3)_2$	−31.46	333.0/348.6				
$Sn(CF_3)_4{}^f$	−33.8	503/531				

[a] All samples run as neat liquids. ^{19}F shifts in ppm and upfield from TFA (external). *J* in Hz. [b] Doublet. [c] Triplet. [d] Reference 9: CHF_2 (49.5), $J_{HF} = 45.0$, $J_{^{117/119}SnF} = 254.5/265.5$. [e] Reference 10: CF_3 (−29.05). [f] Chemical shift taken from ref 11.

Table III. Mass Spectra of Polyfluorotetramethyltin Compounds

m/e	Rel intens	Ion
	$Sn(CHF_2)(CH_3)_3$ (Mol Wt 214)	
14	9.1	CH_2
15	30.3	CH_3
51	18.2	CHF_2
118[a]	32.3	Sn
133[a]	100.0	$Sn(CH_3)$
148[a]	40.4	$Sn(CH_3)_2$
163[a]	68.7	$Sn(CH_3)_3$
167[a]	25.2	$Sn(CH_3)_2F$
199[a]	9.1	$Sn(CH_3)_2(CH_2F)$
	$Sn(CH_2F)(CH_3)_3{}^b$ (Mol Wt 196)	
14	6.3	CH_2
15	24.0	CH_3
33	21.5	CH_2F
118[a]	40.5	Sn
133[a]	100.0	$Sn(CH_3)$
148[a]	35.4	$Sn(CH_3)_2$
163[a]	98.7	$Sn(CH_3)_3$
181[a]	22.8	$Sn(CH_3)_2(CH_2F)$
	$Sn(CH_2F)_2(CH_3)_2$ (Mol Wt 214)	
14	24.6	CH_2
15	78.0	CH_3
33	34.7	CH_2F
51	31.4	CHF_2
118[a]	44.1	Sn
133[a]	100.0	$Sn(CH_3)$
137[a]	69.5	SnF
148[a]	14.4	$Sn(CH_3)_2$
163[a]	15.2	$Sn(CH_3)_3$
171[a]	11.0	$Sn(CH_3)F_2$
181[a]	66.1	$Sn(CH_3)_2(CH_2F)$
199[a]	13.6	$Sn(CH_3)(CH_2F)_2$

[a] Sn isotope pattern. [b] Reference 12: *m/e* 45, 118, 133, 148, 163, 181.

Table IV. Infrared Spectra of Polyfluorotetramethyltin Compounds (cm^{-1})[a]

$Sn(CH_2F)(CH_3)_3{}^b$	3070 m, 3010 s, 2960 sh, 2940 s, 2860 sh, 2400 w, 1740 vw, 1717 vw, 1450 w, 1269, 1260, 1255 (pqr) m, 1215, 1205, 1200 (pqr) m, 1078 m, 989 vs, 779 vs, 531 vs
$Sn(CH_2F)_2(CH_3)_2$	3000 w, 2960 sh, 2940 m, 1745 vw, 1455 vw, 1380 vw, 1320 vw, 1275 m, 1221 m, 1151 m, 1081 m, 1045 w, 1015 w, 989 s, 951 m, 920 m, 878 w, 820 m, 770 m, 530 m
$Sn(CHF_2)(CH_3)_3{}^c$	3060 w, 3010 m, 2910 s, 2400 w, 1745 vw, 1725 vw, 1480 vw, 1400 vw, 1330 w, 1285 s, 1205 m, 1155 m, 1124 s, 1090 s, 1055 vs, 1011 vs, 780 vs, 725 s, 535 vs, 510 sh
$Sn(CF_3)(CH_3)_3$	3080 vw, 3010 m, 2940 m, 1330 vw, 1220, 1210, 1205 (pqr) m, 1160 vs, 1075 vs, 810 sh, 785 s, 730 m, 541 s, 520 sh
$Sn(CF_3)_2(CH_3)_2$	3010 vw, 2930 vw, 1330 vw, 1220 m, 1165 vs, 1140 vs, 1095 vs, 1075 vs, 979 vw, 810 sh, 771 m, 735 w, 715 w, 550 m, 525 m

[a] Key: w, weak; vw, very weak; m, medium; s, strong; vs, very strong; sh, shoulder. [b] Reference 8: 2950, 2900, 1450, 1400, 1250, 1150, 980, 790, 530 cm^{-1}. [c] Reference 9: 3043 (w) 2993 (w) 2910 (m) 1282 (m) 1200 (m) 1120 (w) 1085 (w) 1052 (s) 775 (s) cm^{-1}.

the compounds was analyzed by their infrared, NMR, and mass spectra.

Reaction 5. A quantity of 0.757 g of $Sn(CH_3)_2F_2$ was placed in a nickel boat and placed in a nickel reactor. The following fluorination conditions were used at room temperature.

F_2 flow, cm^3/min	He flow, cm^3/min	Time, h
1.0	60	6
2.0	30	18
4.0	15	24
0.0	30	22

$Cd(CH_3)_2$ was added to a portion of the material in the boat after fluorination. The ^1H NMR spectrum showed only $Sn(CH_3)_4$. The mass spectrum showed only starting material. No apparent fluorination seemed to have occurred under the above conditions.

Infrared Spectra of Fluorine-Containing Methyltin Fluorides. The "off-white" tin fluorides etch glass slowly, as most tin fluorides do. The compounds are also hygroscopic, and the loose powder tends to adhere together after remaining at room temperature for days. A KBr pellet of the material shows the following infrared absorptions (cm^{-1}): 2960 (br, m), 2400 (br, w), 1260 (m), 1200 (m), 1160 (vs), 1080 (vs), 1040 (br, s), 800 (m), 750 (m), 570 (m), 380 (br, s); also present were the characteristic broad water peaks.

Discussion

From the experiments described, it is evident that the cleavage of the tin–carbon bond is the limiting factor toward the synthesis of $Sn(CF_3)_4$. It appears that during the fluo-

Table V. Melting Points of Polyfluorotetramethyltin Compounds

Compd	Mp, °C	Compd	Mp, °C
$Sn(CH_3)_4$	−54.2 to −53.5[a]	$Sn(CHF_2)(CH_3)_3$[d]	−70.5 to −66.4
$Sn(CH_2F)(CH_3)_3$[b]	−62.5 to −59.0	$Sn(CF_3)(CH_3)_3$	−57.0 to −53.2
$Sn(CH_2F)_2(CH_3)_2$[c]	<−80	$Sn(CF_3)_2(CH_3)_2$	−34.5 to −32.0

[a] Lit. mp −54.8 °C. [b] Bp 97–101 °C (745 mm).[8] [c] Cloudy until −63 °C. [d] Cloudy until −55 °C. Bp 111.5 °C.[9]

Table VI. Solvent Effect on ^{19}F Chemical Shifts of CF_3 Groups on $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$[a]

Solvent	$Sn(CF_3)(CH_3)_3$	$Sn(CF_3)_2(CH_3)_2$
Neat	−29.14	−31.46
Pyridine	−28.10	−29.25
$Sn(CH_3)_4$	−29.51	−32.36
$Cd(CH_3)_2$	−31.61	−34.11
CCl_4	−29.05[b]	

[a] Chemical shifts in ppm downfield from external TFA. [b] Reference 10.

Table VII. Weight Percent of Products of Polyfluorotetramethyltin Compounds and Gas Chromatographic Retention Times[a]

Compd	Wt %	GC retention time
$Sn(CH_3)_4$	48.4	38 min 47 s
$Sn(CH_3)_3(CF_3)$	12.9	67 min 0 s
$Sn(CH_3)_3(CH_2F)$[b]	12.9	69 min 55 s
$Sn(CH_3)_3(CHF_2)$	3.2	74 min 40 s
$Sn(CH_3)_2(CF_3)_2$[c]	12.9	77 min 13 s
$Sn(CH_3)_2(CH_2F)_2$	9.7	98 min 15 s

[a] Gas chromatograph conditions: 10% fluorosilicon on Chromosorb P, 3/8 in. × 25 ft Cu tubing, 0 °C isothermal/15 min, 2.5 °C/min → 50 °C/15 min, 2.5 °C/min → 80 °C/50 min. [b] Anal. Calcd: C, 24.40; H, 5.59; F, 9.66. Found: C, 24.31; H, 6.07; F, 9.40. [c] Anal. Calcd: C, 16.74; H, 2.09; F, 39.76. Found: C, 16.51; H, 2.28; F, 40.13.

rination process, a considerable number of Sn–C bonds are cleaved to produce Sn–F bonds. The methyltin fluorides produced are involatile, and this may account for the relatively small amount of volatile tin-containing materials recovered from the reaction of $Sn(CH_3)_4$ with fluorine. From the volatile materials, it is apparent that fluorination is occurring in that one obtains CF_4, CF_3H, and CF_2H_2 in considerable amounts. The various experiments described were intended to minimize these cleavage products in hope of obtaining $Sn(CH_3)_4$. However, it is apparent that $Sn(CF_3)_4$ was not produced in the reaction or that if $Sn(CF_3)_4$ did form, it was unstable in the fluorine atmosphere.

The question whether fluorination can convert methyl groups on tin to trifluoromethyl groups can be resolved by looking at the results of reaction 4. The reaction of the "off-white" powder with $Cd(CH_3)_2$ is most encouraging in that $Sn(CH_3)_4$, $Sn(CH_2F)(CH_3)_3$, $Sn(CH_2F)_2(CH_3)_2$, $Sn(CHF_2)(CH_3)_3$, $Sn(CF_3)(CH_3)_3$, and $Sn(CF_3)_2(CH_3)_2$ formed. The compounds form only after the addition of $Cd(CH_3)_2$. This implies that all existed as a tin fluoride, although it is not possible to report with confidence the number of fluorine atoms bonded directly to the tin. No effort was made to separate and study the physical properties of the tin fluorides formed here. Also no effort was made to study the thermodynamics of the CH_3 exchange of $Cd(CH_3)_2$ with the Sn–F compound to see if any redistribution had occurred. No $Cd(CF_3)(CH_3)$ or $Cd(CF_3)_2$ was formed in the addition of the $Cd(CH_3)_2$ to the "off-white" powder. Therefore it appears that no CF_3 transfer occurred. This is perhaps a consequence of an excess of "off-white" powder used and no solvent present. Speculation on the number of fluorines bonded to tin itself can proceed by first listing the possible fluorides that could result. $Sn(CH_3)_4$: $Sn(CH_3)_3F$, $Sn(CH_3)_2F_2$, $Sn(CH_3)F_3$, SnF_4; $Sn(CH_2F)(CH_3)_3$: $Sn(CH_2F)(CH_3)_2F$, $Sn(CH_2F)(CH_3)F_2$, $Sn(CH_2F)F_3$; $Sn(CH_2F)_2(CH_3)_2$: $Sn(CH_2F)_2(CH_3)F$, $Sn(CH_2F)_2F_2$; $Sn(CHF_2)(CH_3)_3$: $Sn(CHF_2)(CH_3)_2F$, $Sn(CHF_2)(CH_3)F_2$, $Sn(CHF_2)F_3$; $Sn(CF_3)(CH_3)_3$: $Sn(CF_3)(CH_3)_2F$, $Sn(CF_3)(CH_3)F_2$, $Sn(CF_3)F_3$; $Sn(CF_3)_2(CH_3)_2$: $Sn(CF_3)_2(CH_3)F$, $Sn(CF_3)_2F_2$.

Since the tin fluorides would be nonvolatile and ionic,[13] it is possible that for each of the compounds any of the listed fluorides or a combination are possible precursors. However, it is probable that the most important fluorides are $Sn(CH_3)_3F$, $Sn(CH_2F)(CH_3)_2F$, $Sn(CH_2F)_2(CH_3)F$, $Sn(CHF_2)(CH_3)_2F$, $Sn(CF_3)(CH_3)_2F$, and $Sn(CF_3)_2(CH_3)F$. Once one tin–carbon bond is replaced with a tin–fluoride bond, these compounds might be expected to become very much unreactive toward fluorine at low temperatures and to remain unfluorinated.

To summarize the reaction of fluorine with $Sn(CH_3)_4$, the following schematic is presented

$$Sn(CH_3)_4 + F_2/He \xrightarrow{\text{low temp}} SnR_x(CH_3)_yF + CF_4 + CF_3H + CF_2H_2 + HF$$

$$R = CH_3, CH_2F\ (x = 1, 2), CHF_2\ (x = 1), CF_3\ (x = 1, 2);\ x + y = 3$$

$$SnR_x(CH_3)_yF + Cd(CH_3)_2 \rightarrow Sn(CH_3)_4 + Sn(CH_2F)(CH_3)_3 + Sn(CH_2F)_2(CH_3)_2 + Sn(CHF_2)(CH_3)_3 + Sn(CF_3)(CH_3)_3 + Sn(CF_3)_2(CH_3)_2$$

It is interesting to note that there was no $Sn(CF_3)_3(CH_3)$ formed in the reaction.

It is apparent, as mentioned earlier, that a major process in the reaction of $Sn(CH_3)_4$ with fluorine is the cleavage of the tin–carbon bond. This can be seen in Table VII which lists the percentage of products obtained in the reaction with $Cd(CH_3)_2$. Assuming no redistribution, almost half of the amount of material formed is $Sn(CH_3)_4$. However, enough material survives the initial stages of fluorination to give equal amounts of $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$, which comprise approximately 25% of the products. This may indicate that it might be possible to synthesize $Sn(CF_3)_4$ from $Sn(CH_3)_4$ and fluorine under conditions other than those employed here.

The infrared spectra of CF_3-containing compounds are very characteristic and lead to ready identification of the number of CF_3 groups on the compound. (See Table IV.)

The mass spectra of $Sn(CH_2F)(CH_3)_3$, $Sn(CH_2F)_2(CH_3)_2$, and $Sn(CHF_2)(CH_3)_3$ are given in Table III. The highest m/e in each spectrum corresponds to the parent minus a methyl group, $P^+ - 15$ (CH_3). Also, the largest m/e for each is $Sn(CH_3)^+$. $Sn(CH_2F)_2(CH_3)_2$ gives some apparent rearrangements resulting in a m/e of 51 for CHF_2^+ and 163 for $Sn(CH_3)_3^+$. The mass spectra for $Sn(CF_3)_2(CH_3)_2$ and $Sn(CF_3)(CH_3)_3$ are those expected from halide exchange with bromine and chlorine in the mass spectrometer as observed in our laboratory.[14]

Both ^1H and ^{19}NMR spectra lead to conclusive identification of the tin compounds. Also present are the very characteristic tin-117 and -119 isotope satellites. Tables I and II give the proton and fluorine NMR data for the compounds. Although the number of compounds are few, several trends can be seen. (1) Increasing the number of CF_3 groups from one to two causes a large deshielding of the proton to cause the CH_3 resonance to drop from 0.09 to 0.39 ppm. (2) When there are no CF_3 groups, the CH_3 chemical shift is near 0.0 ($Sn(CH_3)_2(CH_2F)_2$ appears to be an anomaly). (3) $J_{^{117/119}Sn-H}$

increases with the number of fluorines on the molecule. (4) J_{HF} for a Sn–CH_2F group is greater than J_{HF} for a Sn–CHF_2 group. (5) $J_{117/119_{Sn-F}}$ values are much greater than $J_{117/119_{Sn-H}}$ values and appear to be dependent on the number of fluorines on the molecule. (6) Increased number of CF_3 groups causes a trend which lowers ^{19}F chemical shifts.

Besides the characteristic doublet and triplet patterns as a result of proton–fluorine coupling, the chemical shifts (in ppm) lead to ready identification of the groups. For protons: CH_3 (~0), CH_2F (~4.8), CHF_2 (~6.0). For fluorine: CF_3 (~−30), CHF_2 (~48), CH_2F (~190). Integration of the partially fluorinated species gives the number of CH_3 groups on tin.

The observation[10] that chlorine cleaves a methyl group rather than trifluoromethyl group from $Sn(CH_3)_3(CF_3)$ is intriguing for this reaction. If fluorine behaves in a similar manner, then once the groups CH_2F, CHF_2, and CF_3 form, they remain on the tin and a methyl group is cleaved. Schematically, the following is possible:

$$Sn(CH_3)_4 + F_2/He \rightarrow$$
$$Sn(CH_3)_3(CH_2F) + F_2/He \rightarrow Sn(CH_3)_2(CH_2F)F$$
$$Sn(CH_3)_2(CH_2F)_2 + F_2/He \rightarrow Sn(CH_3)(CH_2F)_2F$$
$$Sn(CH_3)_3(CHF_2) + F_2/He \rightarrow Sn(CH_3)_2(CHF_2)F$$
$$Sn(CH_3)_3(CF_3) + F_2/He \rightarrow Sn(CH_3)_2(CF_3)F$$
$$Sn(CH_3)_2(CF_3)_2 + F_2/He \rightarrow Sn(CH_3)(CF_3)_2F$$

It is possible that direct fluorination can be used for the two-step synthesis of fluorine-containing tetramethyltins. Previous to this report two fluoromethyltin compounds were reported: $Sn(CH_3)_3(CH_2F)$[8] and $Sn(CH_3)_3(CHF_2)$.[9] Quite vigorous conditions were required for the synthesis of the two compounds.

We are confident that with improvements in our fluorine technology, it may still be possible to synthesize $Sn(CF_3)_4$ by direct fluorination techniques. We have demonstrated that direct fluorination is indeed a useful method for the synthesis of trifluoromethyl compounds.[3–5] We are presently exploring other metal–alkyl systems.

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Registry No. $Sn(CH_3)_4$, 594-27-4; $Sn(CH_2F)(CH_3)_3$, 4554-91-0; $Sn(CH_2F)_2(CH_3)_2$, 65059-35-0; $Sn(CHF_2)(CH_3)_3$, 29723-38-4; $Sn(CF_3)(CH_3)_3$, 754-25-6; $Sn(CF_3)_2(CH_3)_2$, 65059-36-1; $Sn(CH_3)_2F_2$, 3582-17-0; $Cd(CH_3)_2$, 506-82-1; F_2, 7782-41-4.

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Decarbonylation of 2-Germaacetic Acid in Aqueous Solutions

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In dilute aqueous acid solutions (0.05–0.5 M H^+), 2-germaacetic acid decomposes to form carbon monoxide, an orange-yellow solid of approximate composition $GeH_{0.6}$, and small amounts of germane. The rate law for the reaction is $-d[GeH_3COOH]/dt = k[H^+][GeH_3COOH]$; $k = (5.59 \pm 0.14) \times 10^{-4}$ M^{-1} s^{-1} at 22.5 °C and ionic strength 1.0 M. From rate measurements in the temperature interval 0–39.5 °C, the activation energy was determined to be 16.9 kcal/mol. When the reaction is carried out in strongly acidic solutions (e.g., >6 M HCl, >4 M H_2SO_4, or >6 M $HClO_4$), carbon monoxide is evolved quantitatively, but no solid hydride or germane forms. The resulting solution contains the GeH_3^+ group, probably stabilized in the form of the germyloxonium ion, $GeH_3OH_2^+$. The data implicate GeH_2 as an intermediate of the reaction in dilute acid solutions.

Introduction

The decarbonylation of 2-germaacetic acid in aqueous acid was first studied by Kuznesof and Jolly.[1] They reported that the reaction produces 1 mol of carbon monoxide/mol of acid decomposed, variable small amounts of germane, and an insoluble orange solid containing germanium and hydrogen:

$$GeH_3COOH \xrightarrow{H^+} CO + xGeH_4 + \text{solid } (x << 1)$$

The purpose of this study was to determine more precisely the stoichiometry of the reaction and to investigate the mechanism of the reaction by the identification of intermediates and by a kinetic study.

Experimental Section

General Procedure. All manipulations were carried out using a standard vacuum line or a nitrogen-filled glovebag. Commercial 1,2-dimethoxyethane was dried with potassium hydroxide, filtered, refluxed with sodium metal, and then distilled. Germane gas from the Matheson Co. (minimum purity 99.8%) was used without further purification.

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