REACTION OF ARSENIC, ANTIMONY, BISMUTH AND SULFUR FLUORIDES WITH (t-BUTYLTHIO) TRIMETHYLSILANE

A. F. JANZEN* and O. C. VAIDYA Department of Chemistry, University of Manitoba, Winnipeg, Canada R3T 2N2

and

C. J. WILLIS

Department of Chemistry, University of Western Ontario, London, Canada N6G 5B7

(Received 28 July 1980; received for publication 29 August 1980)

Abstract—Tris(t-butylthio) derivatives of arsenic, antimony and bismuth have been prepared in high yield by the reaction of metal fluoride with (t-butylthio)trimethylsilane. The products have been characterized by elemental analysis, IR, Raman, proton NMR and mass spectrometry. Attempts to prepare As(V), Sb(V) or S(IV) derivatives were unsuccessful, although the reaction of SF₄ or Et₂NSF₃ suggests the formation of S(IV) intermediates.

INTRODUCTION

The reaction of metal halides with silicon-sulfur compounds has proved to be a convenient method for the preparation of new sulfur derivatives [1]. With metal fluorides, the reaction is also quite feasible [2] and, in this way, Schmutzler *et al.* have prepared As(SPh)₃ from Me₃SiSPh and arsenic trifluoride [3]. We have studied the reaction of Me₃SiSCMe₃ with arsenic, antimony, bismuth and sulfur fluorides and characterized the products by elemental analysis and spectroscopy. Although thioesters of As(III) and Sb(III) have been prepared by other synthetic routes and are well known, those of Bi(III) are still relatively rare [4].

EXPERIMENTAL

Volatile fluorides were handled in a metal vacuum system. Me₃SiSCMe₃[1] and Et₂NSF₃[5] were prepared by the literature methods; other compounds were of commercial origin. Proton NMR spectra were obtained on a Varian A-56/60A spectrometer and mass spectra were obtained on a Finnigan 1015 mass spectrometer at 70 eV. IR spectra were recorded on Perkin-Elmer 337 and Beckman IR-12 instruments in dichloromethane solution or as KBr pellets. In the far IR, Nujol mulls and polyethylene cells were used. Raman spectra were obtained using a Cary 82 krypton-ion laser operating at 647 nm. Elemental analyses were carried out by Analytische Laboratorien, Engelskirchen, Germany.

Preparation of As(SCMe₃)₃. AsF₃ (1.6 g, 12 mmol) was condensed onto Me₃SiSCMe₃ (5.9 g, 36 mmol) at -196° C. Reaction occurred on warming to 25°C to give a white solid, As(SCMe₃)₃, in essentially quantitative yield, m.p. 108–110°C, ¹H NMR 1.4 ppm. Anal. Calc. for C₁₂H₂₇S₂As: C, 42.09; H, 7.09%. Found: C, 41.70; H, 7.74%.

Preparation of Sb(SCMe₃)₃. SbF₃ (1.8 g, 10 mmol) was introduced slowly from a sidearm attached to a reaction vessel containing Me₃SiSCMe₃ (4.9 g, 30 mmol) and the progress of the reaction monitored by observing the pressure changes due to volative Me₃SiF. Removal of Me₃SiF left behing Sb(SCMe₃)₃, a pale-yellow solid, in quantitative yield, m.p. 148–150°C, ¹H NMR 1.5 ppm. Anal. Calc. for C₁₂H₂₇S₃Sb: C, 37.02; H, 6.99%. Found: C, 36.80; H, 6.98%.

Preparation of Bi(SCMe₃)₃. BiF₃ (2.0 g, 7.5 mmol) and Me₃SiSCMe₃ (3.7 g, 23 mmol) were sealed in a reaction tube and shaken for 3 days at 25°C. Removal of volatile products left

behind a yellow solid Bi(SCMe₃)₃ in quantitative yield, m.p. 150°C dec. ¹H NMR 1.5 ppm. Anal. Calc. for $C_{12}H_{27}S_3Bi$: C, 30.25; H, 5.71%. Found: C, 30.43; H, 5.60%. The product is stable if stored in an evacuated tube but decomposes in air and in dichloromethane solution.

Treatment of Bi(SCMe₃)₃ with mercury gave Hg(SCMe₃)₂. Anal. Calc. For $C_8H_{18}S_2Hg$: C, 25.35; H, 4.79%. Found: C, 25.22; H, 4.79%.

Reaction of Me₃SiSCMe₃ with As(V) and Sb(V)

 Ph_3AsCl_2 (1.3 g, 3.4 mmol) and $Me_3SiSCMe_3$ (1.2 g, 7.4 mmol) in CH_2Cl_2 at 25°C for 48 hr gave Ph_3As and $Me_3CSSCMe_3$.

Ph₃SbCl₂ (1.4 g, 3.3 mmol) and Me₃SiSCMe₃ (1.1 g, 6.8 mmol) in CH₂Cl₂ at 25°C for 48 hr gave Ph₃Sb and Me₃CSSCMe₃.

SbCl₅ (1.2 g, 4.0 mmol) was added dropwise to Me₃SiSCMe₃ (3.3 g, 20 mmol) at 0°C. Me₃SiCl was removed under vacuum and Sb(SCMe₃)₃ and Me₃CSSCMe₃ remained behind. All products were identified by ¹H NMR and mass spectrometry and by comparison with authentic samples.

Reaction of $Me_3SiSCMe_3$ with Sn(IV). $SnCl_4$ (1.9 g, 7.3 mmol) and $Me_3SiSCMe_3$ (4.7 g, 29 mmol) at 25°C for 5 days in a sealed tube gave $Sn(SCMe_3)_4$, ¹H NMR 1.5 ppm. Anal. Calc. for $C_{16}H_{36}S_4Sn: C$, 40.42; H, 7.63; S, 26.98%. Found: C, 40.60; H, 7.43; S, 27.08%. The mass spectrum of $Sn(SCMe_3)_4$ showed the following characteristic peaks: $Sn(SCMe_3)_4^+$, $Sn(S)(SCMe_3)_3^+$, $Sn(SCMe_3)_3^+$, $Sn(SH)(SCMe_3)_2^+$, $Sn(SH)_2SCMe_3^+$, $Sn(SH)_3^+$.

Reaction of Me₃SiSCMe₃ with S(IV) fluorides. SF₄ (1.2 g, 11 mmol) was condensed onto Me₃SiSCMe₃ (7.2 g, 44 mmol) at -196° C and the temperature increased to -63° C and finally to 25°C. Me₃SiF was removed under vacuum and an oil (4.1 g) remained which was identified as a 1:1 mixture of Me₃CSSCMe₃ and Me₃CSSSCMe₃ by the following experiments: (a) A cryoscopic molecular weight study in benzene gave a molecular weight of 193.1. Calc. for a 1:1 mixture 194.4. (b) The mass spectrum showed peaks due to Me₃CSSCMe₃ and Me₃CSSSCMe₃ but no peaks at higher *mle* values. (c) An authentic mixture gave the same ¹H NMR spectrum.

The reaction of Et_2NSF_3 with $Me_3SiSCMe_3$, using the above procedure, gave a 1:1 mixture of $Et_2NSSCMe_3$ and $Me_3CSSCMe_3$. Mass spectrum of $Et_2NSSCMe_3$: m/e 193(M⁺), 137(Et_2NSSH^+). ¹H NMR of $Et_2NSSCMe_3$: 1.26 ppm (s, Me_3C), 1.06 ppm (t, CH₃), 2.74 ppm (q, CH₂), ³J_{HH} = 7.0 Hz.

RESULTS AND DISCUSSION

The reaction of (t-butylthio)trimethylsilane with arsenic, antimony and bismuth trifluoride is a convenient, high yield method of preparing tris(t-butylthio) derivatives of these metals. Reaction with AsF₃ or SbF₃ occurs

^{*}Author to whom correspondence should be addressed.

Table 1. Vibrational spectra of M(SCMe₃)₃ in region 600-80 cm⁻¹, M=As, Sb, Bi

As(SCMe3)3			Sb(SCMe $_3$) $_3$			Bi(SCMe3)3		
IR Solid	Raman		IR	Raman		IR	Raman	
	Solid	Soln	Solid	Solid	Soln	Solid	Solid	Assignment
576	581	578(p)	577	579	578(p)	578	580	CS str.
						443		
	458	457	433	434	439	420	424	
447	449	448	384	384	390			MS str.
						377	383	
387	389	393	358	362	362			MS str.
362	370	369				348	351	
250	257	255(p)	238	243	246(p)		227	MSC bend
	157	159(p)		134	136(p)		120	SMS bend
	101	98		82				

below 25°C while reaction with

$$MF_3 + 3Me_3SiSCMe_3 \rightarrow M(SCMe_3)_3 + 3Me_3SiF \quad (1)$$

$$1 M = As$$
$$2 M = Sb$$

3 M = Bi

BiF₃ is slower and requires 3 days at 25°C. Complete substitution occurs in each case and the reaction is presumably favoured by the formation of volatile Me₃SiF.

Compounds 1-3 are monomeric in the gas phase, as judged by their mass spectra. In each case, the following ions are present: $M(SCMe_3)_3^+$, $M(SH)(SCMe_3)_2^+$, M(S) $(SCMe_3)_2^+$, $M(SCMe_3)_2^+$, $M(S)(SH)SCMe_3^+$, $M(SH)SCMe_3^+$, $M(S)SCMe_3^+$, $M(S)(SH)_2^+$, $M(SH)_2^+$. The formation of these ions is adequately accounted for by the successive loss of SCMe₃, $CH_2=CMe_2$ and H from the molecular ion.

The vibrational spectra of 1 and 2 as solids or in dichloromethane solution are very similar in the region 600-80 cm⁻¹, as seen in Table 1, and these compounds are undoubtedly monomeric in the solid and liquid state. Mehrotra *et al.* found Sb(SCMe₃)₃ to be monomeric in benzene solution[6]. In view of the similarity of the vibrational spectrum of 3 with that of 1 and 2, we assume 3 to be monomeric in the solid state, although it may be noted that *t*-butylthio derivatives of the heavier elements, e.g. Hg(SCMe₃)₂ are polymeric[7].

The reaction of Me₃SiSCMe₃ with SnCl₄ gave the expected Sn(SCMe₃)₄[8], however, attempts to prepare S(IV) derivatives by reaction with SF₄ or Et₂NSF₃ were unsuccessful, instead, reduction occurred, eqns (2) and (3). The decomposition of the postulated

intermediates of eqns (2) and (3) is analogous to the decomposition of $(CF_3)_2S(OCF_3)_2$ to CF_3SCF_3 and $CF_3OOCF_3[9]$.

Attempts to prepare As(V) or Sb(V) derivatives [6, 10] by reacting $Me_3SiSCMe_3$ with SbCl₅, Ph₃SbCl₂ or Ph₃AsCl₂ at 25°C were unsuccessful, instead, As(III) or Sb(III) products were formed, plus $Me_3CSSCMe_3$.

$$SbCl_{5} + 5Me_{3}SiSCMe_{3} \xrightarrow{-5Me_{3}SiCl} \\Sb(SCMe_{3})_{3} + Me_{3}CSSCMe_{3}$$
(4)

$$Ph_3AsCl_2 + 2Me_3SiSCMe_3 \xrightarrow{-2Me_3SiCl} \rightarrow$$

$$Ph_3As + Me_3CSSCMe_3.$$
(5)

Acknowledgement—The financial assistance of the Natural Sciences and Engineering Research Council of Canada is grate-fully acknowledged.

REFERENCES

- 1. E. W. Abel and D. A. Armitage, Adv. Organomet. Chem. 5, 1 (1967).
- S. C. Peake and R. Schmutzler, J. Chem. Soc. (A) 1049 (1970); D. H. Brown, K. D. Crosbie, J. I. Darragh, D. S. Ross and D. W. A. Sharp. J. Chem. Soc. (A) 914 (1970); G. H. Sprenger and A. H. Cowley. J. Fluorine Chem. 7, 333 (1976); R. G. Cavell, D. D. Poulin, K. I. The and A. J. Tomlinson, J. Chem. Soc., Chem. Commun. 19 (1974).
- R. J. Singer, M. Eisenhut and R. Schmutzler, J. Fluorine Chem. 1, 193 (1971-72).
- W. Herrmann, In Houben-Weyl Methoden der Organischen Chemie IV/2, p. 411. Georg Thieme Verlag, Stuttgart (1963);



M. Dub, Organometallic Compounds, Vol. 3, 2nd Edn. Springer-Verlag, New York (1968); G. O. Doak and L. D. Freedman, Organometallic Compounds of Arsenic, Antimony and Bismuth, Chap. IX. Wiley, New York (1970); T. B. Brill and N. C. Campbell. Inorg. Chem. 12, 1884 (1973); M. Wieber and U. Baudis, Z. Anorg. Allgem. Chemie. 423, 40 (1976).

- G. C. Demitras and A. G. MacDiarmid. *Inorg. Chem.* 6, 1903 (1967); S. P. von Halasz and O. Glemser, *Chem. Ber.* 103, 594 (1970).
- R. C. Mehrotra, V. D. Gupta and S. Chatterjee, Austral. J. Chem. 21, 2929 (1968).
- 7. N. R. Kunchur. Nature 204, 468 (1964).
- R. C. Mehrotra, V. D. Gupta and D. Sukhani. J. Inorg. Nucl. Chem. 29, 1577 (1967).
- T. Kitazume and J. M. Shreeve, J. Am. Chem. Soc. 99, 4194 (1977).
- 10. H. Schmidbaur and K.-H. Mitschke, Chem. Ber. 104, 1837, 1842 (1971).