Trimethylsilylmethyl Derivatives of Mercury

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Bis(trimethylsilylmethyl)mercury is only slowly decomposed at 200 °C whereas photolysis causes extensive decomposition. The vibrational and ^{1}H n.m.r. spectra of Me_3SiCH_2HgX (X = Me_3SiCH_2, Cl, Br, or I) are reported and discussed together with the mass spectrum of $(Me_3SiCH_2)_2Hg$.

THE Me_3SiCH_2 group is of current interest because of the high kinetic stability of its bonds to a variety of transition metals.[1] This enhanced stability over, for example, ethyl–metal bonds has been attributed to the position of the silicon atom, so that decomposition by a β-hydride elimination process is not possible. In this paper we describe some properties of $(Me_3SiCH_2)_2Hg$, first prepared by Seyferth [2] in 1961, together with a spectroscopic study of its halide derivatives, Me_3SiCH_2HgX.

Bis(trimethylsilylmethyl)mercury (1) was readily prepared in 73% yield from Me_3SiCH_2MgCl [3] and mercuric chloride in tetrahydrofuran as a colourless liquid.[2,4] In an evacuated system slight decomposition was observed (formation of a small globule of mercury) after 60 h at 160 °C, but even after 100 h at 200 °C over 95% could be recovered unchanged. Tetramethylsilane was identified as a decomposition product together with $Me_3SiCH_2HgCH_2Si(Me)_2CH_2CH_2SiMe_3$ (2), both doubtless formed by radical processes. By comparison [5,6] Et_2Hg decomposes explosively at 205 °C and $Pr^i{}_2Hg$ is 85% decomposed after 15 h at 150 °C. Like other organomercurials, (1) decomposes photochemically but, even after repeated irradiation (medium-pressure Hg lamp) in an evacuated quartz vessel, unreacted material remained. Tetramethylsilane was the main photolysis product together with methane. Coupled g.l.c.–mass spectroscopic examination of the remaining liquid fraction confirmed the presence of both mercury-containing and organosilicon compounds resulting from reactions involving the radicals, $Me_3SiCH_2\cdot$, $Me_3Si\cdot$, and $Me\cdot$, and allowed the identification of products with the following probable structures: $(Me_3SiCH_2)_2$, Me_6Si_2, $(Me_3SiSiMe_2)_2$, $(Me_3SiCH_2CH_2SiMe_2CH_2)_2$, $Me_3SiCH_2HgCH_2SiMe_2CH_2SiMe_3$, (2).

The trimethylsilylmethylmercuric halides Me_3SiCH_2HgX (X = Cl, Br, I) were isolated in theoretical yield according to equation (1), as white crystalline solids

$$(Me_3SiCH_2)_2Hg + HgX_2 \xrightarrow[20\ ^\circ C]{EtOH} 2Me_3SiCH_2HgX \qquad (1)$$

having considerably lower melting points than the corresponding methylmercuric halides (Table 1). As with other diorgano-mercurials, reaction (1) was noticeably slower for X = I than for Cl or Br, and above 35° the molten iodide deposited yellow HgI_2; this disproportionation could be reversed in boiling EtOH. The chemical reactivity of (1) appeared to be lower than that of Me_2Hg and it did not react with powdered beryllium at 200 °C or with $(Ph_3P)_2PtCl_2$ in benzene.

TABLE 1

Trimethylsilylmethyl-derivatives of mercury

		Found			Calc.		
Compd.	M.p.(b.p.)/°C	C	H	Hg	C	H	Hg
R_2Hg	(34—36°, 0·17mmHg)	25·2	5·9	53·3	25·6	5·9	53·5
RHgCl	71[76] [a]	14·9	3·4	62·4	14·9	3·4	62·1
RHgBr	54	13·2	2·9	54·4	13·1	3·0	54·6
RHgI	29	11·6	2·7	48·4	11·6	2·7	48·4

[a] F. C. Whitmore and L. H. Sommer, *J. Amer. Chem. Soc.*, 1946, **68**, 481.

Vibrational Spectra.—Data are collected in Table 2. For $(Me_3SiCH_2)_2Hg$, although the 'rule of mutual exclusion' demanded by the presence of a centre of symmetry is not obvious above 750 cm^{-1} (through accidental degeneracies among the CH_3– and –CH_2– vibrations), the idealised C_{2h} symmetry is reflected in features arising from the vibrations of the $C_3SiCHgCSiC_3$ skeleton. In the i.r. or Raman spectrum, there is only one band attributable to ν(HgC), the Raman shift at 513 cm^{-1} being strongly polarised (A_g mode) with the i.r. absorption at slightly higher frequency (B_u). Similarly, although all the ν(SiC) modes ($3A_g + B_g + A_u + 3B_u$) cannot be distinguished, two polarised Raman bands (612 and 720 cm^{-1}) have no i.r. counterparts and can be identified as A_g fundamentals. In a recent study,[7] the vibrational spectrum of Et_2Hg was shown to be consistent with predictions based on the Point Group C_{2h} whereas $Pr^n{}_2Hg$ and $Bu^n{}_2Hg$ appear to be of lower symmetry, and this has been explained [8] in terms of restricted rotation about C–C bonds. The δ(CHgC) modes are Raman-inactive ($A_u + B_u$) and were not detected.

For the halides Me_3SiCH_2HgX (C_s symmetry), ν(HgX) (a') is found in the Raman effect at 327 (p), 225 (p), and 189 cm^{-1} (X = Cl, Br, or I; EtOH soln.),

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[1] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533; and references therein.

[2] D. Seyferth and W. Freyer, *J. Org. Chem.*, 1961, **26**, 2604.

[3] L. H. Sommer, R. M. Murch, and F. A. Mitch, *J. Amer. Chem. Soc.*, 1954, **76**, 1619.

[4] M. Kumada and M. Ishikawa, *J. Organometallic Chem.*, 1966, **6**, 451.

[5] G. A. Razuvaev, O. N. Druzhkov, S. F. Zhil'tsov, and G. G. Petukhov, *J. Gen. Chem. U.S.S.R.*, 1965, **35**, 176.

[6] E. Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1769.

[7] J. L. Bribes and R. Gaufrès, *Spectrochim. Acta*, 1971, **27A**, 2133.

[8] D. Seybold and K. Dehnicke, *J. Organometallic Chem.*, 1968, **11**, 1.

close to the values for other RHgX compounds.[9] Interestingly however, for X = Cl or Br large shifts to 304 and 211 cm^{-1} occur for solid samples. In addition, for X = Br the ν(HgC) fundamental [538 cm^{-1} (p)] splits into two well separated components of equal intensity in the solid at 528 and 540 cm^{-1}. These solid state effects may arise from some interaction between adjacent Hg atoms with a contribution from halogen-bridged structures. Similar splitting of ν(HgC), reported [10] for cyclopropylmercury azide, has been discussed in terms of rotational isomerism.

TABLE 2

Vibrational spectra/cm^{-1}

$(Me_3SiCH_2)_2Hg$ [a]		Me_3SiCH_2HgCl		Me_3SiCH_2HgBr		Me_3SiCH_2HgI		Approximate description
I.r.	Raman	I.r.[b]	Raman [c]	I.r.[b]	Raman [c]	I.r.[b,d]	Raman [d]	
2950s	2955m(dp)	2955m	2960s	2955s	2960s	2960s		$\nu_{as}(CH)$
2880m	2897vs(p)	2895w	2900vs	2900m	2900vs	2905m,sh		$\nu_s(CH)$
1403w	1410m(dp)	1405w	1410w	1410w	1410w	1415m		$\delta(CH_3) + \delta(CH_2)$
1350w,br	1360s(p)	1350w	1355m	1350w	1350w	1352m		
1258s,sh	1262s(p)	1260s,sh				1260s,sh	1265m	
1247vs	1250s(dp)	1250vs	1250m(dp)	1248vs	1250w	1250vs		
		1000m	1028s(p)	1000m	1018vs	1000m	1009s	$\delta(CH_2)$
980s	985vs(p)					960w,br	950w	
950m,sh								
850vs,br		850vs,br		850vs,sh		840vs,br		$\rho(CH_3)$
826vs	830w(dp)	832vs	840w	834vs	840vw,br		840vw,br	
760s	755w(dp)	768s		765m		768s		
		750m	755w(p)	752m	750m	750m		
709s	720m(p)	710s	725m(dp)	705m	720s(dp)	705s	718m	$\nu_{as}(SiC)$
681s	690m(dp)	690m	693m(dp)	687m	690s(dp)	690s	695m	
	612vs(p)							$\nu_s(SiC)$
600w		605w	618s(p)	610w	615s(p)	603m	613m	
530m								$\nu_{as}(HgC)$
	522vs(p)	525w	535vs(p)	530vw,br	538vs(p) *	525w	530vs	$\nu(HgC)$
		320w,br	327vs(p) *					$\nu(HgCl)$
	270s(p)	267vw	270s(p)		270w	260vw	270vw	$\delta(SiC_3)$
	234s(dp)		235m(dp)		230w,sh		225w	
					225vs(p) *			$\nu(HgBr)$
							189s	$\nu(HgI)$
	170vs(p)		175vs(p)		171s(p)		160s	$\delta(SiCHg) + \delta_s(SiC_3)$
	120m(dp)							
							114s	$\rho(SiC_3)$
					104s(dp)			

[a] Pure liquid. [b] KBr disc, Nujol mull. [c] Powdered solid: (p) polarised, (dp) depolarised (EtOH solution). [d] Molten sample.
* Raman shifts in EtOH soln.; marked wavenumber-change or splitting observed in solid state (see text).

Wavenumbers reported for ν(HgC) span the range 430—604 cm^{-1} so that the present values are typical. Available data [9] for δ(CHgX) suggest that these should be found below 100 cm^{-1}; the remaining skeletal vibrations are those involving CSiC and SiCHg angle bending. By analogy with other Me$_3$Si– derivatives,[11] Raman bands near 270 (p), 230 (dp), and 170 (p) cm^{-1} may be assigned to $\delta(SiC_3)$, (*a*′, *a*″, and *a*′ respectively) with some contribution to the strong 170 cm^{-1} band possibly arising from $\delta_s(SiCHg)$. Bands observed below 150 cm^{-1} are probably due to $\rho(SiC_3)$ as suggested in Table 2.

Wilkinson and co-workers [1] have found i.r. and Raman bands near 1000 cm^{-1} (–CH$_2$– wag/twist) for a number of Me$_3$SiCH$_2$–M derivatives which are M-sensitive. We observe similar bands for the mercury derivatives; little variation in frequency occurs with X in Me_3SiCH_2HgX (X = Me$_3$SiCH$_2$–, Cl, Br, or I).

N.m.r. Spectra.—The large increase in $^2J(^{199}HgH)$ and the downfield shift of τCH_2 between (1) and Me_3SiCH_2HgX (Table 3) parallel changes observed for related methyl- and ethyl-mercurials. As expected a noticeable increase in τCH_2 occurs from values with chloroform as solvent to those measured in benzene solution, due to the anisotropy effects associated with the latter. Altering X in RHgX results in only small variations in τCH_2

TABLE 3

^{1}H N.m.r. data [a]

	Solvent [b]	τCH_3	τCH_2	$\lvert ^2J(^{199}HgH)\rvert$	$\lvert ^4J(^{199}HgH)\rvert$
$(Me_3SiCH_2)_2Hg$	Neat [c]	9·95	9·90	127·3	*d*
$(Me_3SiCH_2)_2Hg$	CDCl$_3$	9·90	9·85	130·4	*d*
Me_3SiCH_2HgCl	CDCl$_3$	9·89	8·97	249·9	7·1
Me_3SiCH_2HgBr	CDCl$_3$	9·92	8·92	246·0	7·2
Me_3SiCH_2HgI	CDCl$_3$	9·90	8·81	*d*	*d*
$(Me_3SiCH_2)_2Hg$	C$_6$H$_6$	9·80	9·90	128·1	*d*
Me_3SiCH_2HgCl	C$_6$H$_6$	10·05	9·67	250·0	7·0
Me_3SiCH_2HgBr	C$_6$H$_6$	10·11	9·56	252·8	6·7
Me_3SiCH_2HgI	C$_6$H$_6$	10·00	9·36	*d*	*d*

[a] Chemical shifts measured upfield from C_6H_6 or C^1HCl_3 at 35 °C: τ values (±0·01) calculated assuming $\delta(C_6H_6) = 7{\cdot}26$ and $\delta(C^1HCl_3) = 7{\cdot}25$ p.p.m. downfield from Me$_4$Si. Coupling constants, Hz, ±0·3. [b] *Ca.* 5—10% *v*/*v* solutions. [c] τ Values measured from external Me$_4$Si. [d] *J* not determined.

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[9] Z. Meic and M. Randic, *Trans. Faraday Soc.*, 1968, **64**, 1438; E. Maslowsky and K. Nakamoto, *Inorg. Chem.*, 1969, **8**, 1108.

[10] A. F. Shihada and K. Dehnicke, *J. Organometallic Chem.*, 1971, **26**, 157.

[11] J. R. Durig, K. K. Lau, J. B. Turner, and J. Bragin, *J. Mol. Spectroscopy*, 1969, **31**, 419; R. D. George, K. M. Mackay, and S. R. Stobart, *J. Chem. Soc.* (*A*), 1970, 3250.

although a downfield trend (Cl > Br > I) is observed. For Me_3SiCH_2HgI, satellites arising from $^2J(^{199}HgH)$ were not observed. An absence of satellites is likewise found for MeHgI, and has been attributed[12] to a relaxation through quadrupolar interaction between ^{127}I and ^{199}Hg, rather than exchange of Me with spin-zero Hg nuclei.

TABLE 4

Mass spectrum of $(Me_3SiCH_2)_2Hg$

m/e [a]	% Ion current	Formula or probable structure
376	5·5	$(Me_3SiCH_2)_2Hg^{+\cdot}$
361	39·0	$Me_3SiCH_2HgCH_2SiMe_2^+$
304	<0·1	$Me_3SiCH_2HgMe^{+\cdot}$
289	0·4	$Me_3SiCH_2Hg^+$
275	<0·1	Me_3SiHg^+
274		$Me_2SiCH_2Hg^{+\cdot}$
259	0·2	$MeSiCH_2Hg^+$
202	1·3	$Hg^{+\cdot}$
173	2·2	$[(Me_2SiCH_2)_2Hg]^{2+}$
145	0·1	$C_6H_{17}Si_2^+$
143	0·1	$C_6H_{15}Si_2^+$
131	1·2	$C_5H_{15}Si_2^+$
129	0·6	$C_5H_{13}Si_2^+$
115	0·6	$C_4H_{11}Si_2^+$
101	0·2	Hg^{2+}
87	2·4	$C_4H_{11}Si^+$
86	0·2	$C_4H_{10}Si^{+\cdot}$
85	0·6	$C_4H_9Si^+$
73	7·6	Me_3Si^+
72	8·9	$Me_2SiCH_2^{+\cdot}$
71	0·7	$C_3H_7Si^+$
70	0·5	$C_3H_6Si^{+\cdot}$
59	8·9	Me_2SiH^+
58	3·6	$C_2H_6Si^{+\cdot}$
57	1·4	$C_2H_5Si^+$
45	2·2	CH_5Si^+
44	4·2	$CH_4Si^{+\cdot}$
43	4·4	CH_3Si^+
31	1·8	H_3Si^+
29	1·0	HSi^+

[a] For ^{202}Hg and ^{28}Si.

Aluminium chloride is known to catalyse the exchange of alkyl groups in Me_2Hg and Et_2Hg.[13] We find that addition of $AlCl_3$ to chloroform solutions of (1) and of Me_3SiCH_2HgCl results in immediate collapse of peaks due to $^2J(^{199}HgH)$ and $^4J(^{199}HgH)$ and broadens the τCH_2 resonances, together with the appearance of small peaks in the τ 9·5—10·5 region which can be assigned to alkylated aluminium species.

Mass Spectra.—The photolysis products referred to earlier were separated and identified by combined g.l.c.–mass spectrometry. Each compound produced a parent ion, and fragment ions were consistent with the structures given although these were not rigorously established.

The mass spectrum of (1) (Table 4) was examined in greater detail. It is unusual in relation to other diorganomercurials in that *ca.* 50% of the ion current is carried by mercury-containing species, the most abundant ion being (parent — CH_3). The group of ions showing a mercury isotope pattern at 171—174 a.m.u. was identified as the doubly charged species $[(Me_2SiCH_2)_2Hg]^{2+}$ and, since the corresponding singly charged ion is not observed, it is probably formed by the process

$$Me_3SiCH_2HgCH_2SiMe_2^+ \longrightarrow Me^- + [(Me_2SiCH_2)_2Hg]^{2+}$$

There was evidence for the occurrence of rearrangement processes resulting in ions with Si–Hg and CH_3–Hg bonds as well as even-electron ions containing two Si atoms, the most abundant of these being $C_5H_{15}Si_2^+$.

EXPERIMENTAL

I.r. spectra were obtained with a Perkin-Elmer 457 spectrometer, and Raman spectra from 488·0 nm (Ar ion laser) with a Cary 83 instrument, to give measurements considered accurate to ±2 cm^{-1} for sharp peaks. Me_3SiCH_2HgI decomposed in the laser beam and polarisation data were not obtained, but the rate of sample deterioration could be reduced by unfocussing the laser at the sample point. For n.m.r. experiments and mass spectrometric measurements, the instruments used were Varian A60-D and A.E.I. MS 902 or 30 with linked g.l.c.

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