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ORGANOSILYLMERCURIALS, A MASS SPECTRAL STUDY *

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Summary

The mass spectra of a number of organosilylmercurials and related compounds have been examined. Although the spectra are dominated by mercury free fragments, all compounds showed parent molecular ions and most showed other mercury containing fragments.

Extrusion of mercury was found to be the most important fragmentation process and was supported by metastable peaks in several examples. Bis(triethylsilyl)mercury showed a metastable peak for the formation of Et_3Si^+ from the parent molecular ion. This was the only other example of the fragmentation of a parent molecular ion supported by a metastable fragment. The effect of substitution of longer chain alkyl, alkene, phenyl, and chlorine groups on bis(trimethylsilyl)mercury are reported and discussed.

Introduction

Despite considerable interest in the mass spectra of organometallic compounds [1], only a few studies have been reported on mercury derivatives. Among these, several reports [2—8] have appeared providing information on the electron impact induced fragmentations of a variety of organomercurials. In addition a few studies have appeared in which mass spectroscopy has been used to determine the molecular weight of organosilyl-mercurials, [9—11] and to determine the bond dissociation energy of bis(trimethylsilyl)mercury [12]. The only report of the fragmentation of a silyl mercurial was by Bentler and Urry [13], who reported that 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane (I) showed a molecular ion and loss of one or two mercury atoms. Bennett et al. [14] reported seeing the two symmetric and mixed species in a mixture of bis(trimethylsilyl)- and bis(trimethylgermyl)mercury, while Eaborn et al. [15] report the intensities of the lines of the parent and loss of one methyl

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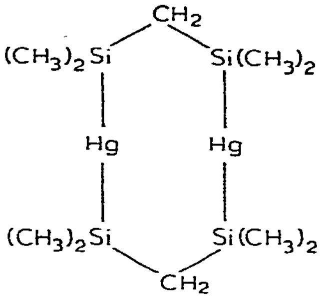
group from bis(trimethylgermyl)mercury. We now wish to report the mass spectra of a variety of silylmercury derivatives in an effort to determine their



(I)

characteristic fragmentation patterns and to provide additional details concerning their decomposition paths.

Experimental

All syntheses and sample preparations were carried out in a glove box or under a nitrogen or argon atmosphere using standard techniques for handling air sensitive compounds. The following compounds were prepared by methods reported in the literature: di-tert-butylmercury [16], bis(trimethylsilyl)mercury [17], bis(trimethylgermyl)mercury [15], bis(dimethyl-1-pent-4-enylsilyl)-mercury [9], bis(methyldichlorosilyl)mercury [18], bis(dimethylchlorosilyl)-mercury [19], bis(trichlorosilyl)mercury [20], 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane, and 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasilacyclohexane [13].

All other symmetrical compounds were prepared by either of two procedures: The first of these is the direct reaction of a silane with di(tert-butyl)mercury. The typical procedure illustrating this method is given for the preparation of bis(dimethylphenylsilyl)mercury. The reactants, 1.36 g, $HSiMe_2Ph$ and 1.57 g $Hg(t\text{-}Bu)_2$ in a mole ratio of 2 : 1 were placed in a reaction tube which then was evacuated, sealed and placed in an 85°C oil bath for two days. The reaction mixture turned green during this time and small amounts of elemental mercury were noted. At the end of this arbitrary time, the reaction vessel was attached to the vacuum system and the volatile products were removed leaving a viscous yellow-green liquid with a very low vapor pressure. This liquid was dissolved in cyclopentane and the solution placed in a dry ice chest for several days. During this time 0.6 g of light green-yellow crystals formed and were removed by filtration, m.p. 92—94°C. Found: C, 41.14; H, 4.97; Hg, 42.37; Si, 11.73; calcd. C, 40.78; H, 4.67; Hg, 42.60; Si, 11.93%.

Other compounds prepared by this method include $(Ph_3Si)_2Hg$, m.p. 210—213°C; $(MePh_2Si)_2Hg$, m.p. 62—66°C; $[(Me_2SiCH_2)Me_2Si]_2Hg$; $[(Me_3Si)_3Si]_2$-Hg, m.p. 194—197°C, found: C, 31.31; H, 7.87; Hg, 28.90; Si, 32.65; $C_{18}H_{54}Si_8H_9$, calcd.: C, 31.03; H, 7.176; Si, 32.18; Hg, 29.02%; $[Me_2(PhCH_2)$-$Si]_2Hg]$; $(Me_2n\text{-}PrSi)_2Hg$; and $(MeEt_2Si)_2Hg$.

(continued on p. 178)

TABLE 1

THE INTENSITIES OF THE MERCURY CONTAINING FRAGMENTS AND THE PRINCIPAL MERCURY FREE FRAGMENTS PRODUCED ON ELECTRON IMPACT FRAGMENTATION OF $(R_3E)_2Hg$ DERIVATIVES AND OF COMPOUND I

Compound	Ions	*m/e*	Σ [a] (%)	Relative [b] abundance	Σ Hg [c] containing ions (%)
$[(CH_3)_3Si]_2Hg$ (70°C) [d]	$C_6H_{18}HgSi_2$	348	15.58	37.12	44.01
	$C_5H_{15}HgSi_2$	333	5.50	13.10	15.54
	C_3H_9HgSi	275	2.16	5.16	6.10
	C_2H_6HgSi	260	0.38	0.90	1.07
	Hg^+	202	11.06	26.37	31.24
	$C_6H_{18}Si_2$	146	1.66	4.25	
	$C_5H_{15}Si_2$	131	4.00	10.25	
	Hg^{++}	101	0.72	1.71	2.03
	C_3H_9Si	73	39.04	100	
$[(C_2H_5)(CH_3)_2Si]_2Hg$ (70°C) [d]	$C_{16}H_{44}HgSi_4$ [e]	550	trace	—	
	$C_{14}H_{38}HgSi_3$ [e]	492	0.16	0.41	1.92
	$C_{12}H_{33}HgSi_3$ [e]	463	trace	—	
	$C_{10}H_{28}HgSi_3$ [e]	434	1.28	3.27	15.35
	$C_9H_{25}HgSi_3$ [e]	419	0.04	0.10	0.48
	$C_{10}H_{27}HgSi_2$ [e]	405	0.07	0.18	0.84
	$C_8H_{22}HgSi_2$	376	3.14	8.01	37.65
	$C_7H_{19}HgSi_2$	361	0.21	0.54	2.52
	$C_6H_{17}HgSi_2$	347	0.42	1.07	5.04
	$C_4H_{11}HgSi$	289	0.16	0.41	1.92
	Hg	202	2.35	6.00	28.18
	$C_6H_{17}Si_2$	145	3.98	10.16	
	$C_4H_{14}Si_2$	117	4.87	12.43	
	Hg^{++}	101	0.51	1.30	6.12
	$C_4H_{11}Si$	87	39.18	100.0	
	C_3H_9Si	73	3.56	9.09	
	C_2H_7Si	59	19.73	50.36	
	C_2H_8Si	58	2.76	7.04	
	CH_3Si	43	1.62	4.13	
$[(C_2H_5)_2(CH_3)Si]_2Hg$ (80°C) [d]	$C_{15}H_{39}HgSi_3$ [e]	505	trace		
	$C_{13}H_{21}HgSi_3$ [e]	476	trace		
	$C_{13}H_{15}HgSi_2$ [e]	418	0.10	0.26	1.23
	$C_{10}H_{26}HgSi_2$	404	5.31	13.79	65.47
	$C_9H_{23}HgSi_2$	389	0.08	0.21	0.98
	$C_8H_{21}HgSi_2$	375	0.12	0.31	1.48
	$C_5H_{13}HgSi$	303	0.32	0.83	3.95
	Hg^+	202	1.86	4.86	22.93
	$C_6H_{17}Si_2$	145	1.67	4.34	
	$C_5H_{13}Si$	101	38.51	100.0	
	Hg^{++}	101	0.32	0.83	3.95
	$C_4H_{11}Si$	87	1.19	3.09	
	C_3H_9Si	73	23.84	61.90	
	C_2H_7Si	59	1.19	6.09	
	C_2H_5Si	57	2.29	5.95	
	CH_5Si	45	3.21	8.33	
	CH_3Si	43	1.28	3.32	
$[(C_2H_5)_3Si]_2Hg$ (80°C) [d]	$C_{12}H_{30}HgSi_2$	432	4.83	15.13	70.17
	$C_{11}H_{27}HgSi_2$	403	0.14	0.44	2.03
	$C_6H_{15}HgSi$	317	0.12	0.38	1.74
	$C_{12}H_{30}Si_2$	230	0.68	2.13	
	Hg^+	202	0.97	3.04	14.00
	$C_6H_{15}Si$	115	31.92	100.0	
	Hg^{++}	101	0.83	2.43	12.06

(continued)

TABLE 1 (continued)

Compound	Ions	m/e	Σ [a] (%)	Relative [b] abundance	Σ Hg [c] containing ions (%)
	$C_4H_{11}Si$	87	1.79	5.61	
	$C_4H_{10}Si$	86	17.94	56.20	
	C_2H_7Si	59	10.12	31.70	
	C_2H_6Si	58	2.10	6.58	
	C_2H_5Si	57	1.48	4.64	
$[n\text{-}C_3H_7(CH_3)_2Si]_2Hg$ (80°C) [d]	$C_{10}H_{26}HgSi_2$	404	2.44	11.53	17.16
	$C_9H_{23}HgSi_2$	389	0.14	0.66	0.98
	$C_7H_{19}HgSi_2$	361	0.24	1.13	1.68
	$C_5H_{13}HgSi_2$	303	0.22	1.04	1.55
	$C_{10}H_{26}Si_2^+$	202	1.57	7.42	
	Hg^+	202	9.48	4.48	66.68
	$C_5H_{15}Si_2$	131	1.65	7.78	
	$C_4H_{14}Si_2$	117	3.09	15.60	
	$C_5H_{13}Si$	101	21.16	100.0	
	Hg^{++}	101	1.70	8.03	11.95
	$C_3H_9Si^+$	73	9.04	42.72	
	C_2H_7Si	59	20.65	97.59	
	C_2H_6Si	58	2.65	12.52	
$[(C_6H_5CH_2)(CH_3)_2\text{-}Si]_2Hg$ (100°C) [d]	$C_{18}H_{26}HgSi_2$	500	5.01	20.29	67.98
	$C_{17}H_{23}HgSi$	485	0.20	0.81	2.71
	$C_{11}H_{19}HgSi_2$	409	0.04	0.16	0.54
	$C_{11}H_{19}Si_2$	207	15.66	63.43	
	Hg^+	202	1.81	7.33	24.56
	$C_9H_{13}Si$	149	24.69	100.0	
	$C_7H_{11}Si$	121	13.60	55.08	
	Hg^{++}	101	0.31	1.22	4.21
	CH_3Si	43	2.10	8.51	
$\{[(CH_3)_3SiCH_2]\text{-}(CH_3)_2Si\}_2Hg$ (80°C) [d]	$C_{12}H_{34}HgSi_4$	492	2.44	7.27	36.26
	$C_{11}H_{31}HgSi_4$	477	0.50	1.49	7.43
	$C_8H_{23}HgSi_4$	419	0.03	0.09	0.45
	$C_6H_{17}HgSi_2$	347	0.05	0.15	0.74
	Hg^+	202	3.60	10.72	53.49
	$C_6H_{17}Si_2$	145	33.57	100.0	
	$C_5H_{15}Si_2$	131	10.85	32.32	
	$C_5H_{14}Si_2$	130	2.77	8.25	
	$C_4H_{11}Si_2$	115	1.76	5.24	
	$C_5H_{13}Si$	101	4.20	12.51	
	Hg^{++}	101	0.11	0.33	1.63
	C_3H_9Si	73	16.58	49.39	
	C_2H_7Si	59	2.03	6.05	
$\{[(CH_3)_3Si]_3Si\}_2Hg$ (120°C) [d]	$C_{18}H_{54}HgSi_8$	696	6.52	30.24	74.51
	$C_{17}H_{51}HgSi_8$	681	0.55	2.55	6.29
	$C_{15}H_{45}HgSi_7$	623	0.07	0.32	0.80
	$C_9H_{27}Si_4$	247	21.56	100.0	
	$C_8H_{24}Si_4$	232	1.33	6.17	
	Hg^+	202	1.40	6.49	16.00
	$C_6H_{18}Si_3$	174	2.85	13.22	
	$C_6H_{17}Si_3$	173	14.72	68.27	
	$C_5H_{15}Si_3$	159	2.16	10.02	
	$C_5H_{13}Si_3$	157	1.54	7.14	
	$C_6H_{17}Si_2$	145	1.42	6.58	

(continued)

TABLE 1 (continued)

Compound	Ions	*m/e*	Σ [a] (%)	Relative [b] abundance	Σ Hg [c] containing ions (%)
	$C_5H_{15}Si_2$	131	3.13	14.52	
	$C_5H_{13}Si_2$	129	2.09	9.55	
	$C_4H_{11}Si_2$	115	1.97	9.14	
	$C_4H_9Si_2$	113	1.40	6.49	
	Hg^{++}	101	0.21	0.97	2.40
	$C_3H_7Si_2$	99	1.75	8.12	
	C_3H_9Si	73	15.34	71.15	
	C_2H_7Si	59	1.40	6.49	
	CH_5Si	45	1.23	5.70	
$[(CH_2{=}CHCH_2)(CH_3)_2Si]_2Hg$ (80° C) [d]	$C_{10}H_{22}HgSi_2$	400	4.18	19.86	36.26
	Hg^+	202	6.45	30.64	56.09
	$C_7H_{17}Si_2$	157	3.67	17.43	
	$C_5H_{13}Si_2$	129	2.98	14.16	
	Hg^{++}	101	0.88	4.18	7.65
	$C_5H_{11}Si$	99	21.05	100.0	
	C_3H_9Si	73	3.94	18.72	
	C_2H_7Si	59	10.98	52.16	
	CH_3Si	43	3.84	18.24	
$[CH_2{=}CH(CH_2)_2(CH_3)_2Si]_2Hg$ (60° C) [d]	$C_{12}H_{26}HgSi_2$	428	2.48	8.56	41.13
	Hg^+	202	2.99	10.32	49.59
	$C_6H_{13}Si$	113	28.97	100.0	
	Hg^{++}	101	0.56	1.93	9.29
	C_5H_9Si	97	5.33	18.40	
	C_4H_9Si	85	13.91	48.02	
	C_3H_9Si	73	1.93	6.66	
	C_2H_7Si	59	23.17	79.98	
	CH_3Si	43	2.27	7.84	
$[CH_2{=}CH(CH_2)_3(CH_3)_2Si]_2Hg$ (70° C) [d]	$C_{14}H_{30}HgSi_2$	456	1.45	4.44	28.60
	Hg	202	2.99	9.15	58.97
	$C_7H_{15}Si$	127	18.76	57.41	
	$C_6H_{11}Si$	111	2.00	6.12	
	Hg^{++}	101	0.63	1.93	12.43
	$C_5H_{11}Si$	99	32.68	100.0	
	C_4HgSi	85	2.71	8.29	
	C_3H_9Si	73	2.83	8.66	
	C_2H_7Si	59	11.34	34.70	
	CH_3Si	43	1.50	4.59	
$[(C_6H_5)(CH_3)_2Si]_2Hg$ (100° C) [d]	$C_{16}H_{22}HgSi_2$	472	2.14	3.52	51.4
	$C_{15}H_{19}HgSi_2$	455	0.13	0.22	3.1
	$C_{10}H_{17}HgSi_2$	395	trace		
	$C_{16}H_{22}Si_2$	270	1.64	2.98	
	Hg	202	1.59	2.89	38.0
	$C_8H_{11}Si$	135	54.98	100	
	C_7H_8Si	120	0.74	1.35	
	C_6H_5Si	105	3.22	5.86	
	Hg^{++}	101	0.31	0.67	7.5
	CH_3Si^+	43	4.55	8.28	
$[(C_6H_5)_2(CH_3)Si]_2Hg$ (120° C) [d]	$C_{26}H_{26}HgSi_2$	596	1.38	2.57	32.0
	$C_{26}H_{26}Si_2$	394	2.91	6.31	
	Hg^+	202	2.50	4.65	57.9
	$C_{13}H_{13}Si$	197	46.12	100.0	
	C_6H_5Si	105	5.14		
	Hg^{++}	101	0.43	0.81	10.1

(continued)

TABLE 1 (continued)

Compound	Ions	*m/e*	Σ [a] (%)	Relative [b] abundance	Σ Hg [c] containing ions (%)
$[(C_6H_5)_3Si]_2Hg$ (150—170° C) [d]	$C_{36}H_{30}HgSi_2$	720	2.05	3.05	65.9
	$C_{18}H_{15}Si$	259	56.05	100.0	
	Hg^+	202	0.87	1.29	28.0
	$C_{12}H_{11}Si$	182	2.47	4.41	
	$C_{12}H_{10}Si^+$	181	5.32	9.49	
	$C_6H_5Si^+$	105	2.86	5.10	
	Hg^{++}	101	0.19	0.28	6.1
$[(CH_3)_2(Cl)Si]_2Hg$ (50° C) [d]	$C_4Cl_2H_{12}HgSi_2$	388	2.63	6.74	19.97
	$C_3Cl_2H_9HgSi_2$	373	0.23	0.59	1.74
	$C_4ClH_{12}HgSi_2$	353	0.76	1.94	5.77
	C_2ClH_6HgSi	295	0.90	2.31	6.83
	$CClH_3HgSi$	280	0.08	0.20	0.61
	$ClHgSi$	265	0.12	0.31	0.91
	C_2H_6HgSi	260	0.06	0.15	0.46
	Hg^+	202	7.26	18.61	55.12
	CCl_2H_3Si	113	1.76	4.51	
	Hg^{++}	101	1.13	2.90	8.58
	C_2ClH_6Si	93	39.0	100.0	
	$ClSi$	63	4.11	10.54	
	C_2H_6Si	58	9.18	23.54	
	CH_3Si	43	3.11	7.97	
$[(CH_3)Cl_2Si]_2Hg$ (80° C) [d]	$C_2Cl_4H_6HgSi_2$	428	4.26	8.61	26.48
	$CCl_4H_3HgSi_2$	413	0.31	0.63	1.93
	$C_2Cl_3H_6HgSi_2$	395	0.70	1.41	4.35
	CCl_2H_3HgSi	315	4.51	9.11	28.03
	Cl_2HgSi	300	0.64	1.29	3.98
	$CClH_3HgSi$	280	0.42	0.85	2.61
	$ClHgSi$	265	0.49	1.00	3.04
	$C_2Cl_4H_6Si_2$	226	1.43	2.89	
	$CCl_4H_3Si_2$	211	0.85	1.72	
	Hg^+	202	2.96	5.98	18.40
	Cl_3Si	133	2.08		
	C_2H_6Si	113	46.47	100.0	
	Hg^{++}	101	1.80	3.64	11.24
	$CClH_3Si$	78	17.35		
	$ClSi$	62	20.04		
$[Cl_3Si]_2Hg$ (70—80° C) [d]	Cl_6HgSi_2	468	1.72	7.01	6.85
	Cl_5HgSi_2	433	1.14	4.65	4.54
	Cl_3HgSi	335	4.58	18.66	18.25
	Cl_2HgSi	300	1.09	4.44	4.34
	Cl_6Si_2	266	1.19	4.85	
	$ClHgSi$	265	0.25	1.02	1.01
	Cl_5Si_2	231	4.53	18.46	
	$HgSi$	230	0.30	1.22	1.19
	Hg^+	202	14.50	59.09	57.79
	Cl_4Si_2	196	1.83	7.46	
	Cl_4Si	168	4.28	17.44	
	Cl_3Si	133	24.54	100.0	
	Hg^{2+}	101	1.51	6.15	6.02
	Cl_2Si	98	14.57	59.37	
	$ClSi$	63	17.65	71.92	
$[(CH_3)_3C]_2Hg$ (100° C) [d]	$C_8H_{18}Hg$	316	2.48	15.10	24.92
	C_4H_8Hg	258	0.18	1.10	1.81
	Hg	202	6.13	37.33	61.61

(continued)

Compound	Ions	m/e	Σ [a] (%)	Relative [b] abundance	Σ Hg [c] containing ions (%)
	Hg^{++}	101	1.16	7.06	11.66
	C_4H_9	57	16.42	00.0	
	C_4H_8	56	10.82	65.90	
	C_3H_7	43	7.06	43.00	
	C_3H_5	41	14.77	89.95	
	C_3H_3	39	6.71	40.86	
	C_2H_5	29	9.63	58.65	
	C_2H_4	28	4.03	24.54	
$[(CH_3)_3Ge]_2Hg$ (50°C) [d]	$C_6Ge_2H_{18}Hg$	436	11.97	25.27	48.34
	$C_5Ge_2H_{15}Hg$	421	5.41	11.42	21.85
	C_3GeH_9Hg	319	1.83	3.86	7.39
	C_2GeH_6Hg	304	0.27	0.57	1.09
	$CGeH_3Hg$	289	0.24	0.51	0.97
	GeHg	274	0.47	0.99	1.90
	$C_6Ge_2H_{18}$	234	1.39	2.93	
	$C_5Ge_2H_{15}$	219	4.01	8.46	
	Hg^{+}	202	3.71	7.83	14.98
	C_3GeH_9	117	47.37	100.0	
	C_2GeH_6	102	3.66	7.73	
	Hg^{++}	101	0.86	1.82	3.47
	$CGeH_3$	87	5.51	11.63	
$[(CH_3)_3Ge]Hg[Si(CH_3)_3]$	$C_6Ge_2H_{18}Hg$	436	0.82	2.25	6.94
	$C_5Ge_2H_{15}Hg$	421	0.42	1.15	3.56
	$C_6GeH_{18}HgSi$	392	2.07	5.67	17.53
	$C_5GeH_{15}HgSi$	377	0.91	2.49	7.71
	$C_6H_{18}HgSi_2$	348	0.70	1.92	5.93
	$C_5H_{15}HgSi_2$	333	0.29	0.79	2.46
	C_3GeH_9Hg	319	0.27	0.74	2.29
	C_2GeH_6Hg	304	0.07	0.19	0.59
	$CGeH_3Hg$	289	0.04	0.11	0.34
	C_3H_9HgSi	275	0.45	1.23	3.81
	Hg^{+}	202	4.67	12.80	39.54
	C_3GeH_9	117	23.67	64.88	
	C_2GeH_6	102	2.72	7.46	
	Hg^{++}	101	1.10	3.02	9.31
	$CGeH_3$	87	3.55	9.73	
	C_3H_9Si	73	36.48	100.0	
	C_2H_7Si	59	1.50	4.11	
	CH_5Si	45	2.19	6.00	
	CH_3Si	43	1.16	3.18	
I (150°C) [d]	$C_{10}H_{28}Hg_2Si_4$	664	1.31	8.11	14.92
	$C_9H_{25}Hg_2Si_4$	649	0.58	3.59	6.61
	$C_{10}H_{28}HgSi_4$	462	3.80	23.51	43.28
	$C_{10}H_{28}Si_4$	260	5.26	32.55	
	$C_9H_{25}Si_4$	245	5.04	31.19	
	Hg^{+}	202	2.62	16.21	29.84
	$C_7H_{19}Si_3$	187	16.16	100.0	
	$C_5H_{14}Si_2$	130	2.76	17.68	
	$C_4H_{11}Si_2$	115	9.46	58.54	
	Hg^{++}	101	0.47	2.91	5.35
	C_3H_9Si	73	3.10	19.18	
	C_3H_7Si	59	4.72	29.21	

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[a] The intensity of each ion is listed as a percentage of the total ion current. Intensities of polyisotopic species are summations corrected to the 202 isotope of Hg set equal to 100% — corrections for other isotopes have not been made. All reported values are for 70 V ionizing potential. [b] Relative abundances compare the intensities for the entire spectrum. [c] Represents the percentage ion current produced for each mercury containing species compared to the total current produced by all mercury fragments. [d] Source and probe temperature. [e] High molecular weight mercury containing fragments was obtained in low abundance in two instances which could not be explained. Possible source for these ions is impure starting materials, decomposition products, or molecule-ion reactions. These spectra were obtained at relatively high sample

The second general procedure used for preparation of symmetrical compounds was the direct reaction of a silyl halide with Na/Hg. The procedure used is illustrated for the preparation of bis(dimethylallylsilyl)mercury. $Me_2(CH_2{=}CHCH_2)SiCl$, 4 ml, Marshallton, Inc., was placed in a tube containing excess Na/Hg (0.5%) and approximately 10 ml of cyclopentane solvent. The tube was evacuated, sealed, and placed on a rotary shaker for 10 days. The solution, which turned green shortly after the reaction started, was then separated from the mercury and the volatile components removed on the vacuum system leaving a yellow liquid (1.3 g, 30% yield) which slowly decomposes to the disilane and mercury on exposure to light. Found: C, 30.75; H, 5.78; Hg, 48.57; Si, 14.50. calcd.: C, 30.50; H, 5.55; Hg, 50.2; Si, 14.10%. Similarly, each of the following compounds were prepared: $[Me_2(CH_2{=}CH(CH_2)_3Si]_2Hg$. Found: C, 36.95; H, 6.60; Hg, 44.12; Si, 13.01; calcd.: C, 37.19; H, 6.85; Hg, 43.99; Si, 12.38%; $(EtMe_2Si)_2Hg$; $(Et_3Si)_2Hg$ and $(Me_2PhSi)_2Hg$ (also prepared by the hydride reaction).

The mixed derivative was obtained by placing samples of the two symmetric species in cyclopentane, stirring for several minutes and removing the solvent.

Mass spectra were recorded on an AEI-MS 902 operating with an ionization potential of 70 V, ionizing current of 5 μA, 3 V repeller potential and 3 V trap potential. As the organosilylmercurials are in most cases extremely air-sensitive compounds of low volatility, samples were introduced to the spectrometer via the direct probe insertion method, the probe being surrounded by a glove bag purged with $N_2(g)$. The probe and ionization chamber were normally operated above room temperature in the range of 70—150°C. The temperature is given for each sample. This was required to provide sufficient pressure but also lead to the complication resulting from thermal decomposition.

Results and discussion

The principal ions observed in the mass spectra of a number of silyl, germyl- and organomercury derivatives are given in Table 1 along with their relative abundances. Examination of these data and the spectra given in Fig. 1—5 clearly show that these spectra are dominated by mercury free fragments, but also show that the parent molecular ion (PMI) is present in every case. Detailed study of a number of these spectra show that the simple extrusion of mercury

TABLE 2

ORGANOSILYLMERCURIALS EXHIBITING METASTABLE SUPPORTED EXTRUSION OF MERCURY AT 70 eV

Compound	m^*
$[(C_6H_5)(CH_3)_2Si]_2Hg$	155
$[(C_6H_5)_2(CH_3)Si]_2Hg$	260
$[(C_6H_5)_3Si]_2Hg$	373
$[(C_2H_5)_3Si]_2Hg$	123 [a]
$[(C_6H_5CH_2)(CH_3)_2Si]_2Hg$	178
$\{[(CH_3)_3Si]_3Si\}_2Hg$	350
I	322

[a] Extrusion of mercury was also metastable supported at 14 V ionizing potential.

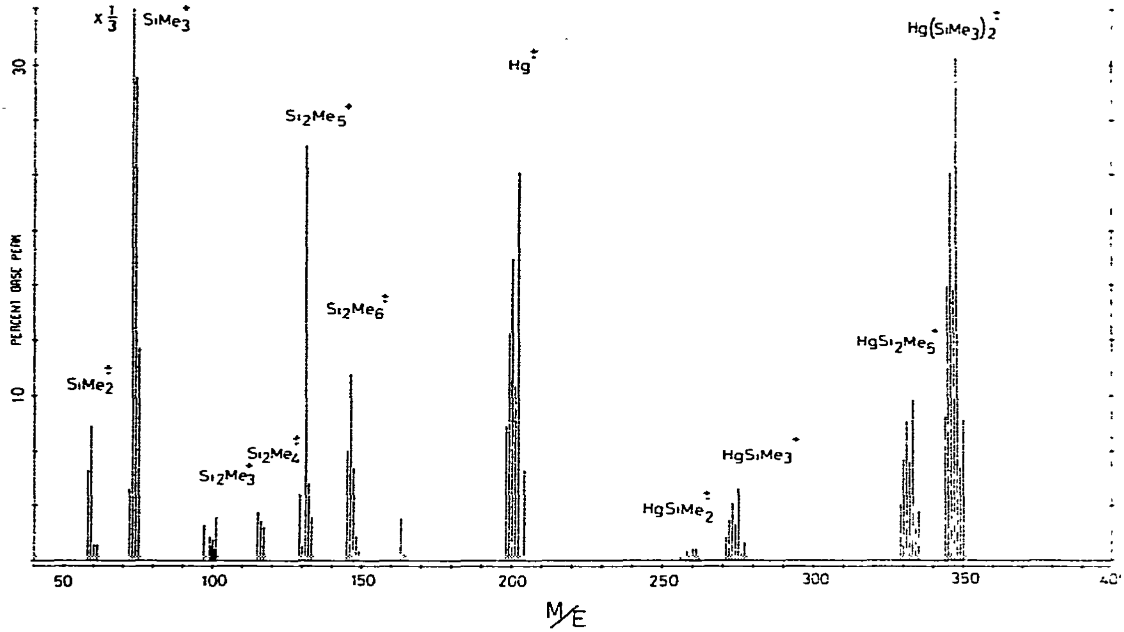


Fig. 1. Mass spectrum of bis(trimethylsilyl)mercury.

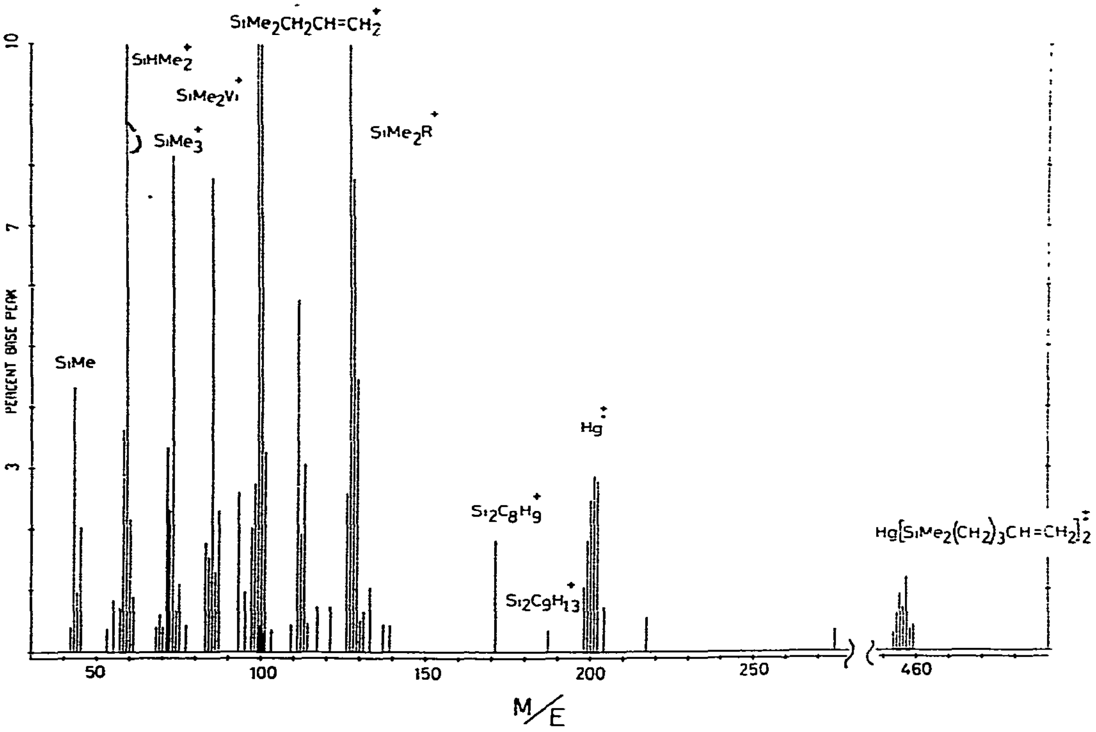


Fig. 2. Mass spectrum of bis(dimethyl-1-pent-4-enylsilyl)mercury.

given in eq. 1 is supported by observation of

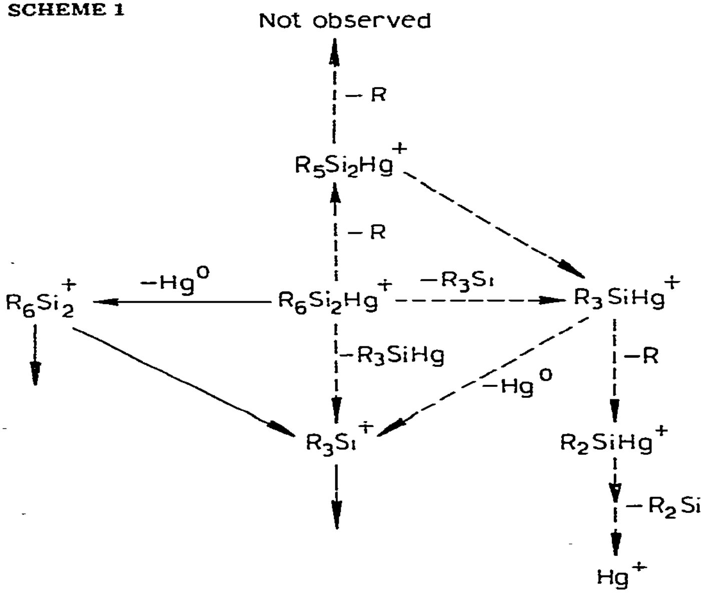
$$(R_3E)_2Hg^+ \rightarrow R_3EER_3^+ + Hg \qquad (1)$$

metastable species for this process. Several of these species are listed in Table 2. A second path for loss of mercury from the PMI is given in eq. 2 and was supported by observation of a metastable species arising from

$$(Et_3Si)_2Hg^+ \rightarrow Et_3Si^+ + HgSiEt_3 \qquad (2)$$

bis(triethylsilyl)mercury. These studies provide the basis for the general fragmentation, Scheme 1.

SCHEME 1



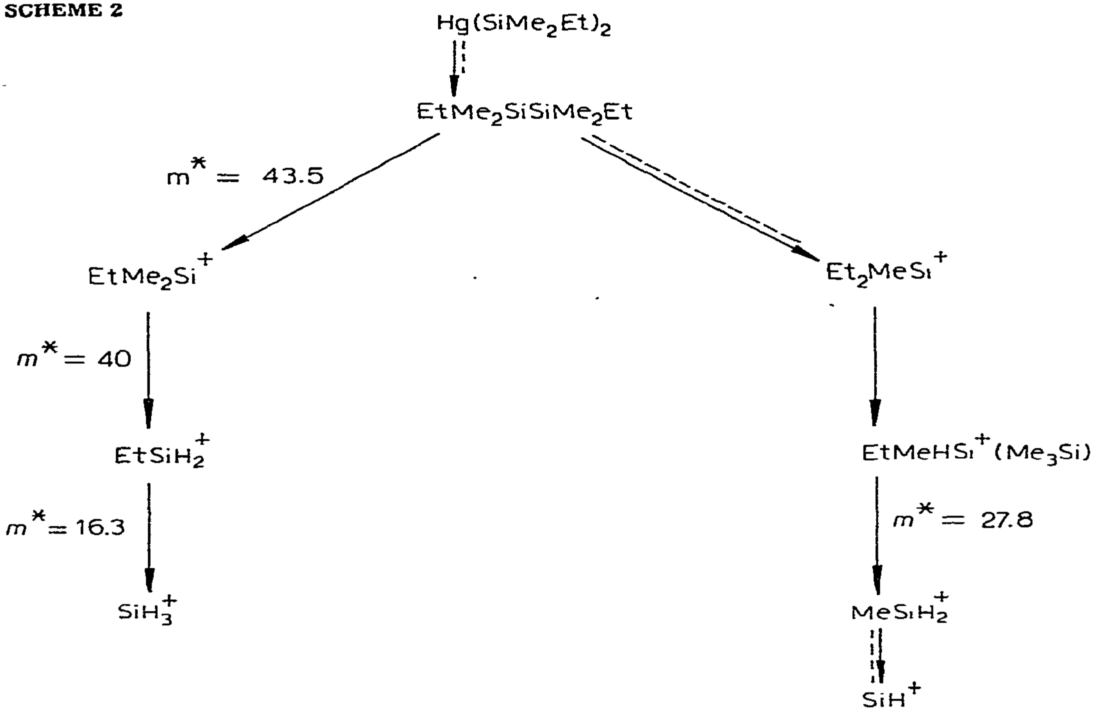
Further examination of the data suggests that Scheme 1 may not account for all of the mercury free fragments observed. In fact, it can be established that under the operating conditions used for the mass spectrometer in the present study (70—150° C), the bis(triorganosilyl)mercury compounds undergo some thermolysis as shown in eq. 3

$$(R_3Si)_2Hg \xrightarrow{\Delta} R_3SiSiR_3 + Hg \qquad (3)$$

This clearly indicates that the mercury free fragments may arize from either of two paths, the extrusion of mercury as indicated in Scheme I or from thermolysis followed by fragmentation as shown in Schemes 2 and 3.

Despite the difficulties introduced by the two paths for decomposition, one may still gain a substantial amount of information about the behavior of these derivatives by careful examination of the data, especially that for the mercury containing ions. Clearly all of the organosilylmercurials studied yield a parent molecular ion (PMI) on electron impact which represent from 1 to 6% of the total ions produced. The single exception to this is bis(trimethylsilyl)mercury

SCHEME 2



for which the PMI represents 15.6% of the ions formed. Further, one should note that three other ions containing both mercury and silicon are present in significant concentrations: Me_5Si_2Hg + (5.50%); Me_3SiHg (2.16%) and Me_2SiHg (0.38%). This is illustrated in Fig. 1.

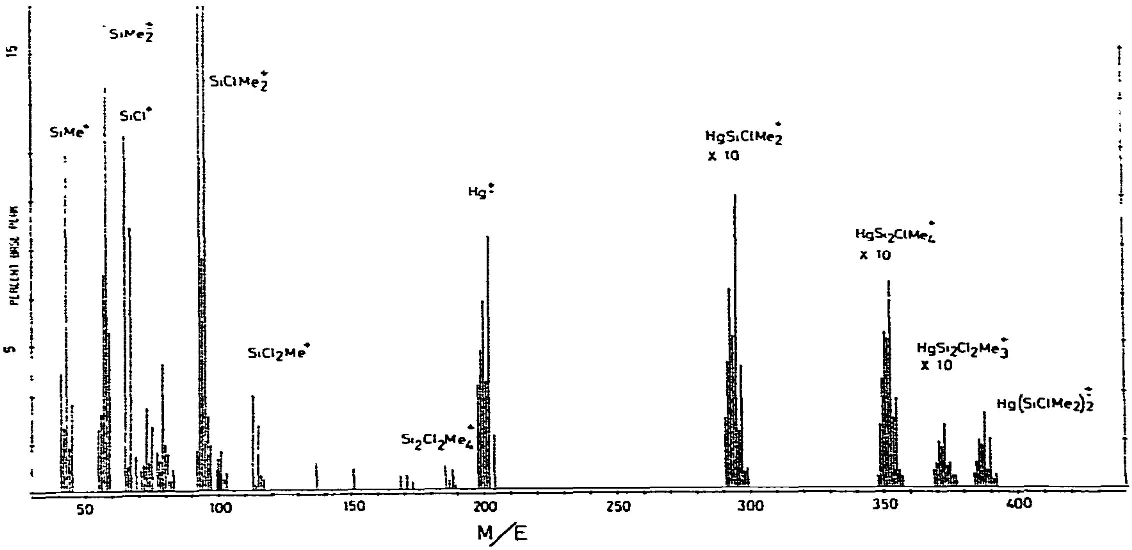


Fig. 3. Mass spectrum of bis(dimethylchlorosilyl)mercury exhibiting competitive loss of Cl and Me and rearrangement ion $Cl_2(CH_3)Si^+$.

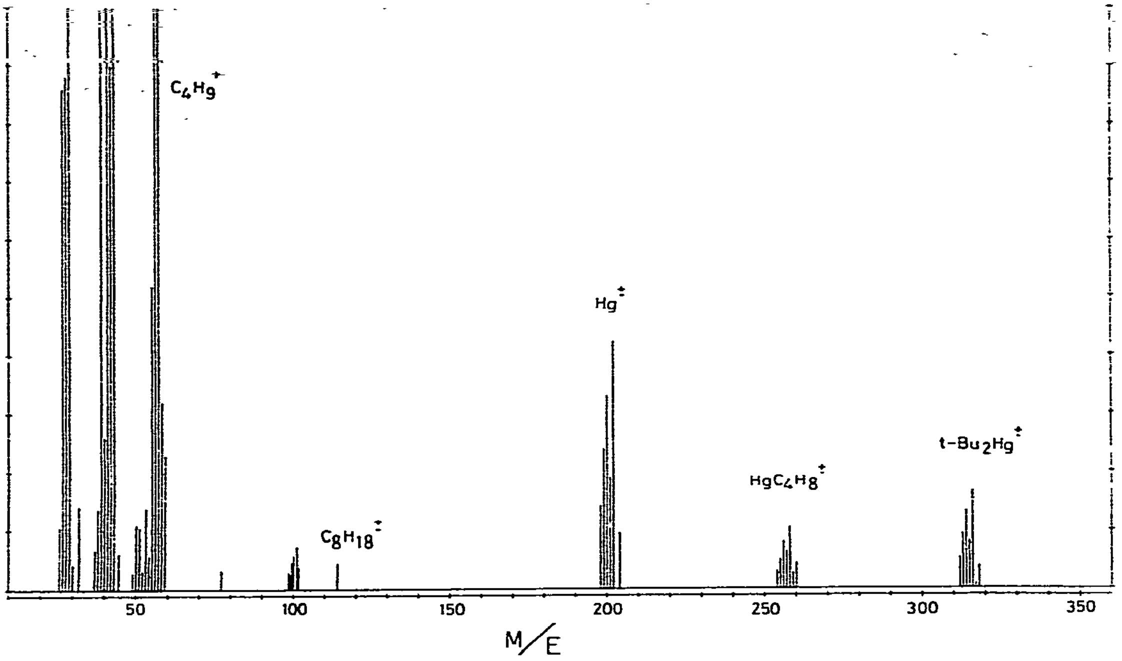


Fig. 4. Mass spectrum of di-tert-butyl-mercury.

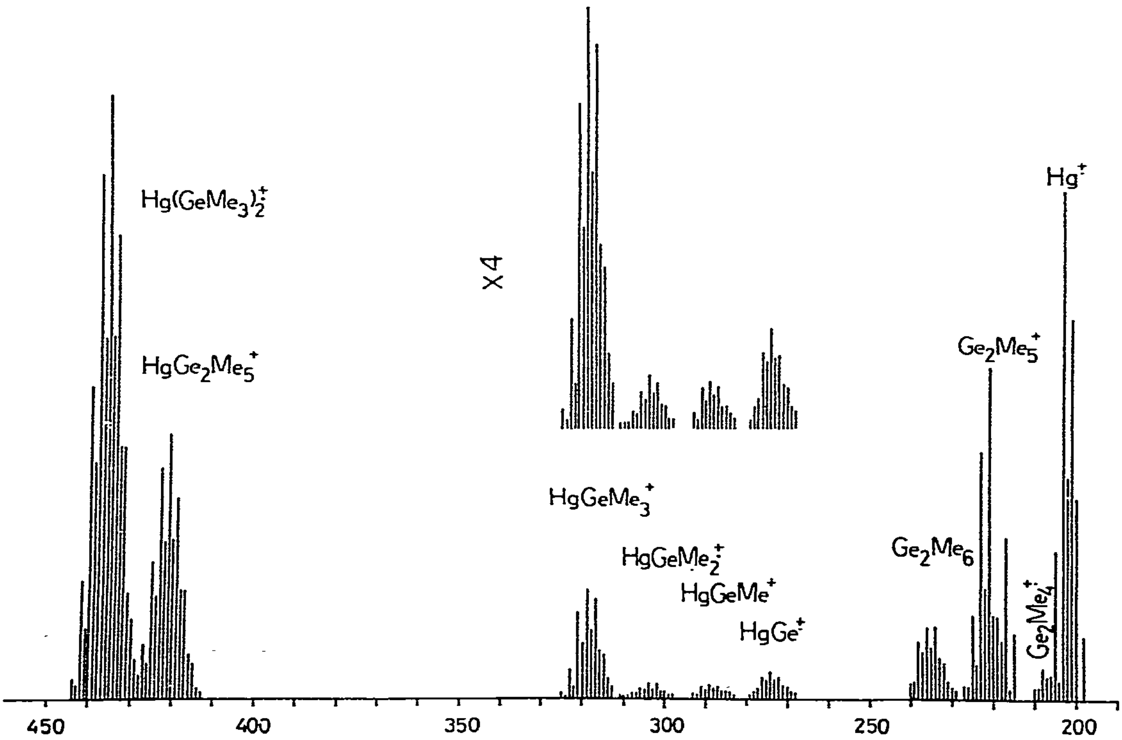
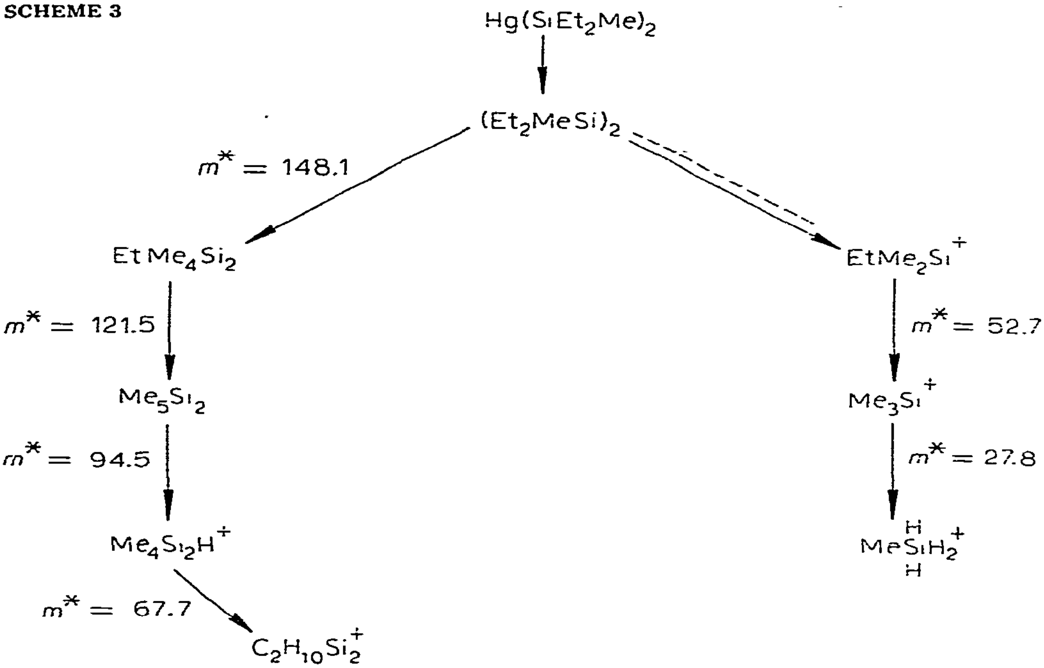


Fig. 5. Mass spectrum of bis(trimethylgermyl)mercury.

SCHEME 3



The absolute values of these numbers must be treated with great care as indicated earlier because of the thermal decomposition, but the ratio of the PMI to other mercury silicon fragments does provide some interesting trends.

Examination of the data collected in Table 1 shows that substitution of alkyl groups for the methyl groups of $(Me_3Si)_2Hg$ results in a substantial decrease in the mercury—silicon fragments. This parallels the apparent thermal stability of the alkyl derivatives and may result either because of lower thermal stability which leads to greater decomposition or because of enhanced extrusion of mercury on electron impact. A further observation is that the ratio of PMI to other mercury—silicon containing fragments is of the order of 5 or 10 to 1 for a variety of samples indicated in Table 1 suggesting that the major path for decomposition of the PMI is through extrusion of mercury.

If a terminal alkenyl group replaces one of the methyl groups, one then obtains spectra such as that shown in Fig. 2 in which no Hg—Si fragments other than the PMI are observed. Data for $[(CH_2{=}CHCH_2)_2Me_2Si]_2Hg$, $[(CH_2{=}CH(CH_2)_2)Me_2]_2Hg$ and $[(CH_2{=}CH(CH_2)_3)Me_2Si]_2Hg$ are collected in Table 1 showing these results. These observations lead to the suggestion that substitution of a terminal double bonded moiety on the silicon destabilizes the Si—Hg species relative to the formation of silicon containing ions with elimination of mercury.

Successive replacement of the methyl groups in the trimethyl derivatives by phenyl groups greatly reduces the number of mercury containing fragments observed. For bis(trimethylsilyl)mercury the intensity of the ion $[Me_3SiHgSiMe_2^+]$ is 35% of the parent, for bis(phenyldimethylsilyl)mercury the corresponding ion, $(PhMe_2SiHgSiMePh]^+$, represents only 6% of parent species with only a trace of the fragment corresponding to loss of one phenyl group observed. In bis(diphenylmethylsilyl)- and bis(triphenylsilyl)mercury, no silylmercury fragments other than the parents were observed. Further, the percentage of the ion current produced by Si—Hg species for the phenyl substituted derivatives is of the order of 1.5—2.5% while for the $(Me_3Si)_2Hg$ over 20% of the ion current is produced by Si—Hg species. This clearly implies a general destabilization of the Hg—Si bonds on phenyl substitution which may result from the change in bonding of the silicon on substitution of an alkyl group by a phenyl group as noted by Gaides et al. [22].

On substitution of chlorine for the methyl groups in bis(trimethylsilyl)-mercury, the spectra became more complex with fragments corresponding to the loss of either methyl groups or chlorine atoms observed. This is shown in Fig. 3. The total ion current produced by the Si—Hg containing species ranged from 3—10% and increased with greater chlorine substitution. This feature, along with the relatively high abundance of species of the form Hg—Si-Cl_n indicates that chlorine substitution stabilized Hg—Si bonds in these ions. This feature becomes more apparent on examination of the data in Table 1 which shows that the Hg—$SiCl_n$ and $Hg(SiCl_n)_2$ ions are in greater abundance than the Hg—Si containing ions for all species except bis(trimethylsilyl)mercury. Additional examination of the mass spectra of the chlorine substituted derivatives indicates that no ions of the form $[HgSiCl_4]^+$ or $HgCl^+$ were present, thus suggesting that the process normally observed for carbene type eliminations as indicated in eq. 4 and 5 do not occur for silyl mercury derivatives.

$$((Cl_3)_2Si)_2Hg \not\rightarrow Cl_3SiHgCl^+ + Cl_2Si \qquad (4)$$

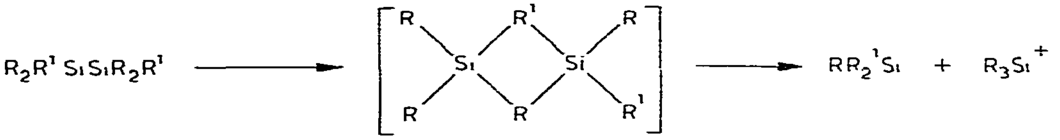
$$HgCiCl_3^+ \not\rightarrow HgCl + Cl_2Si \qquad (5)$$

Another interesting feature of the spectra observed for the phenylmethylsilyl- and methylchlorosilylmercury derivatives was the observation of fragments attributable to the transfer of groups between silicon atoms. Thus, the mass spectrum of bis(phenyldimethylsilyl)mercury contains fragments corresponding to the diphenylmethylsilyl and trimethylsilyl ions while bis(diphenylmethylsilyl)mercury has fragments attributable to the triphenylsilyl and phenyldimethylsilyl ions. The ion which contains more phenyl groups is the more intense in both cases. Similarly, in bis(methyldichlorosilyl)mercury, the trichlorosilyl and dimethylsilyl ions were observed while in bis(dimethylchlorosilyl)mercury, trimethylsilyl and dimethylchlorosilyl ions were observed. Some of these data are collected in Table 3. It is unlikely that these fragments have their origin directly from rearrangement of the PMI but result either from the rearrangement of the disilyl ion resulting from mercury extrusion or from rearrangement of the disilane produced from thermolysis on electron impact. Such rearrangements were observed by Chambers and Glocking [22] and by Gardis et al. [21] in similar systems.

We also have examined the sequence of compounds $(Me_3E)_2Hg$ in which the atom bound to mercury is altered for t-butylmercury, bis(trimethylsilyl)-mercury and bis(trimethylgermyl)mercury. Fig. 4 shows the unique spectrum of di-t-butylmercury. A PMI was observed for this derivative, but no mercury containing fragment with loss of a methyl group was present. A fragment correspond-

TABLE 3

REARRANGEMENT IONS OBSERVED IN MASS SPECTRA OF ORGANOSILYMERCURIALS



Disilane[a]		RR^1_2Si	RA[b]	R_3Si^+	RA
R_2	R^1				
Et	Me	Me_2EtSi	1.19	Et_3Si	0.716
Me	Ph	Ph_2MeSi	2.89	Me_3Si	0.55
Me	$PhCH_2$	$(PhCH_2)Me_2Si$	0.34	Me_3Si	0.42
Cl	Me	Me_2ClSi	0.51	Cl_3Si	2.08
Ph	Me	Me_2PhSi	0.26	Ph_3Si	1.56
Me	Cl	Cl_2MeSi	1.50	Me_3Si	0.78

[a] Disilane derived from extrusion of mercury from respective PMI. [b] Relative abundance.

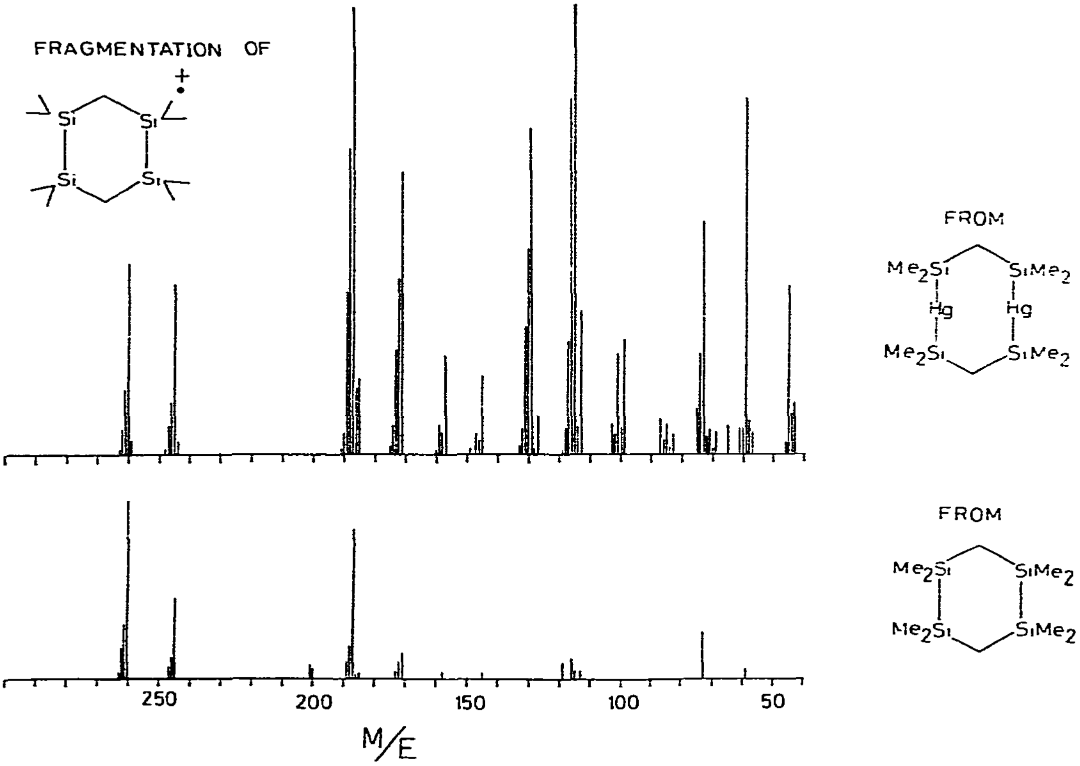


Fig. 6. Low mass region in spectra of I compared with spectrum of authentic tetrasilacyclohexane.

ing to the loss of C_4H_{10} from the PMI was present, but no further fragmentation of this ion retaining the Hg—C bond was observed. This is in marked contrast to dimethylmercury and diethylmercury where the RHg^+ ions are high in intensity and is also unlike the fragmentation observed for the silyl and germyl derivatives as shown in Fig. 1 and 5, both of which have a variety of fragments which contain Hg—Si or Hg—Ge bonds. In fact, these results seem to indicate that a greater variety of species containing Hg—E bonds occur on going through the series $Me_3C < Me_3Si < Me_3Ge$. Again this sequence appears to parallel the thermal stability of the parent molecule with the very unstable di(tert butyl)-mercury decomposing most readily both thermally and on electron impact.

We also have re-examined the cyclic silylmercury compound reported by Bentler and Urry [13] shown in I and have observed both the PMI and the ion corresponding to loss of a single methyl group. In addition, the ion resulting from extrusion of one mercury and the metastable ion supporting this process were observed.

In the fragmentation of I, the extrusion of the first Hg atom could produce ions such as the seven-membered ring II^+ or the open chain IIA^+. Loss of the second mercury, if extruded, could again produce a cyclic III^+ species as shown in Scheme 4.

SCHEME 4

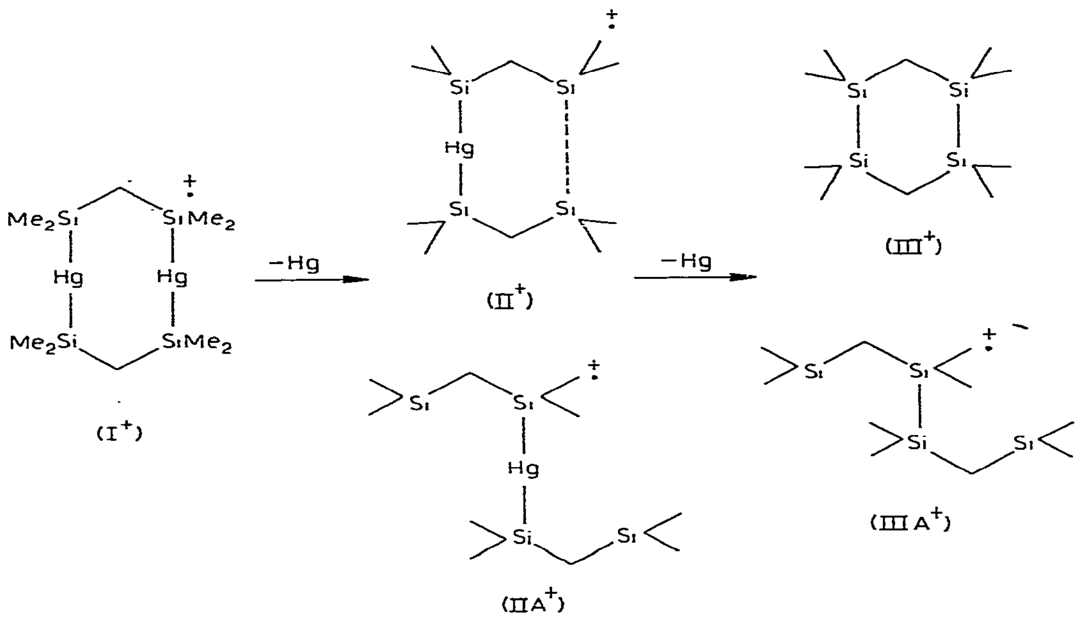


Fig. 6 shows a comparison of the fragmentation of the disilane with an authentic sample of 1,1,3,3,4,4,6,6-octamethyl-1,3,4,6-tetrasilacyclohexane. The much more extensive fragmentation for the silylmercury derived ion indicates at least a large proportion of a species follows a path similar to that suggested in IIA^+ and $IIIA^+$ rather than proceeding through the cyclic intermediates which should show some similarity to the fragmentation of the tetrasilacyclohexane.

In all of the cases studied, the extrusion of mercury ether thermally and/or by electron impact, predominates. For the ions containing mercury, the PMI was found to always carry more ion current than the lighter fragments which contained either one or two silicon to mercury bonds. This is similar to the behavior of the simple organomercury species in which the bond dissociation energies are in the order $D_1 \gg D_2$ and leads to the similar suggestion for other mercury derivatives.

Acknowledgment

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