Methylseleno-derivatives of Group IV. Part II.[1] Hydrides

By **Geoffrey K. Barker, John E. Drake,*** and **Raymond T. Hemmings,** Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3PA, Canada

The following methylseleno-derivatives of Group IV hydrides, SiH_3·SeMe, $SiH_2(SeMe)_2$, $MeSiH_2$·SeMe, GeH_3·SeMe, $MeGeH_2$·SeMe, and Me_2GeH·SeMe have been fully characterised by cleavage reactions and ^1H n.m.r. and vibrational spectroscopy. The silanes were prepared from lithium tetramethylselenoaluminate and the germanes by exchange reactions involving methylseleno(trimethyl)silane. A full assignment of the i.r. and Raman spectra, supported by normal co-ordinate analyses, is presented for MH_3SeMe.

SINCE the commencement of this work, Ebsworth *et al.*[2] reported the preparation of methylselenosilane, SiH_3SeMe, by the reaction of methyl iodide with the ammonium salt of silaneselenol. Before that, the only report of methylseleno-derivatives of Group IV hydrides was as a part of our preliminary note on the preparative use of lithium tetramethyl-seleno- and -thio-aluminates.[3]

As an extension to our work[1] with methylselenolithium, LiSeMe, its use in the synthesis of hydride derivatives was examined initially but without success. When LiSeMe in dimethyl ether is treated with monobromosilane, SiH_3Br, the expected reaction to give SiH_3·SeMe does not occur although a similar reaction of SiH_3Br with Li_2Se in dimethyl ether has been reported to give high yields of $(SiH_3)_2Se$ even at -96 °C.[4] The solubility of methylselenolithium in dimethyl ether could be a problem and a small amount of SiH_3·SeMe is produced if diglyme is substituted as solvent. However, $(SiH_3)_2Se$ and Me_2Se are also formed and are not readily separated from methylselenosilane. An increase in reaction time results in the formation of quantities of silane, an indication of catalysed disproportionation,[5] so this synthetic route was abandoned.

We had shown that SiH_3SeMe could be obtained from lithium tetramethylselenoaluminate, $LiAl(SeMe)_4$.[3] A slight modification to the procedure gives excellent results. The brominated silane (SiH_3Br, SiH_2Br_2, or $MeSiH_2Br$) is added to the solid aluminate in the absence of solvent [*e.g.*, reaction (1)]. The yields are high for the reaction carried out at room temperature, there is no disproportionation, and no solvent present to create problems of separation.

$$LiAl(SeMe)_4 + 2SiH_2Br_2 \longrightarrow 2H_2Si(SeMe)_2 + LiBr + AlBr_3 \quad (1)$$

Methylselenogermane, GeH_3·SeMe, was also prepared from the aluminate,[3] but the simpler preparation of methylseleno(trimethyl)silane, Me_3Si·SeMe,[1] and the general applicability of exchange reactions, lead to a more efficient synthesis of the germanes. When excess of halogenogermane, *e.g.* GeH_3F, $MeGeH_2Cl$, or Me_2GeHCl, is added to Me_3Si·SeMe there is a rapid exchange [*e.g.*, (2)] which is virtually quantitative at room temperature. The methylselenogermane is readily separated from the halogeno(trimethyl)silane and excess of the starting halogenogermane.

$$MeGeH_2Cl + Me_3Si{\cdot}SeMe \longrightarrow MeGeH_2{\cdot}SeMe + Me_3SiCl \quad (2)$$

An attempt to prepare $GeH_2(SeMe)_2$ by use of an exchange reaction with dibromogermane indicated that the species probably forms but that, as with many dipseudohalogeno-[6] or diphosphino-[7]germanes, it is very unstable. Thus reaction of GeH_2Br_2 with excess of SiH_3·SeMe gives the expected amount of SiH_3Br for the formation $GeH_2(SeMe)_2$ and a pale yellow liquid, which on standing turns red, depositing a red solid with the tube exploding after two days. The ^1H n.m.r.

---

[1] Part I, J. W. Anderson, G. K. Barker, J. E. Drake, and M. Rodger, *J.C.S. Dalton*, 1973, 1716.

[2] S. Cradock, E. A. V. Ebsworth, and H. F. Jessop, *J.C.S. Dalton*, 1972, 359.

[3] J. W. Anderson and J. E. Drake, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1007.

[4] S. Cradock, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1969, 1628.

[5] B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 249; T. Yashioka and A. G. MacDiarmid, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 69; A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1534.

[6] J. E. Drake and R. T. Hemmings, *Canad. J. Chem.*, 1973, **51**, 302.

[7] J. E. Drake, N. Goddard, and C. Riddle, *J. Chem. Soc.* (*A*), 1969, 2704.

spectrum of the yellow liquid shows four broad features, two in the region associated with Me attached to Se and two in the region expected for GeH_2; its Raman spectrum includes bands assignable to GeH_2 features and $GeSe_2$ stretching and bending modes.

The other methylseleno-derivatives reported herein could be isolated pure and initially characterised by their cleavage reactions and ^1H n.m.r. spectra (Table 1). Features such as ^{13}C–H coupling were noted so that any amounts of hydride-containing impurities in excess of 1% would have been noted.

RESULTS AND DISCUSSION

^1H *N.m.r. Spectra.*—The ^1H n.m.r. parameters for $SiH_3\cdot SeCH'_3$, $GeH_3\cdot SeCH'_3$, $CH''_3SiH_2\cdot SeCH'_3$, $CH''_3GeH_2\cdot SeCH'_3$, $SiH_2(SeCH'_3)_2$, and $(CH''_3)_2GeH\cdot SeCH'_3$ are in Table 1. The proton chemical shifts of $SiH_3\cdot SeCH'_3$ are close to those reported earlier[2] which had been recorded relative to external tetramethylsilane. The chemical shift of the $SeCH'_3$ methyl-resonance remains fairly constant, as might be expected, for all compounds; the SiH and GeH proton resonances in $SiH_3\cdot SeCH_3$ and $GeH_3\cdot SeCH_3$ are very close to those in $(SiH_3)_2Se$[8] and $(GeH_3)_2Se$;[4] and the CH''_3M resonances (M = Si or Ge) are also in typical regions for methylsilanes[9] and -germanes.[6,10,11] The Si–H and Ge–H proton resonances in the same derivatives fall between those of the corresponding bromides and iodides[8-11] (*e.g.*, δ Ge–*H* = GeH_3Br, 4·50; GeH_3SeMe, 4·19; GeH_3I, 3·75 p.p.m.) which is consistent with their relative electronegativities. The values of the direct coupling constants compare well with related compounds. The value of $J(^{13}CH')$ for CH'_3–Se is very similar in all compounds and the values of $J(^{13}CH'')$ for CH''_3–M (M = Si or Ge) are close to those found in most methyl-silicon[9] and -germanium[10,11] derivatives. It is interesting that the values of $J(^{29}SiH)$ are close to those in related Group VI (oxygen and sulphur) derivatives[12] but differ from those of Group V[12,13] and Group VII[12] derivatives. Thus, if it is assumed that the Fermi contact term is over-riding, the *s*-character in the H–Si bond in a compound H–Si–E is apparently strongly related to the electronic configuration of E rather than its size or electronegativity. Long-range coupling over five atoms, similar to that observed in related compounds, is noted. In the series $H_3M\cdot SCH'_3$, as M changes from C to Si to Ge so the absolute value of $J(HH')$ changes slightly in the order 0·30→0·45→0·60 Hz.[14-16] Similarly, in the series $H_3M\cdot SeCH'_3$ (M = C, Si, Ge) the values of $|J(HH')|$ follow the same trend as the sulphur analogues with $|J(HH')| = 0\cdot15 \rightarrow 0\cdot38 \rightarrow 0\cdot45$ Hz. It has been suggested that the *d*-orbitals of sulphur and selenium could be involved in the transmission of coupling[16,17] because the corresponding oxygen analogues do not display this long-range coupling. It is, however, of interest, that the wider bond angle usually associated with oxygen–silicon or oxygen–germanium bonds results in a greater H–H′ through-space distance for the oxygen compounds than those of sulphur or selenium. Reasonable estimates suggest that in the latter cases the H–H′ non-bonding minimum distance is about *twice* the van der Waals radius of hydrogen whereas for oxygen it is larger.

TABLE 1

^1H N.m.r. parameters of some methylseleno-derivatives of silane and germane *

Compound	δH	$\delta H'$	$\delta H''$	$\lvert J(^{77}SeCH)\rvert$	$\lvert J(^{77}SeMH)\rvert$	$\lvert J(HMH'')\rvert$	$\lvert J(^{13}CH')\rvert$	$\lvert J(^{13}CH'')\rvert$	$\lvert J(HMSeCH')\rvert$	$\lvert J(^{29}SiH)\rvert$
$SiH_3\cdot SeCH'_3$	4·15	1·92	—	9·5	15·2	—	142·7	—	0·3(8)	216·4
$GeH_3\cdot SeCH'_3$	4·19	1·95	—	10·1	12·5	—	141·2	—	0·4(5)	—
$CH''_3SiH_2\cdot SeCH'_3$	4·39	1·86	0·48	9·9	n.o.	4·0	140·0	120·7	0·3(7)	208·5
$CH''_3GeH_2\cdot SeCH'_3$	4·46	1·88	0·74	9·8	n.o.	3·5	n.o.	n.o.	0·3(7)	—
$SiH_2(SeCH'_3)_2$	5·01	1·84	—	9·8	22·2	—	143·7	—	0·3(5)	233·7
$(CH''_3)_2GeH\cdot SeCH'_3$	4·68	1·85	0·67	9·8	n.o.	3·2	139·5	129·6	0·2(7)	—

* The spectra were recorded at ambient temperature in CCl_4 solution (*ca.* 5%). Chemical shifts (±0·02 p.p.m.) are in p.p.m. to low field of tetramethylsilane as internal standard. *J* in Hz, ±0·05 Hz (HH′), ±0·1 Hz (^{13}CH, ^{29}SiH).

Vibrational Spectra.—The assignments of the i.r. and Raman spectra are facilitated by comparison with the spectra of the series $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, or Sn; *n* = 1—4),[1] $(SiH_3)_2Se$,[18] $(GeH_3)_2Se$,[4] $SiH_3\cdot SMe$,[15] $GeH_3\cdot SMe$,[19] SiH_3X,[20] $MeSiH_2X$,[21] GeH_3X,[22] $MeGeH_2X$,[23] and SiH_2X_2[24] (X = F, Cl, Br, or I).

Force-constant calculations are used to confirm the

---

[8] E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, 1963, **67**, 805; E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectroscopy*, 1964, **12**, 299; S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1967, 12.

[9] E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, 1963, **59**, 1518; 1967, **63**, 1574.

[10] J. E. Drake, R. T. Hemmings, and C. Riddle, *J. Chem. Soc.* (*A*), 1970, 3359.

[11] R. T. Hemmings, Ph.D. Thesis, University of Windsor, 1973.

[12] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, 1962, **36**, 2628.

[13] E. A. V. Ebsworth, A. G. Lee, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1968, 2294; E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1966, **62**, 3282.

[14] N. Van Meurs, *Spectrochim. Acta*, 1963, **19**, 1695.

[15] B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1961, **23**, 225.

[16] J. T. Wang and C. H. Van Dyke, *Chem. Comm.*, 1967, 612.

[17] E. A. V. Ebsworth, 'Volatile Silicon Compounds,' Pergamon, Oxford, 1963, p. 135.

[18] H. Burger, V. Goetze, and W. Sawodny, *Spectrochim. Acta*, 1968, **24**, *A*, 2003.

[19] J. T. Wang and C. H. Van Dyke, *Inorg. Chem.*, 1968, **7**, 1319.

[20] W. L. Jolly, *J. Amer. Chem. Soc.*, 1963, **85**, 3083.

[21] E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard, *J. Chem. Soc.*, 1958, 1453.

[22] D. E. Freeman, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, 1963, **39**, 2908.

[23] G. K. Barker, J. E. Drake, R. T. Hemmings, and B. Rapp, *Spectrochim. Acta*, 1972, **28**, *A*, 1113.

[24] D. W. Mayo, H. E. Opitz, and J. S. Peake, *J. Chem. Phys.*, 1955, **23**, 1344.

TABLE 2

Description of the expected fundamentals for the molecules MH_3SeMe (M = Si or Ge)

Vibration *	a'	a''
Probable band contour	A–B	C
CH_3 stretch (a)	ν_1	ν_{14}
CH_3 stretch (s)	ν_2	
MH_3 stretch (a)	ν_3	ν_{15}
MH_3 stretch (s)	ν_4	
CH_3 deformation (a)	ν_5	ν_{16}
CH_3 deformation (s)	ν_6	
CH_3 rock	ν_7	ν_{17}
MH_3 deformation (a)	ν_8	ν_{18}
MH_3 deformation (s)	ν_9	
Se–C stretch	ν_{10}	
MH_3 rock	ν_{11}	ν_{19}
M–Se stretch	ν_{12}	
MSeC bend	ν_{13}	
MH_3 torsion		ν_{20}
CH_3 torsion		ν_{21}

* C_s symmetry.

assignments of the fundamental frequencies in MH_3·SeMe (M = Si or Ge). Initial simple valence-force constants are taken from calculations performed on related molecules, $(SiH_3)_2Se$,[18] Me_2Se,[25] $MeGeH_2X$,[23] and $MeSiH_3$.[26] Similarly, bond lengths/Å: C–H, 1·093;[27] Si–H, 1·516;[18] Ge–H, 1·52;[23] Si–Se, 2·273;[28] Ge–Se, 2·351;[29] C–Si, 1·857;[26] C–Ge, 1·945;[27] and Se–C, 1·943[25] are taken from related molecules. The C–Se–Si and C–Se–Ge bond angles are estimated by taking the mean of the literature values for C–Se–C, 96° 11′;[25] Si–Se–Si, 96·6°;[28] and Ge–Se–Ge, 94·6°.[29] All other angles are assumed to be tetrahedral. The normal-co-ordinate analyses were performed on an IBM S/360-50 series computer with the programme SOTONVIB, a modified version[30] of GMAT and FPERT described by Schachtschneider.[31]

TABLE 3

The vibrational spectra (cm^{-1}) of SiH_3·SeMe and GeH_3·SeMe

	SiH_3·SeMe			Assignment		GeH_3·SeMe		
I.r. (gas)	Raman (liq)	Calc.	PED *	MH_3SeMe	I.r. (gas)	Raman (liq)	Calc.	PED *
B 3032w 3024		3014·8	100(4)	ν_1	3015w		3010·2	100(4)
C 3019w	3015w,dp	3014·8	100(4)	ν_{14}	3015w	3010w,dp	3010·1	100(4)
B 2957m 2943	2936m,p	2036·4	98(4)	ν_2	B 2941m 2930	2930m,p	2929·6	98(4)
A 2193 2188vs 2183	2180sh,dp	2180·0	100(1)	ν_3	2105s	2087sh,dp	2087·0	100(1)
C 2172vs	2180sh,dp	2180·0	100(1)	ν_{15}	2105s	2087sh,dp	2087·0	100(1)
A 2170 2163vs 2150	2158s,p	2158·0	99(1)	ν_4	A 2083 2077s 2071	2064vs,p	2064·0	100(1)
1435m	1428w,dp	1428·0	88(9) + 6(13) + 5(8)	ν_5, ν_{16}	1430w	1429w,dp	1428·5	91(9) + 6(8)
1292 1283m 1274	1279m,p	1279·1	54(8) + 49(9) + 8(3) −6(13) − 9(15)	ν_6	1278w	1276m,p	1278·0	56(8) + 52(9) + 6(3)
963m 950m	949w	949·1	95(5) + 8(6)	ν_8, ν_{18}	864m 856m 839m	863m,dp	866·9	88(5) + 12(6)
A 924sh 912vs (900)	921w	920·7	50(6) + 40(5)	ν_9	A 818 813vs 808	798m,p	800·5	44(5) + 55(6)
900m	906w	905·9	86(8) + 7(15) + 5(9)	ν_7, ν_{17}	920sh	910vw	919·1	85(8) + 9(15) + 6(9)
608sh		603·7	65(6) + 29(3) + 5(5)	ν_{11}	536sh		543·4	82(6) + 11(5) + 7(3)
	598sh,dp					548w,p		
599m		595·2	97(6) + 8(5)	ν_{19}	540w		546·1	88(6) + 12(5)
n.o.	583s,p	580·0	63(3) + 32(6) + 6(8) + 5(9)	ν_{10}	590vw	584w,p	583·8	87(3) + 6(7)
411sh 404s 393sh	400s,p	400·0	97(2)	ν_{12}		290vs,p	290·0	95(2) + 5(7)
	174m,p	173·9	98(7)	ν_{13}		164m,p	164·0	94(7) + 5(2)

* Potential-energy distribution; contributions ⩾5%.

The molecule MH_3SeMe (M = Si and Ge) has **21** normal modes of vibration. Its C_s symmetry, required for a non-linear skeleton, leads to **13** modes of class a' and eight modes of class a'', two of which will be skeletal torsions. The in-plane modes may give A-, B-, or hybrid A/B-type band contours, so the contours are only marginal aids to assignments. The conventional description of the fundamentals is in Table **2**. The i.r. and Raman spectra of SiH_3·SeMe and GeH_3·SeMe (Table **3**) have many features in common. The increased mass of the latter generally results in reduced P–R separations and less well-defined band contours. This is well

---

[25] Y. Shiro, M. Ohsaku, M. Hayashi, and M. Murata, *Bull. Chem. Soc. Japan*, 1970, **43**, 619.

[26] J. A. Lannon, G. S. Weiss, and E. R. Nixon, *Spectrochim. Acta*, 1970, **26**, *A*, 221.

[27] V. W. Laurie, *J. Chem. Phys.*, 1959, **30**, 1210.

[28] A. Almenningen, L. Fernholt, and H. M. Seip, *Acta Chem. Scand.*, 1968, **22**, 51.

[29] J. D. Murdoch, D. W. H. Rankin, and C. Glidewell, *J. Mol. Structure*, 1971, **9**, 17.

[30] I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc.* (*A*), 1971, 2240.

[31] J. H. Schachtschneider, Tech. Rep. No. 57–65, Shell Development Co., Emeryville, California, 1964.

illustrated by the asymmetric CH_3 stretching vibrations. In the i.r. spectrum of SiH_3·SeMe, these are identifiable as a *B*-type band, ν_1, centred at 3028 cm^{-1} and a *C*-type band, ν_{14}, at 3019 cm^{-1} but in GeH_3·SeMe there is only one band envelope (*ca.* 3015 cm^{-1}). Corresponding depolarised Raman bands are observed for both species. The symmetric CH_3 stretching vibration, ν_2, is seen for both species as a polarised Raman band and a *B*-type band in the i.r. spectrum.

The asymmetric CH_3 deformations are typical depolarised bands in the Raman effect and mixed contour bands in the i.r. spectra and so assignable without ambiguity. The symmetric CH_3 deformation, ν_6, is also of mixed contour which in both species has a clear, but weak *Q*-branch centred at 1283 cm^{-1} (Si) and 1278 (Ge). The band is polarised in the Raman spectra.

The CH_3 rocking modes are less readily assigned as they are usually relatively weak bands in both the i.r. and Raman spectra. Shoulders in the region 900—920 cm^{-1} are assigned to these modes. In GeH_3·SeMe there is no ready alternative assignment for these bands and in SiH_3·SeMe they are partially obscured by the SiH_3 deformation modes although a *Q*-branch at 900 cm^{-1} is a reasonable assignment. Comparisons with similar molecules and the normal-co-ordinate analysis lend considerable support to the assignment.

The symmetrical MH_3 stretch, ν_4, is readily identified as an *A*-type band in the i.r. spectrum and a polarised band in the Raman effect. In the Raman spectrum of SiH_3·SeMe, the asymmetric SiH_3 stretches are not resolved and appear as a depolarised shoulder at *ca.* 2180 cm^{-1}; in the i.r. spectrum ν_3 is seen as an *A*-type band centred at 2188 cm^{-1} and ν_{15} as a *C*-type band at 2172 cm^{-1}. In GeH_3·SeMe this separation is not evident. The MH_3 symmetric deformation mode, ν_9, is assigned to the typical prominent feature centred at *ca.* 920 cm^{-1} and 820 cm^{-1} respectively for SiH_3 and GeH_3. The asymmetric deformations are apparently non-degenerate from the fairly complex band contour seen in the broad higher-frequency bands of both compounds.

The MH_3 rocking modes are not resolved, appearing in the same band envelope. In GeH_3·SeMe the i.r. feature is suggestive of overlapping *B*- and *C*-type bands.

The Se–C stretching mode, ν_{10}, shows up most clearly for both SiH_3·SeMe and GeH_3·SeMe as a strong polarised band at 583 cm^{-1} (Si) and 584 cm^{-1} (Ge). Similarly, strong polarised bands are readily assignable to the M–Se stretching mode, ν_{12}, at 400 cm^{-1} (Si–Se) and 290 cm^{-1} (Ge–Se) as well as the M–Se–C bending mode, ν_{13}, at 174 cm^{-1} (Si–Se–C) and 164 cm^{-1} (Ge–Se–C). The two torsional modes are not observed.

The normal-co-ordinate analyses show that there is relatively little mixing of the force constants for most modes particularly for GeH_3·SeMe. In addition, fewer interaction force constants are required for the germane to get a reasonable fit. The force constants associated with the methyl vibrations, as expected, remain fairly constant; there are no significant differences in the interaction terms; and force constants involving Si or Ge are as expected from comparison with other molecules (Table 4). Only for the Se–C stretch, ν_{10}, and one of the SiH_3 rocks, ν_{11}, does the potential-energy distribution show extensive mixing of the force constants. The Se–C stretching force constants differ although the Se–C stretching modes appear in the same position in the spectrum. This is presumably related to the fact that for GeH_3·SeMe the Se–C stretch has a potential-energy distribution containing 87% of the Se–C stretching force constant whilst the potential-energy distribution in the silane analogue contains only 62% of the same constant with 32% of the HSiSe force constant.

TABLE 4

Force constant values for MH_3SeMe (M = Si and Ge) *

Force constant		Value in	
Number	Description	SiH_3·SeMe	GeH_3·SeMe
1	f_{MH}	2·704	2·531
2	f_{MSe}	2·129	1·865
3	f_{CSe}	2·870	2·641
4	f_{CH}	4·879	4·861
5	f_{HMH}	0·463	0·378
6	f_{MHSe}	0·533	0·468
7	f_{MSeC}	0·690	0·746
8	f_{SeCH}	0·518	0·528
9	f_{HCH}	0·476	0·493
10	$f_{MH/MH}$	0·015	−0·007
11	$f_{CH/CH}$	0·043	0·041
12	$f_{HMH/HMH}$	0·017	0·000
13	$f_{HCH/HCH}$	−0·031	−0·014
14	$f_{HMSe/HMSe}$	0·024	0·000
15	$f_{SeCH/SeCH}$	−0·045	−0·053
16	$f_{MSe/HMSe}$	0·000	0·000
17	$f_{SeC/SeCH}$	−0·073	0·000

* Units are: mdyne Å^{-1} for stretching, mdyne Å rad^{-2} for bending, and mdyne rad^{-1} for stretch-bend constants.

The vibrational spectra of the molecules $MeMH_2$·SeMe (M = Si and Ge) are assigned (Table 5) to general types of motion. The CH_3M' stretching and symmetric deformation modes in these and related species,[1,23,32] are characteristic of the nature of M′ (M′ = Ge, Si, and Se) and readily distinguishable. By contrast, the asymmetric CH_3M' deformations are only assignable to one broad feature. The CH_3 rocking modes for the methyl group attached to selenium are apparently consistently weaker than those attached to silicon or germanium. The former are assigned at 920 cm^{-1} in both species with the latter at lower frequency.

The MH_2 stretching vibrations are distinguishable by the polarisation data. The bands at 948 cm^{-1} (Si) and 865 cm^{-1} (Ge) correspond to the MH_2 symmetrical bending (scissors) mode in $MeMH_2X$,[21,23,32] This type of mode is usually at least partially polarised, although there are notable exceptions.[33] The polarised and depolarised bands at 694 and 658 cm^{-1} in $MeSiH_2$·SeMe correspond to the MH_2 wagging and twisting modes in $MeSiH_2X$.[32] The same bands are not resolved in the Raman spectrum of $MeGeH_2$·SeMe although they are clearly identifiable at 728 and 694 cm^{-1} in the i.r. spectrum.

---

[32] A. J. F. Clark and J. E. Drake, to be published.

[33] G. Herzberg, ' Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, 1968, p. 319.

The Se–C stretching mode is readily assigned to a strong polarised band in the 585 cm^{-1} region for both molecules which again emphasises the invariance in frequency with changes in the rest of the molecule. The M–C stretches occur in typical positions and as with the Se–M stretching modes produce strong polarised lines.

The low frequency skeletal deformation modes are seen as polarised lines in the Raman effect. In MeSiH$_2$·SeMe, the M–Se–C deformation is assigned to the lowest-frequency Raman line at 182 cm^{-1} by comparison with SiH$_3$·SeMe (174 cm^{-1}); the C–M–Se deformation is then attributed to the remaining feature at 209 cm^{-1}. In MeGeH$_2$·SeMe the increased mass of germanium leads to a reversal of position.

TABLE 5

The vibrational spectra (cm^{-1}) of MeMH$_2$·SeMe (M = Si and Ge) and SiH$_2$(SeMe)$_2$

	MeSiH$_2$·SeMe		MeGeH$_2$·SeMe		SiH$_2$(SeMe)$_2$	
Assignment	I.r. (gas)	Raman (liq)	I.r. (gas)	Raman (liq)	I.r. (liq)	Raman (liq)
CH$_3$(Se) str. (a)	3019w	3012w,dp	*ca.* 3010sh	3000m,dp	3010w	3014m,dp
CH$_3$(M) str. (a)	2973w	2969w,dp	3001wm	2990m,dp		
CH$_3$(Sc) str. (s)	2949s	2935s,p	2948m	2931s,p	2928m	2935s,p
CH$_3$(M) str. (s)	2915sh	2906s,p	*ca.* 2920sh	2918s,p		
MH$_2$ str. (a)	2160vs	2156sh,dp	2076s	2068sh,dp	2180s	2171sh,dp
MH$_2$ str. (s)	2148vs	2149vs,p	2058vs	2052vs,p	2140sh	2146vs,p
CH$_3$(M,Se) def. (a)	1435w	1425w,dp	1434wm	1430w,dp	1428m,br	1429w,dp
CH$_3$(Se) def. (s)	1287sh	1276m,p	1279s	1275wm,p	1276m	1275m,p
CH$_3$(M) def. (s)	1261s	1254m,p	*ca.* 1250sh	1243wm,p		
MH$_2$ bend (sc)	950sh	948w,p	870sh	865m,dp	855m,br	893w,p
CH$_3$(Se) rock (a, s)		904vw	*ca.* 920br,sh	925w,p	925br,sh	920sh,dp
CH$_3$(M) rock (a)	880br,vs	867w,dp	860m			
CH$_3$(M) rock (s)		875w,p	834vs	825w,p		
M–C stretch	731s	730m,p	604ms	600vs,p		
MH$_2$ wag	700sh	694m,p	728wm		790w,sh	788w,dp
MH$_2$ twist	650w	658w,dp	694s	690m,dp	730w,br	693w,dp
Se–C stretch		583s,p		585vs,p	583w	582s,p
MH$_2$ rock	486m	490vw,dp	438sh	447w,dp	510m,br	515w,dp
M–Se stretch (a)					436s,br	436m,dp
M–Se stretch (s)	389s	387vs,p		282vs,p	362m	381sh,p * 358s,p *
CMSe bend		209s,p		156m,p		
MSeC bend (a)						185m,dp
MSeC bend (s)		182sh,p		184s,p		165sh,p
SiSe$_2$ bend						108m,p * *ca.* 90w,p

* See text.

The molecule SiH$_2$(SeMe)$_2$ is expected to have 33 fundamental vibrations. The splitting of these into symmetry species poses a problem. Several conformers are possible in both eclipsed and gauche forms. In the absence of structural information, only general assignments are made although interesting features in some lower-frequency modes are noted.

The CH$_3$ modes, the SiH$_2$ stretching vibrations, and the Si–C stretching modes are readily assigned by comparison with the silanes just discussed. Bands in the Raman effect at 893, 788, and 693 cm^{-1} are assignable to three SiH$_2$ deformation modes. The i.r. spectrum in this region is far less clear; broad absorptions centred at 855, 790, and 730 cm^{-1} might also be assigned to these modes. The relatively large frequency shifts are unusual and may be indicative of the presence of more than one species. The presence of three i.r.-active modes in this region suggests that at least one of the conformers has symmetry lower than C_{2v}. The fourth deformation is clearly seen as a weak depolarised band in the Raman spectrum at 515 cm^{-1}, and as a broad absorption centred at 510 cm^{-1} in the i.r. spectrum typical of an SiH$_2$ rocking mode.[32]

The asymmetric SiSe$_2$ stretch is assigned to a depolarised band at 436 cm^{-1}. The polarised band at 358 cm^{-1} has a distinct polarised shoulder at 381 cm^{-1}. This is consistent with assignments to two symmetric SiSe$_2$ stretches providing further evidence for more than one conformer.

EXPERIMENTAL

The apparatus and associated spectroscopic techniques were as described previously.[1]

Starting Materials.—The halogeno-silanes and -germanes were prepared by standard methods: monobromosilane by HBr cleavage of PhSiH$_3$;[34] dibromo- and bromo(methyl)-silane by the reaction of BBr$_3$ with SiH$_4$ and MeSiH$_3$ respectively;[35] monoiodogermane from I$_2$ and excess of GeH$_4$ (Matheson) in a sealed tube;[36] monofluorogermane by passage of gaseous GeH$_3$I through lead(II) fluoride;[37] chloro(methyl)- and chloro(dimethyl)-germane by the reaction of BCl$_3$ with MeGeH$_3$ [10] and Me$_2$GeH$_2$.[11] In all cases the purity of the halides was established by comparison with the ^{1}H n.m.r. and i.r. spectra of the pure materials. Methaneselenol was obtained from anhydrous HBr and

---

[34] L. G. Ward, *Inorg. Synth.*, 1968, **11**, 159.

[35] J. E. Drake and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 219.

[36] J. W. Anderson, G. K. Barker, J. E. Drake, and R. T. Hemmings, *Synth. Inorg. and Metalorg. Chem.*, 1973, **3**, 125.

[37] S. N. Srivastava and M. Onyszchuk, *Proc. Chem. Soc.*, 1961, 205.

methylselenolithium as reported earlier.[1] Selenium powder (B.D.H.), methyl-lithium (Alfa Inorganics), and dimethyl ether were used as supplied. Commercial $LiAlH_4$ was recrystallised from anhydrous Et_2O. Solvents (Et_2O, tetrahydrofuran, diglyme, and monoglyme) were distilled from fresh $LiAlH_4$ under nitrogen and stored under vacuum.

Reaction of Monobromosilane with Methylselenolithium.—LiSeMe was first prepared from Se powder (12 mmol) and methyl-lithium (*ca.* 14 mmol) in tetrahydrofuran as described previously.[1] After removal of solvent SiH_3Br (*ca.* 15 mmol) and Me_2O (*ca.* 10 ml) were introduced into the reaction vessel and the mixture allowed to react at −78 °C (*ca.* 24 h). Repeated distillation of the volatile material gave $(SiH_3)_2Se$ and Me_2Se (total *ca.* 3 mmol, identified from ^1H n.m.r. spectra) as the only products condensing in a trap at −95 °C, unchanged SiH_3Br and Me_2O being obtained in a following trap at −196 °C. In a separate experiment diglyme was used for solvent in place of Me_2O (−45 °C, *ca.* 30 min); fractionation of the volatile material gave diglyme in a trap at −22 °C, a trace of SiH_3Br and a mixture of $MeSiH_3$ and SiH_4 (*ca.* 1 : 3, 4 mmol) in a trap at −196 °C, and a mixture of $SiH_3{\cdot}SeMe$ (*ca.* 2 mmol), $(SiH_3)_2Se$ (*ca.* 0·5 mmol)$_4$, and Me_2Se (*ca.* 0·5 mmol) held in a trap at −95 °C; all products were identified by their ^1H n.m.r. spectra.

Reactions of Lithium Tetramethylselenoaluminate.—$LiAl(SeMe)_4$ was prepared in *ca.* 2·5 mmol aliquot portions by the reaction of $LiAlH_4$ with MeSeH as described previously.[1]

(a) *Preparation of methylselenosilane.* In a typical experiment SiH_3Br (12·0 mmol) and diglyme (*ca.* 10 ml) were introduced into a vessel (*ca.* 50 ml) containing an aliquot portion of the $LiAl(SeMe)_4$. The reactants were held at −45 °C (*ca.* 30 min) and the volatile products fractionated. Pure methylselenosilane, $SiH_3{\cdot}SeMe$ (9·2 mmol) (Found: *M*, 124·3. Calc. for CH_6SiSe: *M*, 125·1) (v.p. *ca.* 17 cmHg at 25 °C) was obtained in a trap at −78 °C and SiH_3Br (*ca.* 2 mmol) with a trace of SiH_4 in a trap at −196 °C; a small amount of diglyme was held in a trap at −22 °C.

(b) *Preparation of bis(methylseleno)silane.* In another experiment SiH_2Br_2 (4·0 mmol) was allowed to react with the $LiAl(SeMe)_4$ as above. After 30 min at −45 °C the volatile material was fractionated giving pure bis(methylseleno)silane $SiH_2(SeMe)_2$ [3·7 mmol; v.p. *ca.* 4 mmHg at 25 °C; parent ion in the mass spectrum at *m/e* 216—220 (Calc. for $C_2H_8SiSe_2$: *M*, 220·0)] condensing in a trap at −22 °C and traces of SiH_4 held in one at −196 °C.

(c) *Preparation of methylseleno(methyl)silane.* By the same procedure $MeSiH_2Br$ (10·0 mmol) and $LiAl(SeMe)_4$ gave methylseleno(methyl)silane, $MeSiH_2SeMe$ (9·6 mmol) (Found: *M*, 140·2. Calc. for C_2H_8SiSe: *M*, 139·1) condensing in a trap held at −63 °C and a trace of $MeSiH_3$ (identified spectroscopically) in a following trap at −196 °C.

Reactions of Methylseleno(trimethyl)silane.—(a) *Preparation of methylselenogermane.* In a typical experiment GeH_3F (2·2 mmol) and $Me_3Si{\cdot}SeMe$ (2·0 mmol) were condensed into a reaction vessel (50 ml) held at −196 °C attached to the vacuum line. The reactants were warmed to room temperature and allowed to react (*ca.* 30 min). Fractionation of the volatile products gave pure methylselenogermane, $GeH_3{\cdot}SeMe$ [1·8 mmol; parent peaks in the mass spectrum at *m/e* 166—174 (Calc. for CH_6GeSe: *M*, 169·9)] condensing in a trap at −45 °C and a mixture of GeH_3F (*ca.* 0·1 mmol), Me_3SiF (2·0 mmol; identified by its ^1H n.m.r.[8] and i.r. spectra [38]), and a trace of GeH_4 passing through to a trap at −196 °C.

(b) *Attempted preparation of bis(methylseleno)germane.* GeH_2Br_2 (0·2 mmol) and SiH_3SeMe (0·5 mmol) were condensed into a semimicro n.m.r. tube held at −196 °C attached to the vacuum line. The tube was allowed to warm to room temperature. After *ca.* 15 min the products volatile at room temperature were removed leaving a colourless liquid which rapidly turned yellow. Subsequent ^1H n.m.r. analysis of the involatile material showed singlets at 5·70, 5·23, 2·08, and 1·90 p.p.m. (downfield from tetramethylsilane). The Raman spectrum showed prominent features at: 3014dp, 2927p (CH_3 stretching); 2080dp, 2051p (GeH_2 stretching); 1433dp, 1274p (CH_3 deformation); 920p (CH_3 rocking); 827p (GeH_2 bending); 709p (GeH_2 wag); 644dp (GeH_2 twist); 585p (SeC stretching); 455dp (GeH_2 rocking); 299dp, 266p ($GeSe_2$ stretching); 174p (GeSeC bending); 79p ($GeSe_2$ bending). The volatile fraction was shown from its ^1H n.m.r. spectrum to consist of SiH_3Br (0·4 mmol) and $SiH_3{\cdot}SeMe$ (trace).

(c) *Preparation of methylseleno(methyl)germane.* Typically $MeGeH_2Cl$ (0·96 mmol) and $Me_3Si{\cdot}SeMe$ (0·85 mmol) were condensed into a reaction vessel (10 ml) held at −196 °C. The mixture was brought to room temperature and allowed to react (15 min). Fractionation of the volatile material gave methylseleno(methyl)germane, $MeGeH_2SeMe$ (0·82 mmol) condensing in a trap at −45 °C and a mixture of Me_3SiCl and $MeGeH_2Cl$ (*ca.* 6 : 1, total 0·94 mmol; identified by ^1H n.m.r.[9,10] and i.r. spectra [23,39]) condensing in a following trap at −196 °C.

(d) *Preparation of methylseleno(dimethyl)germane.* In an exactly analogous reaction Me_2GeHCl (0·7 mmol) and $Me_3Si{\cdot}SeMe$ (0·44 mmol) reacted to give methylseleno(dimethyl)germane, $Me_2GeH{\cdot}SeMe$ (0·42 mmol) condensing in a trap at −45 °C and an inseparable mixture of Me_3SiCl and Me_2GeHCl (*ca.* 1·66 : 1; total 0·71 mmol) in a trap at −196 °C. Pure samples of $Me_2GeH{\cdot}SeMe$ gave i.r. and Raman (parentheses) features as follows: 3005sh (3000m), 2994m (2984m,dp), 2949m (2934s,p), 2925sh (2916s,p), CH_3 str; 2041vs (2040s,p), GeH str; 1433m (1431w,dp), 1416sh (1408sh,dp), 1282m (1275m,p), 1251m (1242m,p), CH_3 defs; 905sh (914vw,p), CH_3–Se rock; 850sh (857w,dp), 835vs (835w,p), 765m (754vw,dp), CH_3–Ge rocks; 666s (665m,dp), GeHSe bend; *ca.* 640sh (630m,dp), GeHSe twist; 611s (606sh,dp), GeC str (*a″*); 595s (595vs,p), GeC str (*a′*); 580sh, SeC str; (280vs,p), GeSe str; (*ca.* 191sh), C_2Ge def; (184s,p), CGeSe bend (*a′*); (157sh), GeSeC band.

Cleavage Reactions of the Methylselenides.—Known quantities of the pure compounds were allowed to react with excess of HBr at room temperature (*ca.* 30 min). The well characterised products methaneselenol and a Group IV bromide were identified quantitatively and qualitatively from ^1H n.m.r. and i.r. spectra. The recovery of near-quantitative amounts of cleavage products confirms the stoicheiometric formulation of monomeric methylselenide species.

[3/1428 *Received, 9th July,* 1973]

---

[38] H. Kriegsman, *Z. anorg. Chem.*, 1958, **294**, 113.

[39] A. L. Smith, *Spectrochim. Acta*, 1963, **19**, 1849.