Methylseleno-derivatives of Group IV.†

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The synthesis of a series of methylseleno-derivatives of Group IV, $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, or Sn, n = 1—4), is reported. The preparative routes include reactions of methaneselenol with Group IV amines; the dehydrohalogenation of methaneselenol and a Group IV halide; and the reactions of Group IV halides with ' methylselenolithium ', methylselenomagnesium iodide, lithium tetramethylselenoaluminate, and methylseleno(trimethyl)silane. The n.m.r. and vibrational spectra are reported and discussed. The reactions of the series Me_3MSeMe with some protic reagents were studied.

RECENTLY there has been considerable interest in the chemistry of compounds of sulphur with silicon, germanium, and tin.[1-4] It has been suggested that there may be $p\pi$–$d\pi$ bonding in the S–M bond (M = Si, Ge, or Sn)[5,6] and the compounds have proved useful as ligands for transition-metal complexes[7-9] and as synthetic intermediates in the preparation of Main Group[10] and the

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† For a preliminary communication of part of this work see ref. 22.

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transition-metal[11] sulphur compounds. Analogous selenium compounds have received much less attention but have already been used as ligands[1,12] and intermediates[13] in the preparation of transition-metal selenium compounds. Before commencement of this study the only reported methylseleno-compounds of this type were Me_3MSeMe (M = Sn or Pb)[13] and during the course of this work SiH_3SeMe was reported.[14] This paper describes the preparation, spectra, and reactions with some protic acids of the methylseleno(methyl) derivatives of silicon, germanium, and tin, $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, and Sn; n = 1—4).

Our investigations of Group IV substituted arsines showed that most routes applicable to silyl-, germyl-, and stannyl-arsines gave the highest yields for the silylarsines.[15-18] The latter can be converted quantitatively into the germyl- and stannyl-arsines by reaction with the appropriate halides.[17,18] Expecting similar results in the case of the selenides, we sought a good route to methylseleno(trimethyl)silane, $Me_3SiSeMe$. The most common routes to the methylthio-derivatives of Group IV utilise methanethiol as a starting material[1,5] and thus initially the use of methaneselenol was investigated.

The reaction of methaneselenol with methylsilicon halides in the presence of trimethylamine gave the methylseleno-silanes in 70% yield (1). Silicon–nitrogen,[1,19] germanium–nitrogen,[20] and tin–nitrogen[21] bonds are very susceptible to attack by protic reagents and we found that they are quantitatively cleaved by methaneselenol at room temperature (2). Methaneselenol reacted with lithium tetrahydroaluminate to evolve hydrogen (3). The resulting lithium tetra(methylseleno)aluminate reacted with trimethylsilyl, trimethylgermyl, and trimethylstannyl halides to give the desired products in yields of *ca.* 70%[22] (4).

$$Me_{4-n}SiCl_n + nMeSeH + nMe_3N \longrightarrow Me_{4-n}Si(SeMe)_n + nMe_3NHCl \quad (1)$$

$$Me_3MNMe_2 + MeSeH \longrightarrow Me_3MSeMe + Me_2NH \quad (2)$$
$$(M = Si, Ge, or Sn)$$

$$LiAlH_4 + 4MeSeH \longrightarrow LiAl(SeMe)_4 + 4H_2 \quad (3)$$

$$LiAl(SeMe)_4 + 4Me_3MX \longrightarrow 4Me_3MSeMe + LiX + AlX_3 \quad (4)$$
$$(M = Si, Ge, or Sn;\ X = Cl or Br)$$

The three methods described above are also suitable for the syntheses of germanium[17] and tin[18] arsines whereas only the third method is suitable for silicon arsines. The difference in reactivity between selenols and arsines in the first two methods is presumably related to the greater acidity of Se–H than of As–H.

Methaneselenol is not available commercially, so we searched for a more direct route to $Me_3SiSeMe$. Selenium, like sulphur, is electrophilic and reacts with Grignard reagents.[23] Selenium reacts with methylmagnesium iodide or methyl-lithium in tetrahydrofuran or diglyme to give methylselenide anions [reactions (5) and (6)]. Addition of chloro(trimethyl)silane (after removal of the tetrahydrofuran) gives slightly better yields of $Me_3SiSeMe$ with methyl-lithium (7). The use of a slight excess of methyl-lithium and chloro(trimethyl)silane ensures complete reaction of the selenium. Excess of the chlorosilane and the by-product, tetramethylsilane, are readily removed from $Me_3SiSeMe$. The choice of solvent is important and may be related to the solubility of selenium because monoglyme and dimethyl, diethyl, and dibutyl ether, in which there is no sign of selenium dissolving, all give poor yields.

$$MeMgI + \tfrac{1}{8}Se_8 = MeSeMgI \quad (5)$$

$$MeLi + \tfrac{1}{8}Se_8 = MeSeLi \quad (6)$$

$$MeSeLi\ (or\ MeSeMgI) + Me_3SiCl = Me_3SiSeMe + LiCl\ (or\ MgClI) \quad (7)$$

Excess of selenium in the reactions (5), (6), and (7) does not give polyselenides such as $Me_3Si(Se_n)Me$. It is assumed that when grey selenium dissolves, it does so mainly in the Se_8 form, as does sulphur.[24] The absence of polyselenides suggests that, as with the reaction of organometallo-lithium derivatives with sulphur,[4] the first step to give $LiSe_8Me$ is rate determining and there is rapid further reaction of the idealised type (8) so that no polyselenide ions are present. Had polyselenides formed, a deposit of red selenium would have been observed as they are unstable (9).

$$LiMe + LiE_8Me \longrightarrow LiEMe + LiE_7Me \quad (8)$$

$$Me_3Si(Se)_nMe \longrightarrow Me_3SiSeMe + Se_{n-1} \quad (9)$$

The reactions corresponding to (5), (6), and (7) when attempted with tellurium give $Me_3SiTeMe$ but in poor yield.[25] Tellurium has been shown to react well with aryl

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[20] Ref. 2, p. 557.

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Grignard reagents in tetrahydrofuran but not in diethyl ether. The corresponding reactions with alkyl Grignard reagents were unsuccessful.[26]

Methylseleno(trimethyl)silane can be used as the starting material for the preparation of germanium and tin derivatives (10). These exchange reactions, which

$$n\mathrm{Me_3SiSeMe} + \mathrm{Me}_{4-n}\mathrm{MX}_n = \mathrm{Me}_{4-n}\mathrm{M(SeMe)}_n + n\mathrm{Me_3SiX} \quad (10)$$

$$(\mathrm{M} = \mathrm{Ge\ or\ Sn};\ n = 1\text{—}4;\ \mathrm{X} = \mathrm{F, Cl, or\ Br})$$

occur in the absence of solvent, obey the general rule that the ' harder moiety prefers to be attached to silicon,' so that the reactions to give Ge–Se and Sn–Se bonds are essentially quantitative. Generally, the more readily available chlorides are used although for the formation of $Me_2Ge(SeMe)_2$ the fluoride Me_2GeF_2 is needed. The reaction of methylseleno(trimethyl)silane with chloro(trimethyl)lead did not give the expected methylseleno(trimethyl)lead but a mixture of decomposition products. An attempt to prepare $Me_3PbAsMe_2$ by this method was similarly unsuccessful.[27]

Similar exchanges to (10) between silicon moieties only work effectively for the tetrahalides (11). Even in the presence of an aluminium trichloride catalyst, the

$$4\mathrm{Me_3SiSeMe} + \mathrm{SiX_4} \longrightarrow \mathrm{Si(SeMe)_4} + 4\mathrm{Me_3SiX} \quad (11)$$

corresponding reactions with Me_2SiCl_2 and $MeSiCl_3$ give poor yields of $Me_2Si(SeMe)_2$ and $MeSi(SeMe)_3$. A further exchange reaction of this type (12) leads to the formation

$$\mathrm{Me_3SiSeMe} + \mathrm{SiH_3Br} \longrightarrow \mathrm{SiH_3SeMe} + \mathrm{Me_3SiBr} \quad (12)$$

and identification of methylselenosilane. Further investigation of this type of reaction may be of interest because earlier attempts of exchange between silyl- and trimethylsilyl-moieties have proved unfruitful.[28] Using a deficit of $Me_3SiSeMe$ in reactions (10) and (11) with $Me_{4-n}MCl_n$ (n = 2—4), we identified the mixed species $MCl(SeMe)_3$, $MCl_2(SeMe)_2$, $MCl_3(SeMe)$, $MeMCl(SeMe)_2$, $MeMCl_2(SeMe)$, and $Me_2MCl(SeMe)$ spectroscopically. With M = Si or Ge, the n.m.r. evidence for the mixed species is clear (Table 1) but with M = Sn, only time-averaged signals were observed.

Methylseleno-derivatives of Group IV can also be prepared by the reaction of methaneselenol with an arsine (13) but this reaction is of little practical significance.

$$\mathrm{Me_3MAsMe_2} + \mathrm{MeSeH} \longrightarrow \mathrm{Me_3MSeMe} + \mathrm{Me_2AsH} \quad (13)$$

Group IV element–sulphur bonds can be prepared by the reaction of a Group IV hydride with sulphur(II)–nitrogen compounds [29] but an attempt at similar reactions with selenium(II)–nitrogen compounds was unsuccessful.

The new methylseleno-compounds are all colourless liquids, which turn yellow on standing, and have an obnoxious odour. They are characterised by ^{1}H n.m.r., i.r., Raman, and mass spectra and by the reaction with anhydrous hydrogen halides. The latter cleave the Group IV element–selenium bond quantitatively (14) to give well known compounds.

$$\mathrm{Me}_{4-n}\mathrm{M(SeMe)}_n + n\mathrm{HX} \longrightarrow \mathrm{Me}_{4-n}\mathrm{MX}_n + \mathrm{MeSeH} \quad (14)$$

Methanol and water cleave the Si–Se bond according to reactions (15) and (16) but not the Ge–Se and Sn–Se

$$2\mathrm{Me_3SiSeMe} + \mathrm{H_2O} \longrightarrow \mathrm{(Me_3Si)_2O} + 2\mathrm{MeSeH} \quad (15)$$

$$\mathrm{Me_3SiSeMe} + \mathrm{MeOH} \longrightarrow \mathrm{Me_3SiOMe} + \mathrm{MeSeH} \quad (16)$$

bonds. A similar sequence has been found for M–As [15,18,27] and M–S [1-3] compounds. By contrast, although the M–Se bond (M = Si or Sn) is not affected by H_2S or MeSH, the corresponding M–As bonds are cleaved by these reagents.[27]

The mass spectra are only obtained for the more volatile species. The ready cleavage of the M–Se bond is evident from the high abundance of Me_nM and SeMe fragments relative to the parent peaks and indeed in some cases only the major fragmentation peaks are observed.

The ^{1}H n.m.r. spectra (Table 1) show evidence for various long-range couplings which are an indication of the purity of these compounds. Even traces of impurities have caused the loss of such coupling in related compounds.[30] This was very evident in the case of the series of mixed tin compounds $Me_2SnClSeMe$, $MeSnCl(SeMe)_2$, $MeSnCl_2SeMe$, and $Cl_{4-n}Sn(SeMe)_n$. Mixtures of the compounds exhibited a single SeMe resonance, which exhibited no satellite and whose position varied with the ratio of Cl to SeMe. By contrast, the mixed silicon or germanium compounds exhibited resonances characteristic of each compound. This evidence for more rapid exchange at tin is at least consistent with a greater tendency to form intermediates with co-ordination number greater than four.

The chemical shifts follow similar trends in the analogous series of sulphur and arsenic compounds, $Me_{4-n}M(SMe)_n$ and $Me_{4-n}M(AsMe_2)_n$ where M = Si,[31,32] Ge,[5,17] or Sn;[5,33] n = 1—4. Also the same trends are observed in the series $Me_{4-n}MX_n$ and $(Me_3M)_2E$ where M = Si,[34,35] Ge,[5,36] or Sn;[36,37] X = Cl, Br, or I; E = O,

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S, Se, or Te; $n = 1—4$. For compounds of this type, α-proton shifts ($H_3C–M_{\alpha}$) often appear to be controlled by the inductive effect and hence have been attributed to changes in electronegativity, while β-proton shifts ($H_3C–M–M'_{\beta}$) often appear to be more related to size of the changing substituents and hence have been attributed to anisotropy or dispersion effects.

The same general features are observed for the chemical shifts of the MeSe protons. It is unwise to place emphasis on the significance of the trends but they are useful as an aid to and confirmation of assignments. Thus for the β-proton resonances, *e.g.*, in the series $CH_3Se–MMe_3$, there is a consistent shift downfield (less shielding) of the CH_3Se protons (1·70, 1·78, and 1·83 p.p.m., respectively downfield of tetramethylsilane) as M changes Si to Ge to Sn. This is also noted in the series $(CH_3Se)_2MMe_2$, $(CH_3Se)_3MMe$, and $(CH_3Se)_4M$. The α-proton resonances can be examined in series such as $CH_3O–SiMe_3$,[38] $CH_3S–SiMe_3$,[31] $CH_3Se–SiMe_3$, and $CH_3Te–SiMe_3$ where there is a shift upfield (more shielding) as the electronegativity decreases along the series (3·35, 1·93, 1·70, and 1·43 p.p.m. respectively). By contrast the α-proton resonances for CH_3M show greatest shift downfield for germanium as in the series $CH_3Si–(SeMe)_3$, $CH_3Ge–(SeMe)_3$, and $CH_3Sn–(SeMe)_3$ with values of 0·93, 1·22, and 1·12 p.p.m. respectively. Moreover, this particular trend is also well established.[32,39]

TABLE 1(a)

The ^1H n.m.r. parameters for the series $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, or Sn; $n = 1—4$)

Compound	$\delta SeCH_3$	δMCH_3	$\lvert J(HC^{77}Se)\rvert$	$\lvert J(HCM^{77}Se)\rvert$	$\lvert J(^{13}CH)\rvert(M)$	$\lvert J(^{13}CH)\rvert(Se)$	$\lvert J(MCH)\rvert$	$\lvert J(MSeCH)\rvert$
$Me_3SiSeMe$	1·70	0·36	9·8	3·9	122	141	8·1	3·6
$Me_2Si(SeMe)_2$	1·78	0·62	10·5	4·2	122	143	7·8	4·2
$MeSi(SeMe)_3$	1·84	0·93	10·5	3·3	123	143	7·8	5·4
$Si(SeMe)_4$	2·00	—	10·5	—	—	145	—	5·7
$Me_3GeSeMe$	1·78	0·55	10·2	3·6	128	143	—	
$Me_2Ge(SeMe)_2$	1·85	0·85	10·5	2·7	131	142	—	
$MeGe(SeMe)_3$	1·95	1·22	10·8	2·1	131	141	—	
$Ge(SeMe)_4$	2·04	—	10·9	—	—	144	—	
$Me_3SnSeMe$	1·83	0·52	10·5	4·1	131	144	57·8 53·5	33·3 31·5
$Me_2Sn(SeMe)_2$	1·90	0·74	10·8	4·2	132	144	57·2 55·4	37·4 36·2
$MeSn(SeMe)_3$	2·05	1·12	10·8	4·0	132	143	59·7 57·3	46·1 43·9
$Sn(SeMe)_4$	2·09	—	10·8	—	—	141	—	54·0 52·2

All spectra recorded at room temperature; δ in p.p.m. (±0·02) downfield from internal tetramethylsilane; J in Hz (±0·2 for $J < 12$; ±1 for $J > 12$).

TABLE 1(b)

The ^1H n.m.r. parameters of some chloro(methyl)seleno-derivatives of silicon and germanium

Compound	$\delta SeCH_3$	δMCH_3	$\lvert J(HC^{77}Se)\rvert$	$\lvert J(HCM^{77}Se)\rvert$	$\lvert J(^{13}CH)\rvert(M)$	$\lvert J(^{13}CH)\rvert(Se)$	$\lvert J(MCH)\rvert$
$Me_2SiCl(SeMe)$	1·83	0·66	9·6	3·1	123	145	7·2
$MeSiCl(SeMe)_2$	1·90	0·99	9·9	3·0	122	144	n.o.
$MeSiCl_2(SeMe)$	2·15	1·04	9·7	3·0	122	144	n.o.
$SiCl(SeMe)_3$	2·08	—	10·2	—	—	144	—
$SiCl_2(SeMe)_2$	2·13	—	10·6	—	—	144	—
$SiCl_3(SeMe)$	2·23	—	10·4	—	—	144	—
$Me_2GeCl(SeMe)$	1·99	1·01	9·9	2·4	129	141	—
$MeGeCl(SeMe)_2$	2·03	1·38	9·8	1·8	130	144	—
$MeGeCl_2(SeMe)$	2·19	1·52	10·5	1·8	131	144	—
$GeCl(SeMe)_3$	2·16	—	10·5	—	—	144	—
$GeCl_2(SeMe)_2$	2·26	—	10·5	—	—	145	—
$GeCl_3(SeMe)$	2·44	—	10·0	—	—	144	—

All spectra recorded at room temperature on equilibrium mixtures; δ in p.p.m. (±0·02) downfield from internal tetramethylsilane J in Hz (±0·1 for $J < 12$; ±1 for $J > 12$).

The values of the direct coupling constants $J(^{13}CH)(M)$ for the CH_3M protons are essentially constant for the several compounds where M = Ge or Sn but are 5—6% lower when M = Si. This is similar to the sequence of compounds Me_4M where the lower value for Si was attributed to the effect of orbital overlap obscuring any effects due to electronegativity differences, rather than to an altered electronegativity scale.[39] Nevertheless, the effective electronegativity in these series is apparently Ge ≃ Sn > Si, and the α-proton shifts for CH_3M were ' out of order ' in a similar sense. The values of the direct coupling constant, $J(^{13}CH)(Se)$, for the CH_3Se protons are constant for all the compounds. Thus the *s*-character of these C–H bonds remains relatively insensitive to any changes in the constituents of the molecule.

It has been pointed out that trends in β-coupling

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constants based on the assumption that the Fermi contact term is the most important, could be deceptive.[40] Indeed no very clear pattern of trends emerges in these series. However, the near constancy of the value of J_{HCSe}, combined with the insensitivity of $J(^{13}CH)(Se)$ to β-substitution could indicate a constant hybridisation of the C–Se bond. In other words, the Group IV elements within the moiety CH_3–Se–M behave as if they have similar electronegativities. With any changes due to electronegativity being minimal, it is not surprising that the β-proton shifts, CH_3SeM, were clearly related to size as expected.

TABLE 2 *

The vibrational spectra of the series $M(SeMe)_4$ (M = Si, Ge, and Sn)

Mode		Si	Ge		Sn	
		Raman (liq)	I.r. (liq)	Raman (liq)	I.r. (liq)	Raman (liq)
CH_3 str	(a)	3004vw,dp	3010m	3005w,dp	3010m	3007w,dp
	(s)	2931w,p	2930s	2935m,p	2925s	2927m,p
CH_3 def	(a)	1414vw	1415s	1420w,dp	1417s	
	(s)	1275w,p	1269s	1273w,p	1270s	
CH_3 rock		906vw	905s		903s	
C–Se str		585s,p	578w	584s,p	577w	576s,p
M–Se str	(a)	447w,dp	305sh	300m,dp	263s	250m,dp
			295s		250sh	
	(s)	225s,p	225sh	218s,p		203s,p
MSeC bend		179m,p		178m,p		166s,p
MSe_4 def	(a)	114m,dp		105m,dp		81sh
	(s)	81m,p		78m,p		64sh
SiSe torsion?		53m,dp				

* Tables 2—5. All spectra (cm^{-1}) recorded at room temperature. s = strong, m = medium, w = weak, v = very, br = broad, p = polarised, dp = depolarised, sh = shoulder, str = stretch, def = deformation; (a) = asymmetric, (s) = symmetric.

TABLE 3

The vibrational spectra of the series $MeM(SeMe)_3$ (M = Si, Ge, and Sn)

Mode		Si	Ge		Sn	
		Raman (liq)	I.r. (liq)	Raman (liq)	I.r. (liq)	Raman (liq)
CH_3 str (M)	(a)	2975w,dp	3008m		3010m	
	(s)	2901m,p	2929s	2930w,p	2930s	2930w,p
CH_3 str (Se)	(a)	3005w,dp	3008m		3010m	
	(s)	2938m,p	2929s	2930w,p	2930s	2930w,p
CH_3 def (M)	(a)	1428vw,dp	1380sh		1400sh	
	(s)	1277s,p	1250w		1170w	
CH_3 def (Se)	(a)	1408w,dp	1420m		1419s	
	(s)	1277s,p	1271s		1270s	
CH_3 rock (M)		854vw	838s		752s	
CH_3 rock (Se)		907vw	903s		903s	
M–C str		720m,p	593m	585s,p	520s	530s,p
C–Se str		581s,p	583sh	585s,p	578w	581s,p
M–Se str	(a)	434w,dp	305s	306w,dp	252s	252w,dp
			295sh		247sh	
	(s)	305s,p	249m	248s,p		220s,p
MSeC bend				181m		159m
		179m,p				
MSe_3 rock				164sh		124sh
MSe_3 def	(a)	121vw		92sh		78w
	(s)	101vw		81sh		

The i.r. and Raman spectra of the series $M(SeMe)_4$, $MeM(SeMe)_3$, $Me_2M(SeMe)_2$, and Me_3MSeMe (M = Si, Ge, or Sn) are displayed in Tables 2—5. The assignments can be made with some confidence based on comparisons along the series and with the spectra of Me_2Se,[41] MeSeH,[42] MeSeSeMe,[43] Me_nMBr_{4-n},[44-50] $Me_nM(AsMe_2)_{4-n}$,[17,32] $Me_nM(SMe)_{4-n}$,[6,31] and other Me_nMX_{4-n}[46,47,51-58] compounds (M = Si, Ge, or Sn; n = 0—3).

TABLE 4

The vibrational spectra of the series $Me_2M(SeMe)_2$ (M = Si, Ge, and Sn)

Mode		Si	Ge		Sn	
		Raman (liq)	I.r. (liq)	Raman (liq)	I.r. (liq)	Raman (liq)
CH_3 str (M)	(a)	2967w,dp	2990w	2991vw	3005m	3002vw,dp
	(s)	2901s,p	2910w	2910w,dp	2920sh	2922w,p
CH_3 str (Se)	(a)	3012w,dp	3010sh	3010vw	3005m	3002w,dp
	(s)	2935s,p	2930s	2930w,p	2930s	2932w,p
CH_3 def (M)	(a)	1432w,dp	1405sh		1400sh	
	(s)	1258w,p	1232m		1185m	1185w,p
CH_3 def (Se)	(a)	1412w,dp	1422m		1423s	
	(s)	1274m,p	1273s		1272s	1279w,p
CH_3 rock (M)		839w,p	832m		770sh	
		805w,dp	800s		760s	
		753vw,dp	760sh		725sh	
CH_3 rock (Se)		909w,p	905m		902s	
M–C str	(a)	702vw,dp	613m	612w,dp	533s	534w,dp
	(s)	669m,p	578m	572sh p	512s	516s,p
C–Se str		585s,p		586s,p	580w	580s,p
	(a)	430vw,dp	300sh	290m,dp	255sh	244w,dp
			293s		247s	
M–Se str		378sh,p	266sh			
	(s)	345sh,p	259m	260s,p	230sh	226s,p
		336s,p				
MC_2 def		238sh		181sh		
MC_2 twist						
MC_2 rock		200br,m		174m		155br,m
MC_2 wag						
MSeC bend		180vw,sh		168sh		
MSe_2 def		99vw		96sh		74sh
		70sh				

As might be expected from the n.m.r. data, the position of the characteristic vibrations of both the CH_3–M and CH_3–Se moieties are relatively independent

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of the nature of the Group IV element or on the number of MeSe groups surrounding that element. This uniformity allows us to assign the methyl vibrations unambiguously. A close resemblance is observed in the positions of the CH_3M vibrations to those in the series Me_nMBr_{4-n} (n = 1—3; M = Si, Ge, or Sn). The CH_3 stretches, deformations, and rocks occur at very similar positions while the M–C stretches are at a slightly lower wavenumber, although, in the case of Me_3MSeMe and $Me_2M(SeMe)_2$, the symmetric–asymmetric M–C stretching separation is very similar. This is reasonable since the C–M–C bond angle is not expected to change much on substitution of Br for SeMe.

skeletal and CSeM bending modes appear as one broad envelope in the Raman spectra, an effect also noticed in Me_3SnSMe.[6]

The sulphur compounds $Si(SMe)_4$ and $Ge(SMe_4)$, analogous to the series $M(SeMe)_4$ (Table 2), show splitting of the asymmetric skeletal stretching modes in their i.r. spectra.[31] The nine vibrations of the MSe_4 skeleton based on local T_d symmetry correspond to an a_1 symmetric stretch (i.r.-inactive and Raman polarised), an e symmetric deformation (i.r.-inactive and Raman depolarised), and f_2 asymmetric stretches and deformations (i.r.-active and Raman depolarised). Unfortunately all the symmetric modes for the series appear in the 200 cm^{-1} region of the spectra so it is not possible for us to tell whether the methyl groups on selenium have lowered the symmetry sufficiently to make these modes i.r.-active. They are very strongly polarised in the Raman effect which suggests that local symmetry predominates, although there is some indication of a splitting of the asymmetric MSe_4 stretches from the appearance of shoulders in the i.r. spectra (Table 2) of $Ge(SeMe)_4$ and $Sn(SeMe_4)$. A strong, apparently depolarised band at 53 cm^{-1} in the Raman spectrum of $Si(SeMe)_4$ can be tentatively assigned to a SiSe torsional mode.

Similarly, the skeletal modes of the $MeM(SeMe)_3$ series can be assigned conveniently by assuming that local C_{3v} symmetry about M predominates (Table 3). Again, a slight splitting of the e-type MSe_3 asymmetric stretching vibrations, possibly as a result of the lowering of symmetry by the bent M–Se–C(H_3) bond, is evident from the shoulders at 295 and 247 cm^{-1} respectively in the i.r. spectrum of $MeGe(SeMe)_3$ and $MeSn(SeMe)_3$. As with the $M(SeMe)_4$ series there is no evidence for this splitting in the corresponding weak depolarised Raman bands, although there is a general broadening of the MSeC deformation region.

TABLE 5

The vibrational spectra (cm^{-1}) of the series Me_3MSeMe (M = Si, Ge, and Sn)

Mode		Si		Ge		Sn	
		I.r. (gas)	Raman (liq)	I.r. (liq)	Raman (liq)	I.r. (liq)	Raman (liq)
CH_3 str (M)	(a)	2985s	2971sh,dp	2985m	2985w,dp	2992m	2991w,dp
	(s)	2910m	2904s,p	2912w	2912m,p	2920sh	2919m,p
CH_3 str (Se)	(a)	3029w,sh	3019sh,dp	2985m	2993sh,dp	2992m	2997sh,dp
	(s)	2951sh	2941s,p	2935sh	2939sh,p	2935m	2928m,p
CH_3 def (M)	(a)	1455sh	1472sh,dp	1405sh		1400sh	
		1410w	1430w,dp				
	(s)	1254sh	1254w,p	1245m	1245w,p	1187w	1201w,p
CH_3 def (Se)	(a)	1437w	1420w,dp	1420w		1426m	
	(s)	1262s	1279m,p	1275sh	1275sh,p	1273m	1277w,p
CH_3 rock (M)		845vs	848w	830s	824vw	775s	770w
			831w				
		760m	753w	765vw		725sh	
CH_3 rock (Se)		900sh	910w,p	920vw	920w	900w	900w
M–C str	(a)	700m	701w,dp	610s	609w,dp	530s	530w,dp
	(s)	632m	630s,p	570vw	572s,p	508m	505s,p
C–Se str		580vw	585s,p	590sh	589s,p	581sh	581m,p
M–Se str		378sh	374s,p		282s,p	230sh	237s,p
MC_3 def	(a)		226sh		195sh		
	(s)		214mp		187s,p		
							154br,m
MC_3 rock			197vw,sh		146vw		
MSeC bend			179w,p		163vw		

Methyl vibrations of the methylseleno-group can be assigned characteristic vibrations at *ca.* 3005 cm^{-1} (asym. CH_3 stretch), *ca.* 2930 cm^{-1} (sym. CH_3 stretch), *ca.* 1420 cm^{-1} (asym. CH_3 deformations), *ca.* 1272 cm^{-1} (sym. CH_3 deformation), and *ca.* 910 cm^{-1} (CH_3 rocking modes). Additionally, all compounds exhibit a strong polarised band in the Raman effect, and a weak band in the i.r. spectrum at *ca.* 580 cm^{-1} which can unambiguously be assigned to the C–Se stretching vibration.

The positions of the M–Se stretching vibrations are shown in Tables 2—5. The symmetric–asymmetric splittings in $Me_2M(SeMe)_2$, $MeM(SeMe)_3$, and $M(SeMe)_4$ are, as noted for the M–C stretching separations, very similar to those found in the series Me_2MBr_2, $MeMBr_3$, and MBr_4, which suggests similar bond angles for the two series.

A strong band is seen in the Raman effect at *ca.* 170 cm^{-1} for the $M(SeMe)_4$ (Table 2) series which we can assign to the MSeC bending mode. Similar bands are observed in the other spectra, although they are not so clear in the Me_3MSeMe (Table 5) and $Me_2M(SeMe)_2$ (Table 4) series because of overlap with the Me_3M and Me_2M skeletal modes. In fact, in the tin series, the

The skeletal modes of the $Me_2M(SeMe)_2$ series are similarly assigned by assuming local C_{2v} symmetry which requires $4a_1 + 1a_2 + 2b_1 + 2b_2$ vibrations. Only the a_1 modes should be Raman polarised. On this basis the main peaks are readily assigned (Table 4). However, features remain which cannot be rationalised merely in terms of a lowering of symmetry but may be indicative of the presence of rotational isomers. Depending on the orientation of the methyl groups attached to selenium, symmetries of the type C_{2v}, C_1, and C_s (two such) can be generated. In the Si–Se stretching region of $Me_2Si(SeMe)_2$, the Raman spectrum shows the expected strong polarised a_1-type Si–Se symmetric mode at 336 cm^{-1} and the weak depolarised asymmetric mode at 430 cm^{-1}. However, the 336 cm^{-1} band has two clearly defined shoulder peaks at 354 and 378 cm^{-1} which are also polarised, cannot be reasonably rationalised in terms of Fermi resonance, and so could result from rotational conformers. [The n.m.r. spectrum was run before and after each Raman spectrum and showed no indication of proton-containing impurities nor of more than one species being present. However, the time scale of exchange could account for the latter.] The two features at 70 and 99 cm^{-1} could then be assigned to $SiSe_2$ bending vibrations of different conformers. The i.r. spectra of $Me_2Ge(SeMe)_2$ and $Me_2Sn(SeMe)_2$ show splittings, which are less marked, and there is a distortion of the symmetric M–Se stretching bands in the Raman spectrum. However, the bands assigned to the depolarised asymmetric modes are only slightly less polarised than those designated Raman-polarised which is at least consistent with the presence of compounds having C_1 symmetry for which completely depolarised bands are not expected.

The Me_3M vibrations of the series Me_3MSeMe could be assigned unambiguously by comparison with the spectra of Me_3MBr (M = Si, Ge, or Sn) by assuming local C_{3v} symmetry. No detectable splitting arises from the presence of the methyl group attached to selenium (Table 5). The Me_3 deformation and rocking modes and the MSeC bend all appear in one band envelope in $Me_3SnSeMe$. However, it is possible to make the appropriate assignments for the silicon and germanium analogues.

EXPERIMENTAL

Apparatus.—A conventional Pyrex-glass vacuum system was used for all experiments. The i.r. spectra were recorded at room temperature in the range 4000—200 cm^{-1} on a Beckman IR 12 spectrometer with either a gas cell (5 cm pathlength) fitted with KBr windows or, for liquid samples, an air-tight liquid-film cell fitted with CsI plates. Raman spectra were recorded in the range 4000—50 cm^{-1} with the sample in sealed Pyrex-glass tubes (*ca*. 2 mm o.d.) on a Beckman 700 laser-Raman spectrometer with a helium–neon or argon ion source. Strong bands are estimated to ±1 cm^{-1} in the i.r. spectra and ±4 cm^{-1} in the Raman effect. The ^1H n.m.r. spectra were recorded at 60 MHz on a Jeol C-60 HL high-resolution spectrometer in sealed tubes (*ca*. 2 mm o.d.) and the mass spectra on an AEI MS 10c2 instrument, fitted with a Hitachi–Perkin-Elmer recorder, operating at an ionising potential of 70 eV.

Starting Materials.—Commercial chloro(trimethyl)-silane and -stannane, bromostannane, methyl(trichloro)silane, -germane, and -stannane and tetrachloro-silane, -germane, and -stannane were used as supplied (Alfa Inorganics) and had ^1H n.m.r.[35-38] and/or i.r. spectra corresponding to the pure materials. Anhydrous diethyl ether (Mallinckrodt), tetrahydrofuran (B.D.H.), diglyme (B.D.H.), and monoglyme (Matheson) were distilled from fresh lithium tetrahydroaluminate and stored in vacuum vessels. Methyllithium (Alfa Inorganics) was used as supplied and transferred by use of a syringe. Hydrogen sulphide was prepared by hydrolysis of aluminium sulphide. Anhydrous methanol (Fisher), methanethiol (Eastman), trimethylamine (B.D.H.), dimethylamine (B.D.H.), spectral grade tetramethylsilane, and chloroform were used without further purification, their i.r. and ^1H n.m.r. spectra corresponding to the pure materials. Lithium tetrahydroaluminate was recrystallised from anhydrous diethyl ether. Trimethyl(dimethylamino)silane was prepared by reaction of trimethylchlorosilane with dimethylamine. Selenium powder (B.D.H.) was used as supplied. Anhydrous hydrogen bromide (Matheson) was 'pumped on' at −196 °C to remove any non-condensible gas.

Reactions with Lithium Tetramethylselenoaluminate.—Lithium tetrahydroaluminate (2·6 mmol) was placed in a flask attached to the vacuum line. Diethyl ether (*ca*. 7 ml) was condensed in, followed by methaneselenol (*ca*. 12 mmol). The flask was left for *ca*. 30 h at room temperature with occasional shaking. During this time there was a steady effervescence and a white solid was precipitated. The flask was surrounded by a liquid-nitrogen bath and the non-condensible gas (hydrogen, 9·4 mmol) pumped off. Bromo(trimethyl)germane (10·1 mmol) was condensed in and the mixture allowed to warm. A bath at −45 °C was placed around the flask which was then left for 35 min with regular shaking. All the volatile products were pumped out of the flask and separated on the fractionating column giving methylseleno(trimethyl)germane (7·4 mmol). The other volatile materials were the solvent and traces of trimethylgermane and methaneselenol.

Identical procedures were used to prepare methylseleno(trimethyl)-silane and -stannane from bromo(trimethyl)-silane and bromo(trimethyl)-stannane in yields of 66 and 69% respectively.

Reactions of Group IV *Hydrides with Selenium*(II) *Amines*.—In each case the Group IV hydride was condensed into a diglyme solution of $MeSeNMe_2$ in an n.m.r. tube (5 mm o.d.) attached to the vacuum line and the mixture allowed to warm to room temperature and left for 30 min. In the case of trimethylstannane there was effervescence and *ca*. 40% of the theoretical amount of dimethylamine was evolved. However the n.m.r. spectrum of the solution showed no peak attributable to methylseleno(trimethyl)stannane. With trimethylsilane and trimethylgermane no dimethylamine was evolved.

Reactions of Methaneselenol with Group IV *Arsines*.—In each case approximately equimolar amounts of the arsine and methaneselenol, together with a little benzene for reference, were sealed together in n.m.r. tubes (2 mm o.d.) and left overnight at room temperature. The ^1H n.m.r. spectra showed that dimethylarsine and the appropriate Group IV selenide had been formed almost quantitatively.

Reactions of Group IV *Amines with Methaneselenol*.—

Excess of methaneselenol was condensed into a solution of the amine (*e.g.*, trimethylstannyldimethylamine) in a few ml of ether and the mixture stirred at room temperature for 1 h with occasional cooling to ensure adequate mixing. The mixture was refluxed for 5 min and then separated to give methylseleno(trimethyl)stannane in near quantitative yield. The procedures and yields with the other Group IV amines were similar.

Preparation of ' Methylseleno-lithium.'—Typically tetrahydrofuran (*ca.* 30 ml) was distilled under vacuum from lithium tetrahydroaluminate on to selenium powder (2 g, 25 mmol) contained in a three-necked flask equipped with a rubber septum and a stirring bar. The system was filled with dry nitrogen, cooled to -196 °C, and a solution of methyl-lithium (*ca.* 30 mmol) in diethyl ether was introduced with a syringe. When the system was allowed to warm to room temperature with stirring, a colourless solution was formed. The solvents were distilled out leaving a colourless crystalline solid.

Reaction of ' Methylseleno-lithium.'—(*a*) Anhydrous hydrogen bromide (*ca.* 30 mmol) was condensed at -196 °C into the flask containing the methylseleno-lithium as prepared previously. Upon warming slowly to room temperature a mildly exothermic reaction occurred giving a colourless liquid. After *ca.* 30 min at room temperature the contents of the flask were cooled to -196 °C and any non-condensible gas pumped off through a series of U-traps also held at -196 °C. The products were then distilled through a trap held at -95 °C into one at -196 °C. Methaneselenol (*ca.* 23 mmol; identified by its i.r. spectrum[42]) stopped in the trap at -95 °C and unchanged HBr (*ca.* 1 mmol) passed through into the trap at -196 °C.

(*b*) Trimethylchlorosilane (*ca.* 30 mmol) was condensed at -196 °C into the flask containing the methylselenolithium. The reactants were allowed to warm to room temperature and held there for 2 h to ensure complete reaction. The products were then cooled to -196 °C and distilled through a trap held at -45 °C into one at -196 °C. Methylseleno(trimethyl)silane (*ca.* 24 mmol) (Found: *M*, 164·7. Calc. for $Me_3SiSeMe$: *M*, 167·05) was retained in the trap at -45 °C, unchanged trimethylchlorosilane and tetramethylsilane passed through and were collected in the trap at -196 °C. The mass spectrum of $Me_3SiSeMe$ showed the following major peaks at *m/e* values: 168—166 (10) $Me_3SiSeMe^+$; 153—151 (100) Me_3SiSe^+; 95—93 (60) $MeSe^+$; 80—78 (30) Se^+; 73 (60) Me_3Si^+; 58 (40) Me_2Si^+; 43 (40) $MeSi^+$; and 28 (10) Si^+.

(*c*) Trimethylbromogermane (*ca.* 5 mmol) was distilled into a flask held at -196 °C containing methylselenolithium (*ca.* 5 mmol). After 2 h at room temperature the products were allowed to pass through a trap held at -22 °C into one at -196 °C. Methylseleno(trimethyl)germane (4·7 mmol) remained in the trap at -22 °C and unchanged trimethylbromogermane together with a trace of tetramethylgermane collected in the trap at -196 °C. The mass spectrum of $Me_3GeSeMe$ showed the following major peaks at *m/e* values: 216—208 (5) $Me_3GeSeMe^+$; 186—178 (10) Me_2GeSe^+; 156—148 (10) $GeSe^+$; 121—115 (100) Me_3Ge^+; 91—85 (50) $MeGe^+$; and 76—70 (25) Ge^+.

Reactions of Methylseleno(trimethyl)silane.—A series of reactions of methylseleno(trimethyl)silane with halides in glass fingers attached to the vacuum line are described in Table 6. All reactions were at room temperature. In the reaction with silicon tetrachloride the volatile materials were removed from the reaction vessel every 24 h and separated into trimethylchlorosilane and methylseleno(trimethyl)silane and the latter returned to the reaction vessel.

TABLE 6

Reactions of methylseleno(trimethyl)silane with halides

Halide	[Halide]/mmol	[$Me_3SiSeMe$]/mmol	Reaction time/h	Product	[Product]/mmol	[$Me_3SiSeMe$]/mmol	[Me_3SiCl]/mmol	
Me_2SiCl_2	0·2	0·5	*ca.* 170	No reaction		0·5		
$MeSiCl_3$	0·2	0·7	*ca.* 170	No reaction		0·7	—	
$SiCl_4$	1·0	4·5	72	$Si(SeMe)_4$	0·95	0·5	4·0	
Me_3GeBr	0·6	0·5	0·5	$Me_3GeSeMe$	0·47	Trace	0·49 [a]	Me_3GeBr
Me_2GeF_2	0·5	1·1	1·0	$Me_2Ge(SeMe)_2$	0·5	0·1	*ca.* 1·0 [b]	
$MeGeCl_3$	0·4	1·4	2·0	$MeSe(SeMe)_3$	0·38	*ca.* 0·2	1·2	
$GeCl_4$	0·4	2·0	2·0	$Ge(SeMe)_4$	0·36	0·5	1·5	
Me_3SnCl	0·4	0·5	1·0	$Me_3SnSeMe$	0·38	Trace	0·4	Trace of yellow solid
Me_2SnCl_2	0·9	2·0	1·0	$Me_2Sn(SeMe)_2$	0·86	Trace	1·75	
$MeSnCl_3$	0·8	2·5	1·0	$MeSn(SeMe)_3$	0·75	0·2	2·3	
$SnCl_4$	0·5	2·3	1·0	$Sn(SeMe)_4$	0·45	0·5	2·0	
SiH_3Br	1·0	0·6	1·0	SiH_3SeMe	*c*	—	*c*	SiH_3Br (0·4 mmole)
HBr	0·7	0·5	1·0	HSeMe	0·48	—	0·49 [a]	HBr (0·2 mmole)

[a] Me_3SiBr. [b] Me_3SiF. [c] Inseparable mixture of SiH_3SeMe and Me_3SiBr (approximately equimolar by n.m.r.)

A further series of reactions carried out at room temperature in sealed n.m.r. tubes with tetramethylsilane as reference is detailed in Table 7. Similar conditions were used with the methyltin chlorides.

Reactions of Methylseleno(trimethyl)-germane and -stannane with Water, Methanol, Hydrogen Sulphide, and Methanethiol.—Typically $Me_3GeSeMe$ (0·2 mmol) and H_2O (0·2 mmol) were sealed together in a semimicro n.m.r. tube together with a trace of tetramethylsilane. After *ca.* 1 day no change was observed in the ^1H n.m.r. spectrum. A similar procedure was followed for the other reactions; in each case no change was observed after *ca.* 1 day.

Reactions of Methaneselenol.—(*a*) Dichloro(dimethyl)silane (1·0 mmol) and trimethylamine (3·0 mmol) with MeSeH (2·2 mmol) were condensed at -196 °C into a 50 ml reaction vessel attached to the vacuum line. Upon warming to room temperature a white solid was formed. After *ca.* 1 h the products were distilled out of the flask and fractionated. $Me_2Si(SeMe)_2$ (0·7 mmol) was collected in a trap held at -22 °C whilst excess of Me_3N and MeSeH passed through to one at −196 °C. The mass spectrum of $Me_2Si(SeMe)_2$ showed the following major peaks at *m/e* values: 248—244 (40) $Me_2Si(SeMe)_2^+$; 218—214 (30) $Me_2SiSe_2^+$; 203—199 (80) $MeSiSe_2^+$; 153—151 (100) $Me_2SiSeMe^+$; 138—136 (70) Me_2SiSe^+; 108—106 (80) $SiSe^+$; 95—93 (100) $MeSe^+$; 80—78 (60) Se^+; and 28 (20) Si^+.

(*b*) Trichloro(methyl)silane (1·0 mmol) and trimethylamine (4·0 mmol) with MeSeH (3·5 mmol) were condensed at −196 °C into a 50 ml reaction vessel equipped with a semimicro n.m.r. tube side arm. Upon warming to room temperature a white solid formed. After *ca.* 1 h all volatile products were removed and the remaining colourless liquid was distilled into the side arm which was cooled to −196 °C. The n.m.r. tube was then sealed off, the ^1H n.m.r. spectrum showing that pure $MeSi(SeMe)_3$ (0·6 mmol) was present. Owing to the involatility of the compound no mass spectral data was obtained.

TABLE 7

Reaction of methylseleno(trimethyl)silane with halides and protic reagents followed by n.m.r.

Reactants	[Reactant] mmol	[$Me_3SiSeMe$] mmol	Reaction time	Unchanged $Me_3SiSeMe$ (%)	Products
Me_2SiCl_2	0·5	0·5	1 week [a]	95	$Me_2Si(SeMe)_2$, $Me_2SiCl(SeMe)$, Me_3SiCl
$MeSiCl_3$	0·2	0·7	1 week [a]	95	$MeSi(SeMe)_3$, $MeSiCl(SeMe)_2$, $MeSiCl_2(SeMe)$, Me_3SiCl
$SiCl_4$	0·2	0·9	1 week	50	$SiCl_{4-n}(SeMe)_n$ (n = 1—4), Me_3SiCl
			2 weeks	12	$Si(SeMe)_4$, Me_3SiCl
Me_2GeCl_2	0·2	0·5	2 days	n.m.	$Me_2Ge(SeMe)_2$, $Me_2GeCl(SeMe)$, Me_3SiCl
			2 weeks	n.m.	$Me_2Ge(SeMe)_2$, Me_3SiCl
$MeGeCl_3$	0·1	0·2	15 min [b]	0	$MeGeCl_{3-n}(SeMe)_n$ (n = 0—3), Me_3SiCl
$GeCl_4$	0·2	0·4	1 hour [b]	0	$GeCl_{4-n}(SeMe)_n$ (n = 1—4), Me_3SiCl
SiH_3Br	0·5	0·2	15 min	0	SiH_3SeMe, Me_3SiBr
SiH_3F	0·7	0·5	3 days	90	SiH_3SeMe, Me_3SiF
Me_3PbCl	0·7	1·0	<30 min	n.m.	Black solid, yellow liquid containing Me_3SiCl, Me_2Se, unidentified singlet at δ 0·90
H_2O	0·5	0·3	10 min	0	$(Me_3Si)_2O$, MeSeH, H_2O (1 : 2 : 2·2)
MeOH	0·3	0·2	10 min	0	Me_3SiOMe, MeSeH, MeOH (2 : 2 : 1)
H_2S	0·3	0·2	1 day	100	No reaction
MeSH	0·3	0·2	1 day	100	No reaction

[a] With a crystal of $AlCl_3$ as a catalyst; no further change after 1 month. [b] No further change after 1 week.

Cleavage Reactions of $Me_nM(SeMe)_{4-n}$ (M = Si, Ge, *or* Sn; n = 0—4) *with Anhydrous Hydrogen Bromide.*—Typically $Me_3SnSeMe$ (0·141 g; 0·55 mmol) was placed into a 25 ml reaction vessel attached to the vacuum line. Anhydrous HBr (1·0 mmol) was distilled in at −196 °C and the reactants left at room temperature for *ca.* 30 min. Separation of the products volatile at room temperature gave MeSeH (0·53 mmol) in a trap held at −112 °C and HBr (0·43 mmol) in a trap at −196 °C. Me_3SnBr (0·132 g; 0·54 mmol) remained in the reaction vessel. All products were readily identifiable from their known spectra.

A similar procedure was used for all the pure methylseleno-derivatives reported in this paper; in each case the ratio of halide to methaneselenol was as expected.

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