Interconversion of Derivatives of Germane using Heavy-metal Salts: Synthesis of Germyl Carboxylates †

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Reactions of bromogermane with silver(I) and lead(II) salts have been investigated more fully than hitherto, resulting in the preparation and full characterization of three carboxylato-derivatives of germane, germyl formate, acetate, and trifluoroacetate. The wider scope of conversions using lead rather than the more reactive silver salts are illustrated by facile synthesis of (*i*) digermyl ether from PbO or $Pb[CO_3]$ and (*ii*) the silyl formate from bromosilane with $Pb[CO_2H]_2$. I.r., Raman, mass-spectroscopic, and ^1H n.m.r. data for the compounds are discussed in relation to those for their silyl analogues, for which Raman spectra have also been measured. Protolysis reactions of $GeH_3(NCS)$ are of limited value in the synthesis of germane derivatives but afford $GeClH_3$, $GeH_3(SMe)$, and $[Mn(CO)_5(GeH_3)]$ from HCl, MeSH, and $[Mn(CO)_5H]$ respectively.

INTERCONVERSION of derivatives of silane through reactions with silver salts has been shown by MacDiarmid[1] to be a versatile route to a number of silyl compounds, and has been formalized in terms of a ' silver-salt conversion series '. By contrast, application of similar

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[1] A. G. MacDiarmid, *Quart. Rev.*, 1956, **10**, 208.

methods to the development of the substitution chemistry of germane has remained neglected since exploratory work by Srivastava and his co-workers,[2,3] so that the potential of conversions using heavy-metal salts for synthesizing compounds containing the germyl (GeH_3) group has yet to be fully explored. We have investigated reactions of bromogermane with a variety of silver and lead salts, which afford a range of germyl derivatives including the novel carboxylates germyl formate and trifluoroacetate and provide a facile synthesis of the structurally[4] and chemically[3,5] interesting digermyl ether.

EXPERIMENTAL

General manipulative techniques and the synthesis of bromogermane have been described elsewhere.[6,7] Inorganic silver, lead, and mercury salts were either obtained commercially or prepared by established methods and were thoroughly dried by prolonged pumping *in vacuo* before use. I.r. and Raman spectra (from 488.0 nm, argon-ion laser) were recorded using Perkin-Elmer 457 and Cary 83 spectrometers respectively, ^1H n.m.r. spectra with a Varian A60-D instrument, and mass spectra using an A.E.I. MS902 mass spectrometer.

Reactions were carried out in one of two ways: either (*i*) streaming bromogermane through a U column containing the powdered metal salt diluted with three times its volume of acid-washed dried sand; or (*ii*) condensing bromogermane onto an excess of metal salt in an evacuated round-bottomed flask (50 cm^3). In either method the reaction vessel was incorporated into a vacuum system and volatile products were separated by trap-to-trap fractionation.

Syntheses.—Germyl formate. Bromogermane (90 mg, 0.58 mmol) was condensed onto excess of powdered dry lead(II) formate. After warming to room temperature and allowing reaction for 10 min, volatile products were shown by i.r. spectroscopy to consist of a mixture of CO (incondensible at −196 °C), germane, formic acid, digermyl ether, water, and *germyl formate*, characterized by mass spectroscopy. The product (*ca.* 40% yield) was freed with difficulty from $O(GeH_3)_2$ by repeated condensation in a trap at −63 °C. Further experiments using shorter contact times (2 min) reduced the amount of $O(GeH_3)_2$ formed, giving only traces of formic acid and affording $HCO{\cdot}OGeH_3$ in 75% yield.

Germyl Acetate. Streaming $GeBrH_3$ through a column containing silver(I) acetate diluted with sand gave *germyl acetate* in almost quantitative yield as described earlier.[2] On condensing $GeBrH_3$ (80 mg, 0.51 mmol) onto dry lead(II) acetate, fractionation after 10 min at ambient temperature afforded the same *product* (52 mg, 0.39 mmol) held at −45 °C, together with a mixture of $O(GeH_3)_2$ and GeH_4 at −196 °C.

Germyl trifluoroacetate. Passage of $GeBrH_3$ (115 mg, 0.74 mmol) through a column charged with silver(I) trifluoroacetate gave *germyl trifluoroacetate* (120 mg, 0.64 mmol) condensed at −45 °C and identified spectroscopically, together with a little trifluoroacetic acid and GeH_4 collected at −196 °C.

Germyl benzoate. Bromogermane was passed through a column containing excess of silver(I) benzoate, diluted as described above. The silver salt darkened rapidly but no volatile component was collected. On warming the U tube gently a white solid sublimed out *in vacuo* and was identified (i.r.) as benzoic acid. Examination of the purple residue in the reaction tube by i.r. spectroscopy showed absorptions attributable to the presence of Ge–H bonds; on strong heating it evolved GeH_4.

Silyl esters. Silyl trifluoroacetate was prepared in 73% yield by reaction of bromosilane with the silver salt at −10 °C as described by Ebsworth and Thompson.[8] A similar reaction between $SiBrH_3$ and $Ag[O_2CMe]$ gave *silyl acetate* in 35% yield at 0 °C and 38% at −10 °C. *Silyl formate* was obtained by condensing $SiBrH_3$ (124 mg, 1.12 mmol) onto dry $Pb[O_2CH]_2$; after 15 min at 20 °C fractionation afforded the *product* (41 mg, 0.54 mmol) together with some formic acid, disiloxane, and silane. The purity of each of these compounds was confirmed by i.r. and ^1H n.m.r. spectroscopy.[8]

Reactions of Bromogermane with Lead Salts.—Lead(II) *oxide.* After 10 min at room temperature, $GeBrH_3$ (84 mg, 0.54 mmol) and excess of powdered PbO gave *digermyl ether* (79 mg, 0.47 mmol) and GeH_4 (5 mg, 0.07 mmol) as the only products, separated at −127 °C.

'Red lead'. Under similar conditions, $GeBrH_3$ and Pb_3O_4 afforded only traces of $O(GeH_3)_2$.

Lead(IV) *oxide.* Bromogermane reacted violently with a bluish flash immediately on warming to ambient temperature with PbO_2. Volatile products were water, unchanged $GeBrH_3$, and GeH_4, and elemental lead was recovered from the reaction residue.

Lead(II) *carbonate.* Bromogermane (80 mg, 0.51 mmol) was allowed to react for 10 min at room temperature with excess of $Pb[CO_3]$. A mixture of unchanged $GeBrH_3$ and $O(GeH_3)_2$ was produced which could not be successfully separated by fractionation but which represented *ca.* 50% conversion into the ether.

Lead(II) *nitrate.* During 2 h at ambient temperature, $Pb[NO_3]_2$ turned yellow in contact with $GeBrH_3$. After this time the only volatile products were GeH_4 and nitrogen mono-oxide (i.r.).

Lead(II) *iodide.* Bromogermane (217 mg, 1.39 mmol) was condensed onto PbI_2. After 45 min the only product other than unchanged $GeBrH_3$ (193 mg, 1.24 mmol) was a trace of GeH_4.

Lead(II) *cyanate.* Condensation of $GeBrH_3$ (100 mg, 0.64 mmol) onto $Pb[OCN]_2$ gave, after 25 min at ambient temperature, *germyl isocyanate* (73 mg, 0.62 mmol) with only trace amounts of $O(GeH_3)_2$ and GeH_4.

Lead(II) *thiocyanate.* A similar reaction to that above afforded pure *germyl isothiocyanate* in 80% yield, held in a trap at −45 °C.

Lead(II) *cyanamide.* Reaction as above yielded only unchanged $GeBrH_3$ together with small amounts of $O(GeH_3)_2$. Further experiments firmly established that consecutive treatment of a single sample of the lead salt with

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[2] T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Canad. J. Chem.*, 1962, **40**, 739.

[3] C. H. Van Dyke, 'Preparative Inorganic Reactions,' ed. W. L. Jolly, Interscience, 1971, vol. 6, p. 157; J. E. Drake and C. Riddle, *Quart. Rev.*, 1970, **24**, 263.

[4] C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and S. Cradock, *J. Chem. Soc.* (*A*), 1970, 315.

[5] T. D. Goldfarb and S. Sujishi, *J. Amer. Chem. Soc.*, 1964, **86**, 1679.

[6] P. C. Angus and S. R. Stobart, *J.C.S. Dalton*, 1973, 2374.

[7] L. M. Dennis and P. R. Judy, *J. Amer. Chem. Soc.*, 1929, **51**, 2321.

[8] E. A. V. Ebsworth and J. C. Thompson, *J. Chem. Soc.* (*A*), 1967, 69.

several fractions of $GeBrH_3$ resulted finally in no further formation of ether, and no other product was observed even at elevated temperatures in a heated U column. The conversion of $GeBrH_3$ into $O(GeH_3)_2$ is thus attributable to traces of oxide or oxo-salts in the $Pb[CN]_2$ used, although this could not be detected by microanalysis for C and N.

RESULTS AND DISCUSSION

On passing bromogermane vapour through a column containing silver(I) acetate diluted with an inert support, virtually quantitative conversion into germyl acetate was observed, as reported by earlier workers.[2] We found that the same compound can be obtained in high yield rather more conveniently by condensing $GeBrH_3$ onto undiluted lead(II) acetate and allowing reaction to occur over 10 min at room temperature. Similar treatment of lead(II) formate afforded the hitherto unreported germyl formate, very short reaction times (2 min) limiting the formation of other products. With silver(I) trifluoroacetate, $GeBrH_3$ reacted to yield a further new carboxylate, germyl trifluoroacetate, while with silver(I) benzoate no volatile germyl derivative could be isolated. Silyl trifluoroacetate has been prepared by Ebsworth and Thompson, by treatment of the silver(I) salt with halogenosilanes;[8] with silver(I) formate, however, only traces of silyl formate were isolated and explosive reactions were described. Here, while no difficulty was encountered in synthesizing silyl acetate by this method, although yields were rather low, the advantage of using lead salts is emphasized by the smooth conversion of bromosilane into silyl formate.

The new germyl esters resemble germyl acetate [2,9] in their physical properties; all three compounds are low-melting colourless liquids whose i.r. spectra contain strong absorptions attributable to the presence of the GeH_3 group and bands near 1 600 cm^{-1} due to C=O stretching. A further account of i.r. and Raman data is given below in relation to comparable measurements [10] for the analogous silane derivatives. In the vapour phase at low pressure, thermal decomposition is slow but complete, varying from 3 (formate) to 7 d (acetate) to give the appropriate acid, germane, and some polymeric germanium hydride $(GeH)_x$: by contrast, in the liquid phase the behaviour of the three compounds appears to vary markedly. As found by others, germyl acetate decomposes rapidly only near 100 °C, without formation of GeH_4 or any other volatile germyl species.[2] Decomposition of the formate is fast at ambient temperature (particularly in the presence of $Pb[O_2CH]_2$) and seems to follow equation (1); similar decarbonylation of alkylgermyl formates has been observed.[11] The trifluoroacetate is of intermediate stability, slowly producing a canary-yellow brittle solid for which i.r. spectroscopy

$$2HCO{\cdot}OGeH_3 \longrightarrow O(GeH_3)_2 + 2CO + H_2O \quad (1)$$

confirmed the presence of CF_3CO groups; the spectrum showed no absorption due to Ge–H. Mass spectroscopy indicated a relatively large unit ($m/e \approx 300$) containing only one germanium atom as the basis for a presumably polymeric structure; an appropriate formulation would be $[Ge(O_2CCF_3)_2]_x$ (calc. for $C_4F_6{}^{74}GeO_4$: m/e 300). A very different situation was encountered for the corresponding silyl esters,[8] of which the acetate is much the least thermally stable and loses silane rapidly below 20 °C.

Proton chemical shifts for the germyl carboxylates are collected in Table 1, where they are compared with those for two other germanium–oxygen bonded species. As expected, the Ge*H* resonances occur *ca.* 1 p.p.m. to low field of those for Si*H* in the silyl analogues.[8] However, unlike the latter the shifts in the germanes do follow the order of electron-releasing character of the substituent group, with that for the trifluoroacetate at substantially lower field than the other two esters and that for methoxygermane at highest field.

TABLE 1

^{1}H N.m.r. data [a] for germyl carboxylates and related compounds

Compound	τ(Ge*H*)	τ(C*H*)
$HCO{\cdot}OGeH_3$	4.49	1.89
$MeCO{\cdot}OGeH_3$	4.51	7.88
$CF_3CO{\cdot}OGeH_3$	4.13	
$OMe(GeH_3)$	4.88 [b]	6.51 [b]
$O(GeH_3)_2$	4.72 [c]	

[a] At 35 °C in $CDCl_3$ solution (*ca.* 10% v/v) from internal $SiMe_4$. [b] Ref. 15. [c] S. Cradock, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc. (A)*, 1969, 1628.

Mass-spectroscopic data for the silyl and germyl esters are complicated by the polyisotopic nature of both Si and Ge and by successive hydrogen loss from the MH_3 group (M = Si or Ge), but the abundance of important fragment ions can be summarized as in Table 2. For the formates and acetates a marked increase in the proportion of ion current carried by $[MH_x]^+$ fragments is evident on going from M = Si or Ge, at the expense of that accounted for by (formally) M–O bonded ions. This can be rationalized in terms of the marked decrease in M–O bond energy between Si and Ge, and carries the implication that the low thermal stability of silyl acetate [8] is due to kinetic rather than thermodynamic factors. Such simple fragmentation behaviour is not found for the trifluoroacetate analogues (Table 2), but the predominance of $[GeH_x]^+$ ions in the spectrum of the germane again suggests loss of CF_3CO_2 through Ge–O bond scission, whereas for the silane less selective breakdown of the heavy-atom skeleton of the molecule, attributable to the stronger Si–O bond, results in a complex sequence of ion fragments. Of considerable interest in the spectra of both trifluoroacetates is a rearrangement involving fluorine transfer from the CF_3 group, to give $[MFH_x]^+$ ions, in much higher abundance than $[MH_xO]^+$ despite the prominence of the latter for the unfluorinated compounds.

The mass spectra of the germyl carboxylates differed from those of mono-organogermanes and related compounds in the high abundance for the former of $[GeH_x]^+$

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[9] T. N. Srivastava and M. Onyszchuk, *Canad. J. Chem.*, 1963, **41**, 1244.

[10] A. G. Robiette and J. C. Thompson, *Spectrochim. Acta*, 1965, **21**, 2023; P. C. Angus, unpublished work.

[11] H. H. Anderson, *J. Amer. Chem. Soc.*, 1952, **74**, 2371.

ions. This appears to be a general feature of the fragmentation of GeH_3X derivatives with X an electron-withdrawing group: thus for X = Cl or Br we observed a similar pattern with no X^+ ions. In the case of $GeH_3(NCO)$, the families $[GeH_x(NCO)]^+$, $[GeH_x(NC)]^+$, $[GeH_xN]^+$, and $[GeH_x]^+$ were all found with the first of these most abundant, and an intense family due to $[GeH_x(NCO)]^{2+}$ ions may imply a strong skeletal bonding framework; no Ge–O containing fragments were detected, consistent with the absence[12] of the isomer $GeH_3(OCN)$.

TABLE 2

Mass spectra of silyl and germyl carboxylates

Formates Ion family[a]	Percentage of metal-containing ions[b] Si	Ge
$[MH_x(O_2CH)]^+$	34.8	15.5
$[MH_x(O_2C)]^+$		
$[MH_xO]^+$	41.4	38.2
$[MH_x]^+$	23.8	46.3
Acetates		
$[MH_x(O_2CMe)]^+$	17.9	13.0
$[MH_x(O_2CH)]^+$	3.6	[c] 9.6
$[MH_x(O_2C)]^+$	20.1	
$[MH_xO]^+$	30.6	22.5
$[MH_x]^+$	27.8	54.9

Trifluoroacetates Ion family[a]	Percentage of metal-containing ions[b] Si	Ge
$[MH_x(O_2CCF_3)]^+$	0.5	3.7
$[MH_x(O_2CCF_2)]^+$	0.6	1.1
$[MH_x(O_2CCF)]^+$	0.2	
$[MH_x(O_2CF)]^+$	9.4	7.6
$[MH_x(O_2CC)]^+$	0.8	
$[MH_x(OCF)]^+$	15.9	
$[MH_x(O_2CH)]^+$	4.5	[c] 9.6
$[MH_x(O_2C)]^+$	27.2	
$[MH_x(OC)]^+$	0.7	
$[MH_xF]^+$	12.2	11.2
$[MH_xO]^+$	3.5	2.5
$[MH_x]^+$	24.6	64.2

[a] M = Si or Ge; x = 0—3. [b] Summed over x in each ion family. [c] x = 3.

The spectroscopic data for silyl and germyl esters do not offer any evidence for unusual M–O (M = Si or Ge) bonding characteristics analogous to those which lead to wide M–O–M bond angles in $O(MH_3)_2$ compounds.[4] Thus planar structures, with a *cis* configuration as found for the corresponding methyl esters, remain the most likely for these molecules.[10]

Vibrational Spectra.—A detailed discussion of the i.r. spectra of silyl formate, acetate, and trifluoroacetate, including partial assignments in terms of C_s selection rules, has been published.[10] Raman data reported here for the same compounds substantiate most of these earlier conclusions, which have therefore been used as a basis for interpretation of the vibrational spectra of the germyl esters. Observed bands and assignments for germyl formate are in Table 3, with numbering of vibrations belonging to either a' or a'' symmetry species following that adopted for the silyl analogue,[10] and here are also listed Raman shifts for $HCO{\cdot}OSiH_3$. Similar data for germyl acetate and trifluoroacetate are in Table 4, and again Raman wavenumbers for the silyl analogues are also given.

The proposed assignments are unambiguous for fundamentals above 850 cm^{-1}, but analysis of the low-energy region of the spectra (350—850 cm^{-1}) is much less certain and requires further comment. Vibrations expected to be found in this range include four important a' modes of the heavy-atom skeleton: ν(Ge–O); δ(OCO); δ(CCO) (not for the formate); and δ(COGe); as well as GeH_3 rocking (of both a' and a'' species). The Raman spectrum of $MeCO{\cdot}OGeH_3$ contained four clearly polarized shifts below 700 cm^{-1}, at 612m, 538vs, 331s, and 270w cm^{-1}. Silyl acetate exhibits a similar pattern of polarized Raman bands at somewhat higher energy (702s, 590vs, 381s, and 323w cm^{-1}). Following assignments based on i.r. data for the silyl compound,[10] we attribute the middle two shifts in each case to δ(OCO) and δ(CCO) modes; it then seems reasonable to assign the shift at

TABLE 3

Vibrational spectrum of germyl formate and Raman shifts for silyl formate

(*a*) $HCO{\cdot}OGeH_3$

Bands/cm^{-1} I.r.[a]	Raman[b]	Assignment [approximate description]	
2 938*R* 2 928*Q* 2 917*P* } s	2 935w, p	ν_1	[ν(C–H)]
2 155*R* 2 149*Q* } vs		ν_2 and ν_{13}	[ν_{asym}(Ge–H)]
2 135*Q* 2 128 } vs	2 129vs, p	ν_3	[ν_{sym}(Ge–H)]
1 880 1 870 } vw			
1 730*R* 1 716*P* } vs	1 680vw (?)	ν_4	[ν(C=O)]
1 360w		ν_5	[δ(CH)]
1 215*R* 1 207*Q* 1 200*P* } vs		ν_6	[ν(C–O]
890*R* 879*Q* } s	855m, br, dp	ν_7 and ν_{15}	[$\delta_{asym}(GeH_3)$]
850*R* 842*Q* 835*P* } vs	830vw, p (?)	ν_8	[$\delta_{sym}(GeH_3)$]
633m		ν_{16}	[$\rho(GeH_3)$]
612*R* 605*Q* 598*P* } m		ν_9	[ν(Ge–O)]
562m		ν_{11}	[$\rho(GeH_3)$]
	530m, br, p	ν_{10}	[δ(OCO)]
	254m, br, p (?)	ν_{12}	[δ(COGe)]

(*b*) $HCO{\cdot}OSiH_3$[c]

2 939w, p; 2 205vs, p; 1 700m, p; 1 368w, p; 1 195w, p; 942s, p; 702s, p; 655w, p (?); 590vw; 245m, p

[a] Vapour phase. [b] Benzene solution. [c] Neat liquid.

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[12] K. M. Mackay and S. R. Stobart, *Spectrochim. Acta*, 1970, **A26**, 373; 1971, **A27**, 923.

TABLE 4

Vibrational spectra (cm^{-1}) of germyl acetate and trifluoroacetate and Raman shifts for the silyl analogues

$MeCO{\cdot}OGeH_3$		$CF_3CO{\cdot}OGeH_3$			
I.r. (gas)	Raman (liquid)	I.r. (gas)	Raman (liquid)	Approximate description	
3 033vw, br				ν_{asym}(C–H)	($a' + a''$)
2 960vw, br	2 925s, p			ν_{sym}(C–H)	(a')
2 150 (sh) 2 143 } vs		2 165 (sh) 2 159 } vs		ν_{asym}(Ge–H)	($a' + a''$)
2 135 2 122(sh)) } vs	2 126vs, p	2 148 2 145 (sh) } vs	2 142 2 105sh } vs, p	ν_{sym}(Ge–H)	(a')
1 803w					
1 772w					
1 741 1 738 1 730 } vs	1 678w, br, p	1 782 1 775 } vs	1 734vw, p	ν(C=O)	(a')
1 430w	1 424w, dp			$\delta_{asym}(CH_3)$	($a' + a''$)
1 382 1 377 } s				$\delta_{sym}(CH_3)$	(a')
1 285 1 270 } vs	1 270vw, br, p	1 387s	1 388vw, p	ν(C–O)	(a')
		1 242 (sh) 1 238 } vs		$\nu_{asym}(CF_3)$	($a' + a''$)
		1 190 (sh) 1 174 } vs	1 170vw, p	$\nu_{sym}(CF_3)$	(a')
1 020 1 011 } m	1 008w, p			$\rho(CH_3)$	(a'') (?)
934w 922w }	927m, p			$\rho(CH_3)$	(a')
890 879 862 } m	884s, p	865 860 (sh) } s	874 860 } s, p	ν(C–C) and $\delta_{asym}(GeH_3)$	($2a' + a''$)
845 838 } vs	830s, p	845 840 825 (sh) } vs	835m, p	$\delta_{sym}(GeH_3)$	(a')
			782vw		
		746m	733vw, p	$\delta_{asym}(CF_3)$	(a'')
734m	714vw			$\pi(CCO_2)$ (?)	(a'')
658 646 640 } w	638w, dp	668 664 661 } m		$\rho(GeH_3)$	(a')
619 613 } m	612m, p	627 610 } w	630w, p	ν(Ge–O)	(a')
	585w, dp				
538vw	539vs, p	520vw	545w, p	δ(OCO) [with ρ(GeH) (i.r.) or $\delta_{asym}(CF_3)$]	(a')
			411w	$\rho(CF_3)$	(a')
	332s, p		285m, p	δ(CCO)	(a')
			312s, p	$\rho(CF_3)$	(a')
			265m, dp	$\rho(CF_3)$	(a'')
	270w, p		195s, p	δ(COGe)	(a')

Silyl acetate: 2 930s, p; 2 202vs, p; 1 717w, p; 1 460vw, dp; 1 430vw, p; 1 250vw, p; 1 080w, p; 1 020w, p; 988w, p; 942s, p; 866vw, p; 790w, p; 690s, p; 590s, p; 381m, p; 323w, p

Silyl trifluoroacetate: 2 218vs, p; 1 772w, p; 1 388w, p; 1 160vw, br, p; 944m, p; 869m, p; 765vw, p; 732s, p; 665w, dp; 570w, p; 412m, p; 335s, p; 260m, dp; 235m, p.

highest energy for each compound to the M–O stretching vibration (M = Si or Ge) with that at lowest energy arising from δ(COM). Similar conclusions can be reached for the other four compounds, though with more difficulty due first to the indifferent Raman spectrum obtained for germyl formate (in dilute solution in benzene), due to its low thermal stability in the liquid phase, and secondly to overlap with CF_3 bending modes in the spectra of the trifluoroacetates. This situation is summarized in Table 5, and introduces one difference from the earlier interpretation of i.r. data for the silyl species:[10] reassignment of ν(Si–O) to i.r. absorptions near 700 cm^{-1} (with SiH_3 rocking). For germyl acetate, this leaves the i.r. band at 734m cm^{-1} unaccounted for; its Raman counterpart was very weak with uncertain polarization properties. No similar absorption was present for the formate, but for the trifluoroacetate there was a weak band near 780 cm^{-1}, as well as the strong 745 cm^{-1} feature which can confidently be attributed to a $\nu_{asym}(CF_3)$ mode. We tentatively suggest that this region may be appropriate for the out-of-plane (a'') skeletal deformation mode of the acetate or trifluoroacetate group, by analogy with the structurally

TABLE 5

Skeletal modes (a' symmetry)/(cm^{-1})

	$HCO{\cdot}OMH_3$		$MeCO{\cdot}OMH_3$		$CF_3CO{\cdot}OMH_3$	
Mode	Si	Ge	Si	Ge	Si	Ge
ν(M–O)	702	605	690	612	732	630
δ(OCO)	590 (?)	530	590	539	570	545
δ(CCO)			381	331	335	285
δ(COM)	245 (?)	245	323	270	235	195

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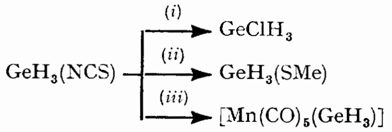
[13] G. Gattow and W. Behrendt, *Angew. Chem. Internat. Edn.*, 1972, **11**, 534.

related compound CO(OH)·OMe (methyl hydrogencarbonate) for which it has been recently claimed[13] that the out-of-plane skeletal bend occurs at substantially higher energy (823s cm^{-1}) than the in-plane component (567w cm^{-1}). Similar weak i.r. bands near 800 cm^{-1} for the silyl esters (previously assigned[10] to Si–O stretching), all with very weak Raman intensity, may be contributed to by the *a''* skeletal bend or by the high-energy component of the SiH_3 rocking motion[10] (also *a''*). Finally, the GeH_3 rocking modes were observed weakly in both i.r. and Raman spectra in the 550—600 cm^{-1} range for all three germyl compounds. As suggested earlier,[10] interaction between a number of *a'* fundamentals in this narrow spectral region undoubtedly contributes to its complexity.

A general feature of the vibrational spectra of the silyl and germyl esters is the marked shift (Tables **3** and **4**, ref. 10) in ν(C=O) between gaseous (i.r.) and liquid phases (Raman) of 30—60 cm^{-1} and increasing in MH_3X as $X = O_2CCF_3$, O_2CH, and O_2CMe for both M = Si and Ge. Similar shifts were not found for other fundamentals, so that this observation may be significant in terms of intermolecular association in the condensed phase, *via* donation of electron density from the carbonyl oxygen atom presumably to a neighbouring M atom.

Synthesis of Other Substituted Germanes.—Further reactions of bromogermane with lead salts substantiate the usefulness of the latter in synthesizing germane derivatives. Thus with PbO or $Pb[CO_3]$ (as well as $Pb[OH]_2$)[4] facile conversion into digermyl ether results, unlike the situation encountered with the corresponding silver salts[2] where only decomposition products were obtained. The thermal instability of $O(GeH_3)_2$ seems from our experience to have been exaggerated,[3] at least when handling material free from impurity as prepared from PbO, so that further investigation of the chemistry of this interesting compound should be possible. Convenient syntheses of germyl pseudohalides can also be achieved similarly; the isocyanate and isothiocyanate were isolated from lead(II) cyanate and thiocyanate respectively, whereas using silver salts experimental conditions are more demanding in order to avoid extensive decomposition. Several other lead salts (nitrate, iodide, and cyanamide) gave no volatile germyl derivatives on treatment with $GeBrH_3$, while lead(IV) oxide was reduced in a violent reaction to metallic lead and lead(II) bromide without formation of $O(GeH_3)_2$. These observations establish a relatively lower reactivity of halogenogermanes towards lead than to silver salts, so that isolation of substitution products is often possible with the former when decomposition in a highly exothermic reaction occurs with the latter. The nature of these interconversion reactions is further complicated by the observation during the course of this work that $O(GeH_3)_2$ reacted quantitatively with mercury(II) iodide at ambient temperature giving iodogermane. Conversely, the reverse reaction between GeH_3I and mercury(II) oxide at −40 °C was used by Goldfarb and Sujishi[5] as a route to pure $O(GeH_3)_2$.

Protolysis reactions of trisilylamine[8] and digermylcarbodi-imide[14] have also been used as routes to substituted silanes and germanes. Attempts to employ germyl isothiocyanate similarly were unsuccessful in efforts to synthesize germyl carboxylates, but with hydrogen chloride, methanethiol, and pentacarbonylhydridomanganese appropriate germyl derivatives[15,16] were isolated (Scheme).



SCHEME (*i*), Dry HCl, 1 min, 20 °C; (*ii*), MeSH, 18 h, 20 °C; (*iii*), $[Mn(CO)_5H]$–tetrahydrofuran, 30 min, 20 °C

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