Characterisation of Bis-methylgermanium and Bis-methylsilicon Carbodi-imides and their Reactivity with Protic Reagents

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Bismethylgermanium and bismethylsilicon carbodi-imides have been prepared in high yield by halide metathesis reactions with lead(II), silver(I), or silicon(IV) species. The new derivatives in the series of general formula $(Me_nH_{3-n}MN{:})_2C$ (M = Si or Ge; n = 1, 2, or 3) have been characterised by ^1H n.m.r., i.r., and Raman spectroscopy as well as mass spectrometry and cleavage reactions. The utility of the germanium carbodi-imides as synthetic intermediates is shown by ready cleavage of the Ge–N bond by Group VI and other protic species leading to the formation of chalcogeno-germanes and related derivatives of the type $(Me_nH_{3-n}Ge)_2E$ (E = O, S, Se, or Te) and $Me_nH_{3-n}GeSR$ (R = Me, Bu^t, Ph, MeC(O), or $-CH_2CH_2-$). Comparative studies show that in the silicon carbodi-imides the Si–N bond is not susceptible to protolysis by the heavier chalcogenols.

NUMEROUS studies have demonstrated the utility of species containing the Si–N bond as synthetic intermediates in silane[1] and organosilicon[2] chemistry. Studies of the analogous Ge–N species have been confined largely to the fully substituted organogermanes.[3]

Several methods for the preparation of fully substituted organometallic carbodi-imides of the type $R_3M{\cdot}NCN{\cdot}MR_3$ (R = alkyl or aryl; M = Si, Ge, or Sn) are described in the literature.[4–6] Early work by Pump and Wannagat[4] showed that bistrimethylsilylcarbodi-imide, $(Me_3SiN{:})_2C$, was formed in a variety of systems such as reaction of $Na(R_3Si)_2N$ with $COCl_2$, Me_3SiCl with $(LiMe_3SiN)_2CO$, or Me_3SiCl with $AgCN_2$. A modification to the silver salt procedure has recently appeared.[5] Other workers report the formation of the germanium species $(Et_3GeN{:})_2C$ and $(Ph_3GeN{:})_2C$ in the reactions of the corresponding oxide or bromide respectively with cyanamide, H_2NCN, under forcing conditions.[6] We find that Me_3SiCl and Me_3GeBr are readily converted into the carbodi-imides, $(Me_3SiN{:})_2C$ and $(Me_3GeN{:})_2C$, by direct heating with lead(II) cyanamide. However, these and the foregoing reactions are not suited for the formation of the thermally unstable hydridic species and, indeed, no reaction occurs between Me_2HSiCl and $PbCN_2$ at room temperature in the gas phase. In keeping with the well known heavy-metal salt exchange series[7] the metathetical reaction of the iodo-silanes and -germanes with lead(II) cyanamide leads to extremely satisfactory yields of the corresponding carbodi-imido-species, $(Me_nH_{3-n}MN{:})_2C$ (M = Si or Ge; n = 0, 1, 2, or 3) [equation (1)].

$$2{\geqslant}M{-}I + PbCN_2 \longrightarrow ({\geqslant}M{-}N{:})_2C + PbI_2 \quad (M = Si \text{ or } Ge) \qquad (1)$$

The comparative reactions of the iodides with silver(I) cyanamide give significantly reduced yields with increased disproportionation as has been observed in other systems employing silver-salt exchange reactions.[8,9]

Alternatively, the germanium carbodi-imides may be obtained from bistrimethylsilylcarbodi-imide by ex-

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change with the corresponding fluorogermanes.[10] While the illustrative example (2) is a high yield reaction it is

$$(Me_3SiN\colon)_2C + 2MeH_2GeF \longrightarrow (MeH_2GeN\colon)_2C + 2Me_3SiF \quad (2)$$

less convenient because the fluoride must first be prepared from heavier halides. Thus the lead cyanamide route is the preferable one.

It is interesting to compare the reactions of the organometallic carbodi-imides to their organic analogues RNCNR. In the hydrolysis of an organic carbodiimide[11] the central carbon atom provides the electropositive centre for nucleophilic attack so that an urea results with no fission of a C–N bond. By contrast, in the germanium or silicon derivatives, the metal atom provides the focus for nucleophilic attack with cleavage of the M–N bond and formation of $(H_2NCN)_n$ and the germyl or silyl chalcogenide.

TABLE 1

Protolysis reactions of $(R_3MN\colon)_2C$ species with chalcogenols

$$\underset{(I)}{(R_3MN\colon)_2C} + H_2E \longrightarrow \underset{(II)}{(R_3M)_2E} + \tfrac{1}{2}(H_2NCN)_2$$

	E = O			E = S			E = Se			E = Te		
R_3M	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)
MeH_2Ge	0.75	0.68	90	1.45	1.38	95	1.42	1.18	83	1.62	1.01	62
Me_2HGe	1.41	1.16	82	1.50	1.32	88	1.52	1.34	88	1.50	1.18	79
Me_3Ge	1.24	1.07	86	0.89	0.74	83	1.55	1.21	78	1.09	0.97	89
Me_3Si	2.40	2.30	96	No reaction			No reaction [a]			No reaction		
H_3Ge	2.36	1.91	98 [b]	0.24	0.22	92	1.25	1.05	84 [c]			

[a] BuSeH is reported to react with $(Me_3SiN\colon)_2C$ (100 °C, 1 h, benzene) to give $Me_3SiSeBu$ (70%), Yu I. Dergunov, I. A. Vostokov, and V. T. Bychkov, *Zhur. obshchei Khim.*, 1972, **42**, 371, 380. [b] Ref. 10. [c] S. Cradock, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc. (A)*, 1969, 1628.

TABLE 2

Protolysis reactions of $(R_3MN\colon)_2C$ species with various thiols

$$\underset{(I)}{(R_3MN\colon)_2C} + 2R'SH \longrightarrow \underset{(II)}{2R_3MSR^3} + \tfrac{1}{2}(H_2NCN)_2$$

	R = Me			R = Bu^t			R = Ph			R = –CH$_2$CH$_2$–			R = MeC(O)		
R_3M	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)	(I) (mmol)	(II) (mmol)	Yield (%)
H_3Ge	0.45	0.72	81	1.41	2.53	90	0.60	0.98	80	0.86	0.42	49	1.05	1.64	78
MeH_2Ge	1.42	2.15	75	1.25	2.13	85	1.41	2.20	78	1.40	1.15	82	1.30	2.31	89
Me_2HGe	1.42	2.38	84	0.95	1.49	78	1.12	1.77	79	1.02	0.70	68	1.12	1.95	87
Me_3Ge	1.08	1.69	78	1.50	2.60	87	0.99	1.41	71	0.99	0.83	83	0.99	1.53	77
Me_3Si	No reaction			2.00	1.56	39	2.70	1.83	34	No reaction			1.90	1.59	42

Rapid and non-reversible reactions occur with weak acid donors (Tables 1 and 2). With hydrogen chalcogenides, H_2E, protolytic cleavage leads to the corresponding germyl–Group VI derivatives and dicyanodiamide [equation (3)].

$$e.g.\ (MeH_2GeN\colon)_2C + H_2E \longrightarrow (MeH_2Ge)_2E + \tfrac{1}{2}(H_2NCN)_2 \quad (3)$$
$$(E = O,\ S,\ Se,\ \text{or } Te)$$

Cleavage also occurs with a wide variety of alkane- and arene-thiols [equation (4)] providing convenient syntheses for the previously reported H_3GeSMe[12] and H_3GeSPh[13] as well as the new hydride derivatives, H_3GeSBu^t, $H_3GeSC(O)Me$, $(H_3GeSCH_2\text{–})_2$, and $Me_nH_{3-n}GeSR$ [equation (4)].

$$(H_3GeN\colon)_2C + RSH \longrightarrow H_3GeSR + \tfrac{1}{2}(H_2NCN)_2 \quad (4)$$
$$R = Me,\ Bu^t,\ MeC(O),\ \text{–}CH_2CH_2\text{–},\ \text{or } Ph$$
$$\text{also } H_3Ge \equiv Me_nH_{3-n}Ge$$

Comparative experiments indicate that the SiNCNSi system is more resistant than is the GeNCNGe linkage to nucleophilic attack by the heavier chalcogenols, SH, SeH, and TeH. Proponents of the importance of $(p\text{–}d)$ π bonding in the Si–N system,[14] relative to Ge–N, would no doubt accept this as further evidence of the 'extra' stability of the Si–N bond or of the decreased polarity of the bond making the silicon atom less open to nucleophilic attack. Unfortunately, supportive thermochemical data, particularly for germyl derivatives, is scant and inconsistent. It seems unlikely that the supposed relative weakness of the Ge–N bond could completely account for the quantitative cleavage of Ge–N to form Ge–O, –S, –Se, and –Te bonds. However, the ready cleavage of Si–N by H_2O and ROH is probably associated with the formation of the strong Si–O bond.[15]

More important than these speculations is that we have

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established that the Ge–N linkage in germanium carbodi-imides makes them excellent and versatile intermediates for the formation of other Ge–M bonds, a property we are utilising in current researches.

EXPERIMENTAL

Manipulations and spectroscopic measurements were as described previously.[16] Silyl and germyl halides were prepared by standard methods,[17–19] and their purity established spectroscopically. Ag_2CN_2 Was obtained from $AgNO_3$ and $CaCN_2$ in basic solution.[20] Hydrogen sulphide, selenide, and telluride were prepared by hydrolysis of aluminum chalcogenides.[21] Other materials were reagent grade of commercial origin.

Preparation of the Carbodi-imides, $(Me_nH_{3-n}MN{:})_2C$ (M = Si or Ge; n = 0, 1, 2, or 3). (i) *Reactions of* $Me_nH_{3-n}MX$ *with* $PbCN_2$ *and* Ag_2CN_2. The gaseous iodo-silane or -germane (*ca.* 5 mmol) was passed at 25 °C over the anhydrous cyanamide (*ca.* 25 g) held in a column on glass wool. Exothermic reactions ensued and after two or three double-passes the ^1H n.m.r. spectra of the colourless, sparingly volatile, material showed no iodide resonances. After fractional condensation at −23 °C the yields of the silyl- and germyl-carbodi-imides were frequently in the region of 90% in the $PbCN_2$ reactions with little evidence for disproportionation: *e.g.* GeH_3I (0.50 mmol) gave $(H_3GeN{:})_2C$ (0.21 mmol, 84%; v.p. *ca.* 0.6 mmHg at 0 °C; m.p. 10 °C, δ Ge*H* 4.94 p.p.m.) and SiH_3I (2.89 mmol) gave $(H_3SiN{:})_2C$ (1.25 mmol, 87%; v.p. 18 mmHg at 0 °C, δ Si*H* 4.45 p.p.m.). Using Ag_2CN_2 yields of only 40—60% could be realised with considerable formation of involatile residues (shown to contain polymeric H_2NCN) and parent hydrides. The corresponding hydrido-chlorides or-bromides showed little or no reactivity in the gas phase. However, the high thermal stability of Me_3SiCl (11.20 mmol) and Me_3GeBr (11.30 mmol) permitted direct heating (*ca.* 100 °C, 5 h) with the cyanamide salt (*ca.* 20 g) in a sealed ampoule when again satisfactory conversion into $(Me_3SiN{:})_2C$ (5.03 mmol, 90%) and $(Me_3GeN{:})_2C$ (5.08 mmol, 90%) occurred.

(ii) *Reaction of* $Me_nH_{3-n}GeF$ *with bis(trimethylsilyl)-carbodi-imide.* Typically $(Me_3SiN{:})_2C$ (0.597 g, 3.21 mmol) was distilled into a reaction vessel (10 ml) held at −196 °C containing a slight excess of MeH_2GeF (0.833 g, 7.67 mmol). The mixture was allowed to react (room temp., 15 min) and then vacuum fractionated. A pure sample of $(MeH_2GeN{:})_2C$ (0.636 g, 2.90 mmol; 90.3%) was retained in a trap at −23 °C; traces of $(Me_3SiN{:})_2C$ (*ca.* 0.3 mmol) in a trap at −45 °C; small amounts of MeH_2GeF (*ca.* 1.8 mmol; identified by i.r. and n.m.r. spectra [17]) in a trap at −95 °C; and Me_3SiF (*ca.* 5.8 mmol; identified by i.r.[22] and n.m.r.[23] spectra) in a −196 °C following trap. By similar procedures Me_2HGeF (8.80 mmol) and Me_3GeF (9.12 mmol) reacted with $(Me_3SiN{:})_2C$ (*ca.* 4 mmol) to give $(Me_2HGeN{:})_2C$ (3.44 mmol, 89.4%) and $(Me_3GeN{:})_2C$ (3.35 mmol; 88.9%) respectively.

Characterisation of the Carbodi-imides.—(i) ^1H *N.m.r. spectra.* All the carbodi-imides give first-order spectra (Table 3) consistent with free rotation about the C–M bonds. The chemical shifts (δ p.p.m.) of M–*H* resonances in the $(Me_nH_{3-n}MN{:})_2C$ species are comparable to those of related compounds containing an M–N bond, *viz.* $(H_3Ge)_3N$ 4.9; $H_3Ge–N_3$ 5.1; –NCO 5.05, –NCS 5.18; $(H_3Si)_3N$ 4.44; $H_3Si–N_3$ 4.49; –NCO 4.42, –NCS 4.46 δ.[24,25] Marked dilution shifts (*e.g. ca.* 0.5 p.p.m. from neat liquid to 5% CCl_4 solution) suggest association. This is supported by line-broadening in the more concentrated solutions. Broadening as a result of interactions involving the ^{14}N quadrupole should be concentration independent.

(ii) *The vibrational spectra of* $(Me_nH_{3-n}MN{:})_2C$ (M = Si or Ge). These spectra are displayed in Tables 3—5. Principal features can be assigned by comparison with the spectra of related but simpler molecules.[9,10,16–18] The N=C=N asymmetric stretch is placed in the i.r. spectra at *ca.* 2 250 cm⁻¹ for the silanes and 2 150 cm⁻¹ for the germanes. Not surprisingly, in view of the effective, local centro-

TABLE 3

The ^1H n.m.r. parameters * of $(Me_nH_{3-n}MN{:})_2C$ (M = Si or Ge) and $(Me_nH_{3-n}Ge)_2E$ (E = O, S, Se, or Te) species

Compound	δ(Me)	δ(MH)	$\lvert J_{HH}^{vic}\rvert$	$\lvert J_{CH}\rvert$
$(MeH_2SiN{:})_2C$ [a]	0.36	4.61	3.75	125.5
$(Me_2HSiN{:})_2C$ [b]	0.25	4.74	3.30	123.4
$(Me_3SiN{:})_2C$ [c]	0.14			118.6
$(MeH_2GeN{:})_2C$	0.58	4.99	3.00	129.6
$(Me_2HGeN{:})_2C$	0.51	5.18	2.63	129.0
$(Me_3GeN{:})_2C$	0.43			128.1
$(MeH_2Ge)_2O$	0.59	5.28	2.91	129.1
$(Me_2HGe)_2O$	0.40	5.40	2.43	128.2
$(Me_3Ge)_2O$ [d]	0.29			125.9
$(MeH_2Ge)_2S$	0.66	4.87	3.30	129.4
$(Me_2HGe)_2S$	0.54	4.93	2.91	129.0
$(Me_3Ge)_2S$ [d]	0.51			127.5
$(MeH_2Ge)_2Se$	0.77	4.55	3.38	129.6
$(Me_2HGe)_2Se$	0.69	4.73	2.96	127.5
$(Me_3Ge)_2Se$ [d]	0.58			127.1
$(MeH_2Ge)_2Te$	0.93	4.12	3.53	132.6
$(Me_2HGe)_2Te$ [e]	0.80	4.65	3.37	131.7
$(Me_3Ge)_2Te$ [f]	0.71			129.1

* The spectra were recorded at ambient temperature in CCl_4 solution (*ca.* 5% v/v). Chemical shifts (δ ±0.02 p.p.m.) are in p.p.m. to low field of Me_4Si as internal standard. Deviations for coupling constants are J(HH) ±0.05 Hz, $J(^{13}CH)$ ±0.2 Hz.

[a] $J(^{29}SiH)$, 218 Hz. [b] $J(^{29}SiH)$, 217 Hz. [c] J_{SiH}^{gem}, 6.9 Hz. [d] Compare with δ$(Me_3Ge)_2E$ (CCl_4 solution) of 0.31(O); 0.53(S); 0.66(Se) p.p.m. in H. Schmidbaur and I. Ruidisch, *Inorg. Chem.*, 1964, **3**, 599. [e] Recorded in cyclohexane (5% v/v). [f] Agrees with approximate value of δ 0.74 p.p.m. (C_6H_6 solution) in H. Schumann, R. Mohtachemi, H. J. Kroth, and U. Frank, *Chem. Ber.*, 1973, **106**, 2049; J_{HTe}^{vic} 5.5 Hz.

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TABLE 4

The i.r. and Raman spectra (cm^{-1}) of the bismethylgermanium carbodi-imides *

Tentative assignment		(MeH$_2$GeN:)$_2$C		(Me$_2$HGeN:)$_2$C		(Me$_3$GeN:)$_2$C	
		I.r. (gas)	Raman (liq)	I.r. (liq)	Raman (liq)	I.r. (liq)	Raman (liq)
CH$_3$ stretch	(a)	2 997m	2 992m, dp	2 990m	2 991m, dp	2 995m	2 985m, dp
	(s)	2 928w	2 919vs, p	2 916w	2 918vs, p	2 918m	2 915vs, p
N=C=N stretch (a)		2 149s	N.o.	2 142vs [a]	N.o.	2 130vs	N.o.
Ge–H stretch		2 086s	2 083vs, p	2 073vs	2 063vs, p		
N=C=N stretch (s)			1 418m, p [b]		1 412m, p [b]		1 409m, p [b]
CH$_3$def.	(a)	1 405vw		1 417w		1 408m	
	(s)	1 259w	1 249m, p	1 249m	1 248m, p	1 252m	1 250m, p
GeH$_2$def (sc)		882m	877m, p				
CH$_3$rock	(a″)	845m	*ca.* 840sh	832s	850w, dp	825s	833vw
	(a′)	802s		816s			
	(a′, a″)			*ca.* 760sh		*ca.* 750sh	763vw
GeH$_2$,GeH def.		728m	731m, dp	712m	705m, p		
					636m, dp		
Skeletal bend		675m	675m, dp	661m		670m	663sh
GeC stretch	(a″)			619s	603m, dp [c]	617s	615m, dp
	(a′)	612m	611vs, p	593m	579vs, p	572m	576vs, p
GeH$_2$ rock		474w	478m, dp				
GeN stretch	(a)	545m		530s	*ca.* 500sh	527s	*ca.* 480sh
	(s)	398w?	421s, p	425w?	420s, p		430s, p
Skeletal modes			227m, p		225m		240sh
			194m, dp		184s, dp		189s
							163ms

* Spectra recorded at room temperature.

m = medium, s = strong, w = weak, v = very, sh = shoulder, p = polarised, dp = depolarised.

[a] Gas. [b] CH$_3$(a) is expected in this region. [c] Polarisation spectrum.

TABLE 5

The i.r. and Raman spectra (cm^{-1}) of the bismethylsilicon carbodi-imides * †

Tentative assignment		(MeH$_2$SiN:)$_2$C		(Me$_2$HSiN:)$_2$C		(Me$_3$SiN:)$_2$C	
		I.r. (gas)	Raman (liq)	I.r. (gas)	Raman (liq)	I.r. (liq)	Raman (liq)
CH$_3$ (stretch	(a)	2 981m	2 972m, dp	2 972m	2 968m, dp	2 967m	2 966m, dp
	(s)	2 924w	2 911vs, p	2 911w	2 906vs, p	2 903w	2 904vs, p
N=C=N stretch (a)		2 258vs	N.o.	2 241vs	N.o.	2 205s	N.o.
Si–H stretch		2 176vs	2 170vs, p	2 149vs	2 147vs, p		
			1 566m		1 552m		
N=C=N stretch (s) [a]		N.o.	1 504m	N.o.	1 518m	N.o.	1 514m
					1 481m		1 453m
CH$_3$ def	(a)	1 419vw	1 418w, dp	1 429w	*ca.* 1 420w, br	1 406w	1 416m, dp
				1 381w			
	(b)	1 267m	1 257m, p	1 262ms	1 259m, p	1 253s	1 262m, p
SiH$_2$ def (sc)		964s	963m, p				
CH$_3$ rock	(a″)	915vs	929w, dp	906s	907w, dp	837s	845w, br
	(a′)	*ca.* 870sh	868w, dp	884vs	883w		
	(a′, a″)			838s	843w	736s	760w, dp
SiH$_2$,SiH def		686w	707vs, p		750m		
		ca. 730m	726m, dp	627m	632m		
Skeletal bend		587m	N.o.	584w	N.o.	581m	N.o.
SiC stretch	(a″)			739s	702m, dp	698m	699m, dp
	(a′)	760s	761vs, p		674vs, p	640w	645vs, p
SiH$_2$ rock		512w	515m, dp				
SiN stretch	(a)	789vs		775s	772w?	760s	
	(s)		493s, p		484s, p	480w	480s, p
Skeletal modes					273m	279m	283E, dp
			232m, p		246m		208s, p
					199s dp		195sh

* See footnote to Table 4. † N.o. = not observed.

[a] See text.

symmetry of the carbodi-imide structure [26] this mode is absent in the Raman effect.[27] The N=C=N symmetric stretch is a polarised medium-intensity band at *ca.* 1 409—1 418 cm^{-1} in the Raman spectra of the germanes. In the silanes, a more complex pattern appears at 1 500—1 570 cm^{-1} which seems to be a characteristic feature of silylcarbodi-imides [9] and so is assigned as the N=C=N symmetric stretch. In (H$_3$SiN:)$_2$C, the feature was attributed to Fermi resonance with the overtone of the i.r.-active SiH$_3$ deformation mode.[9] In (MeH$_2$SiN:)$_2$C it is reasonable to assume that there is Fermi resonance between the N=C=N symmetric stretch and the overtone (2 × 761 cm^{-1}). For

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the other species, the rationale for the complex band-pattern is less obvious, but could involve the overtone of the Si–N asymmetric stretch, which is expected in the region 760—790 cm^{-1} [788 cm^{-1} in $(H_3SiN{:})_2C$[9]]. For the germanium series, the assignment of the Ge–N asymmetric stretch to a strong i.r. band in the region 527—545 cm^{-1} [547 cm^{-1} in $(H_3GeN{:})_2C$] [10] is clear as are the assignments of the Ge–C stretching modes (*ca.* 576—619 cm^{-1}) [17] and the GeH_2 and GeH deformation modes. The M–N symmetric stretches appear in the Raman spectra as strong polarised bands in the regions of 480—493 cm^{-1} for the silanes [496 cm^{-1} in $(H_3SiN{:})_2C$] [9] and of 420—430 cm^{-1} for the germanes [410 cm^{-1} in $(H_3GeN{:})_2C$].[10]

(iii) *Mass spectra.* In all cases the molecular ion, *viz.*, $(Me_nH_{3-n}MN{:})_2C^+$, is detected and provides confirmation of the molecular species. The low normalised abundance (*i.e. ca.* 1 to 20) of this ion is a common feature in the spectra of organo-silanes and -germanes.[28,29] Ions arising from H and Me stripping appear to be most abundant although significant ion current in the germanes is carried by ' rearranged ' ions such as Ge_2N^+ or $Ge_2{}^{2+}$ and ions from N–C bond cleavage, *i.e.* $Me_nH_{3-n}GeN^+$. This is in general agreement with the observations in the spectrum of $(H_3GeN{:})_2C$ but we have been unable to detect ions of the type MN_2C^+ reported in the same study.[10]

(iv) *Chemical characterisation* (i.e. *analysis for* $Me_nH_{3-n}M$*-groups*). This was achieved by protolytic cleavage of the M–N linkage with an excess of gaseous hydrogen halides leading to the isolation of stoicheiometric quantities of familiar halogeno-silanes and -germanes, $Me_nH_{3-n}MX$ (X = Cl, Br, or I), which were identified spectroscopically.[17,18,30,31] The extensive protolysis reactions with chalcogenols (see next section and Table 1) also provide indirect evidence for the stoicheiometric/monomeric nature of the carbodi-imides.

Reactions of the Carbodi-imides with Selected Protic Reagents.—(i) *Reactions of* $(R_3MN{:})_2C$ (R = H or Me) *with* H_2O (E = O, S, Se, or Te). A general procedure was followed for all the volatile protic reagents. The carbodi-imide (*ca.* 1—2 mmol) was distilled into a greaseless reaction vessel (150 ml) with a bulb which could be immersed in a low-temperature bath and a side arm which could be sealed. An excess of the H_2E species was distilled into the vessel with the bulb head at −196 °C. The mixture was allowed to attain room temperature, with quenching as the reaction became too vigorous (particularly for the thermally unstable H_2Te). After typically 60 min, vacuum fractionation of the products was carried out. For the H_2S, H_2Se, and H_2Te reactions examination of the products involatile at −45 °C showed no resonances attributable to unchanged carbodi-imide whilst the excess of H_2E, volatile at this temperature, was identified in a −196 °C trap. For the H_2O reactions the excess of H_2O was retained in a −23 °C trap and spectroscopically pure oxides were collected in a −196 °C trap. An amorphous white material remaining in the reaction vessel was subsequently characterised by i.r. spectroscopy [32] as polymeric H_2NCN. Details of the reactions are given in Table 1 and the ^1H n.m.r. parameters of the new methylgermanium chalcogenides are collected in Table 3. General features in the Raman spectra of $(Me_2HGe)_2E$ characteristic of $Me_nH_{3-n}Ge$- and Ge-E-Ge moieties appear as follows (cm^{-1}): Ge–E stretching (2 bands) at 486m,p and 792s (i.r.) [O]; *ca.* 380vs,p and 409s (i.r.) [S]; 273vs,p and 282 s (i.r.) [Se]; 228vs,p [Te]; Ge–C stretching (2 bands) at *ca.* 585vs,p and *ca.* 610m,dp; Ge–H stretching at *ca.* 2 040—2 080vs,p; CH_3 stretching (2 bands) at *ca.* 2 915 vs,p and 2 985 m,dp; CH_3 def. (2 bands) at *ca.* 1 240m,p and 1 414 w,dp; Ge–E–Ge def. at 169m,p [O]; 95m,p [S]; 76m,p [Se], and 63m,p [Te].

Analysis for the $Me_nH_{3-n}Ge$- groups was carried out by cleavage of the germanium–chalcogen bond with an excess of gaseous HI, which produced stoicheiometric quantities of H_2E and the familiar iodogermanes, $Me_nH_{3-n}GeI$, which were identified spectroscopically.[17,18] The 70 eV mass spectra of the $(Me_nH_{3-n}Ge)_2E$ species further support the formulation of the chalcogenides as well as providing molecular-weight confirmation and support for the *a priori* assignment of n.m.r. and vibrational spectra.

Further preliminary experiments [33] also show that the corresponding germyl chalcogenols $Me_nH_{3-n}GeEH$ (E = S, Se, or Te) are formed rapidly at room temperature when the chalcogenides are treated with an excess of H_2E in sealed tubes.

(ii) *Reactions of* $(R_3MN{:})_2C$ *species with* R'SH *species.* An exactly similar procedure to that described above was followed for the volatile MeSH and Bu^{t}SH. The thiogermanes could be transferred in a pure state to the side arm after pumping off the excess of thiol at −45 °C. Reaction

TABLE 6

^1H N.m.r. parameters * of $Me_nH_{3-n}MSR$ species prepared in this study †

	δ (Me)	δ (GeH)^b	$\lvert J_{HH}{}^{vic}\rvert$	$\lvert J_{CH}\rvert$	δ(CH′)	$\lvert J_{CH'}\rvert$
MeH_2GeSMe'	0.65	4.77	3.52	130.7	2.11	143.4
$Me_2HGeSMe'$	0.56	4.86	3.24	129.5	2.04	142.8
Me_3GeSMe' ^{b}	0.51			125.7	1.97	141.0
$H_3GeSCMe_3'$		4.35			1.42	125.5
$MeH_2GeSCMe_3'$	0.64	4.90	3.75	134.9	1.49	132.9
$Me_2HGeSCMe_3'$	0.55	5.02	3.06	130.3	1.42	129.6
$Me_3GeSCMe_3'$ ^{c}	0.50			127.5	1.40	126.3
$Me_3SiSCMe_3'$	0.05			119.2	1.42	128.6
MeH_2GeSPh'	0.50	5.01	3.67	135.1	7.43	
$Me_2HGeSPh'$	0.47	5.17	3.36	132.3	7.38	
Me_3GeSPh' ^{c}	0.40			N.o.	7.16	
Me_3SiSPh' ^{b}	0.25			123.0	7.15	
$(H_3GeSCH'_2-)_2$		4.74			2.86	N.o.
$(MeH_2GeSCH_2'-)_2$	0.71	4.89	3.53	133.8	2.79	N.o.
$(Me_2HGeSCH_2'-)_2$	0.61	5.04	3.45	132.7	2.72	N.o.
$(Me_3GeSCH_2'-)$	0.50			N.o.	2.60	N.o.
$H_3GeSC(O)Me'$		4.62			2.49	127.2
$MeH_2GeSC(O)Me'$	0.78	4.92	3.42	133.8	2.47	135.0
$Me_2HGeSC(O)Me'$	0.68	5.03	3.18	131.7	2.41	132.0
$Me_3GeSC(O)Me'$	0.60			128.1	2.35	128.8
$Me_3SiSC(O)Me'$	0.39			120.8	2.54	131.1

* See footnote to Table 3. † N.o. = not observed.

[a] Compare with values of δ(H_3GeSR): 4.71 (R = Ph), C. Glidewell and D. W. H. Rankin *J. Chem. Soc. (A)*, 1969, 753 (C_6H_{12}); 4.48 (R = Me), J. T. Wang and C. H. Van Dyke, *Inorg. Chem.*, 1968, **7**, 1319. [b] See K. A. Hooton and A. L. Allred, *Inorg. Chem.*, 1965, **4**, 671. [c] E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometallic Chem.*, 1966, **5**, 130.

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times of the order of 60 min at room temperature gave essentially quantitative conversion. The less-volatile species, PhSH, $HSCH_2CH_2SH$, and MeC(O)SH, were handled volumetrically and syringed into the reaction vessel and degassed thoroughly before distilling in the carbodi-imides. For these reactions it was found advantageous to use a deficit of the thiol (see Table 2). Unchanged $(R_3MN\dot{:})_2C$ species were pumped from the reaction vessel leaving involatile oily sulphides which could be transferred to the side arm and sealed for subsequent spectroscopic analysis (Table 6). The amorphous white material adhering to the walls of the reaction vessel was again shown to be $(H_2NCN)_n$. The very low reactivity of $(Me_3SiN\dot{:})_2C$ towards the thiols was evident even when the mixtures were held at higher temperatures (*ca.* 60—100 °C). Preliminary experiments show that, as expected, $(Me_3SiN\dot{:})_2C$ reacts rapidly with the more acidic alcohols R′OH, leading to Me_3SiOR' species which together with analogous derivatives of the hydridosilanes and -germanes are currently under study and will be presented at a later date. Thus Me_3SiOMe' [88%; δ(Me) 0.07 and δ(Me′) 3.37 p.p.m], Me_3SiOPh [90%; δ(Me) 0.25 p.p.m], $Me_3Si(OCH_2)_2$ [80%; δ(Me) 0.08 and δ(CH_2) 3.57 p.p.m.] and $Me_3SiOC(O)Me'$ [92%; δ(Me) 0.26, δ(Me′) and 1.99] were obtained from $(Me_3SiN\dot{:})_2C$ with MeOH, PhOH, $HOCH_2CH_2OH$, and HOC(O)Me respectively.

The ^1H n.m.r. parameters of the new $Me_nH_{3-n}GeSR'$ species are presented in Table 6. The i.r. and Raman spectra show features characteristic of both $Me_nH_{3-n}Ge-$ and $-SR'$ moities but we have not attempted any detailed analysis at this stage. By comparison with the spectra of H_3GeSMe [34] and H_3GeSPh [13] and other thiogermanes [35] the Ge–S stretching frequency has been assigned as follows in the Raman spectra of the liquids: *viz.* 386—396 cm^{-1} (R = Me); 450—451 cm^{-1} (R = Bu^t); 378—381 cm^{-1} (R = Ph); 393—398 cm^{-1} (R = $-CH_2CH_2-$); 288—293 cm^{-1} [R = MeC(O)]. The Ge–H stretching frequency appears surprisingly low in the range 2 040—2 088 cm^{-1} for all species. The mass spectra of the more volatile $Me_nH_{3-n}GeSMe$ have also been obtained and show the expected molecular ions in low abundance consistent with their formulation.

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