Formation of Germanium–Nitrogen Double Bonds in Reactions of the Electron-rich Germylene Bis[bis(trimethylsilyl)amido]germanium(II) with a Range of Diazo-compounds

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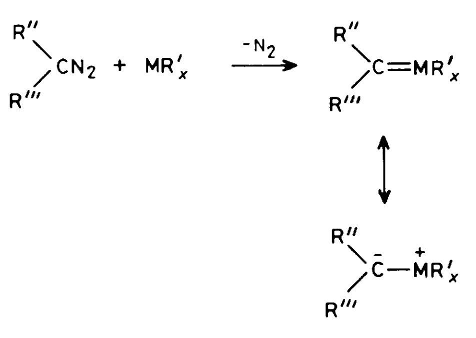
The electron-rich germylene $Ge[N(SiMe_3)_2]_2$ reacts with the diazo-compounds $R^1CH_2COC(N_2)R^2$ [$R^1 = H$, $R^2 = CO(OEt)$, $SO_2C_6H_4Me$-*p*, or COPh; $R^1, R^2 = -CMe_2CH_2C(O)-$], which contain an enolisable function, to yield the heterocycles $\overline{Ge[N(SiMe_3)_2]_2NHN{=}C(R^2)C({=}CHR^1)O}$; the weakly acidic diazo-compounds ethyl diazoacetate and diazoacetophenone yield bis-adducts $Ge[N(SiMe_3)_2]_2[C(N_2)COR][NHN{=}C(H)COR]$ (R = OEt or Ph). Diazo-compounds containing two non-enolisable substituents yield mono-adducts with $Ge[N(SiMe_3)_2]_2$ which can be hydrolysed to yield the diol $Ge(OH)_2[N(SiMe_3)_2]_2$ and, in one example, the corresponding hydrazone $H_2NN{=}C(COPh)CO(OEt)$. These adducts appear to be thermodynamically stable in an aprotic solvent, but can be trapped by addition of ethanol, to yield $Ge[N(SiMe_3)_2]_2(OEt)\{NHN{=}C[CCO(OMe)]_2\}$, or of diazoacetophenone to yield $Ge[(SiMe_3)_2]_2[C(N_2)COPh]\{NHN{=}C[CO(OMe)]_2\}$. All the reactions of the germylene with diazo-compounds can be rationalised in terms of the initial formation of a germyleneazine $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(X)Y$, which readily adds any available protic species to give a germane derivative. MNDO calculations on model systems are in accord with the experimental findings and also explain their differences from results previously obtained using the simpler germylene $GePh_2$.

Compounds containing doubly bonded germanium, $R_2Ge{=}MR'_x$, are still rare.[1,2] When M = C, reactive intermediates have generally been identified using trapping experiments,[3,4] although mass spectral data on $Me_2Ge{=}CH_2$ suggest[5] appreciable π bonding. Such Ge=C bonds are undoubtedly polarised in the sense $>\overset{+}{Ge}{-}\overset{-}{C}<$, and we reasoned that if in a compound $R''_2Ge{=}CR'''_2$, the substituent R″ is an electron donor and R‴ is an electron acceptor, then it might be possible to synthesise 'germaethenes' which possess true thermodynamic stability, rather than mere kinetic stability (persistence) induced by sterically demanding substituents.[1,2] Such compounds would be examples of stabilised push–pull hetera-alkenes.†

One approach which has proven successful[7,8] in the synthesis of stable ylidic systems containing elements of Groups 15 and 16‡ is the use of a diazo-compound as a carbene source, equation (1) (M = P, As, Sb, Bi, S, Se, or Te).



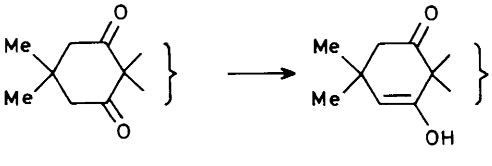
(1)

Accordingly we have studied the reactions of a range of diazo-compounds which contain carbonyl or sulphonyl functions α to the central carbon, with the germylene $Ge[N(SiMe_3)_2]_2$. Evidence was obtained[4] from trapping experiments for the transient existence of germaethenes in the reactions of the monosubstituted diazo-compounds $HC(N_2)CO(OEt)$ with the simple germylenes GeF_2, GePhCl, and $GePh_2$, and we have therefore also studied the reaction of this diazo-compound with $Ge[N(SiMe_3)_2]_2$.

Results and Discussion

Reactions of $Ge[N(SiMe_3)_2]_2$ *with Enolisable Diazo-compounds.*—Each of the diazo-compounds (**1**)—(**4**) reacted smoothly with $Ge[N(SiMe_3)_2]_2$ in benzene solution at room temperature to yield the corresponding products (**5**)—(**8**). The products had compositions, determined by elemental analysis and high-resolution mass spectrometry, corresponding to 1:1 addition of the diazo-compound to the germylene, so that both nitrogen atoms of the diazo-group are retained rather than being lost as dinitrogen as in many reactions of diazo-compounds with carbene acceptors: however, many phosphines react similarly with retention of nitrogen to form phosphinazines, $R_3P{=}N{-}N{=}CR'_2$.[9]

For each of (**5**)—(**7**) the ^1H n.m.r. spectrum showed (see Experimental section) as well as signals for $SiMe_3$ groups, and for Et, C_6H_4Me-*p*, and Ph respectively, an AB spectrum with $^2J(H_AH_B)$ in the range expected[10] for a methylene ($=CH_AH_B$) exocyclic to a six-membered ring together with a rather broad absorption, assignable to NH (or possibly OH) which was not however exchangeable with D_2O. Hence in each of (**5**)—(**7**) the acetyl group had enolised, $MeC(O){-} \longrightarrow CH_2{=}C(OH){-}$. Similarly in (**8**), the ^1H spectrum contained in addition to $SiMe_3$ (36 H) and CMe_2 (6 H), signals for a CH_2 group at δ 2.49, a =CH– proton at δ 5.19, and a broader proton signal, again not exchangeable with D_2O, at δ 6.81: these data indicated a single enolisation in the cyclohexanedione system, equation (2).



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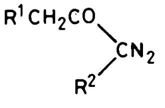
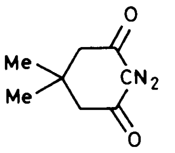
† For some discussion on push–pull alkenes see ref. 6.

‡ Formerly Groups 5B and 6B; refers to the new 18-Group format of the Periodic Table.



(1) $R^1 = H, R^2 = CO(OEt)$
(2) $R^1 = H, R^2 = SO_2C_6H_4Me\text{-}p$
(3) $R^1 = H, R^2 = COPh$



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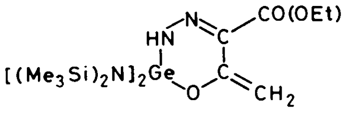

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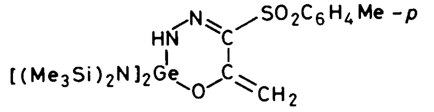

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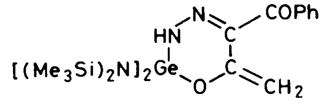

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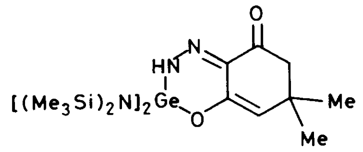
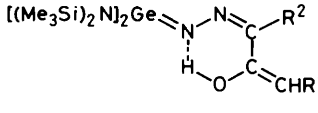


(8)

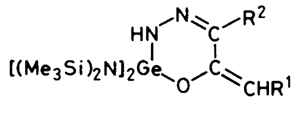
These enolisations were further confirmed, first by the presence of a band at *ca.* 1 600 cm^{-1}, assignable to ν(C=C), in the i.r. spectrum for each of (**5**)—(**8**), and the absence of any carbonyl absorption for (**6**), and secondly, by the ^{13}C spectra of (**5**)—(**7**) each of which showed an exocyclic =CH_2 fragment: the spectrum of (**5**) showed only a single Me unit (from the ethyl group), and the spectrum of (**8**) showed the presence of both CH_2 and =C– ring fragments.

In the mass spectra of (**5**)—(**8**) molecular ions were observed, whose accurate mass confirmed the molecular formulae deduced from elemental analysis, and from ^{1}H and ^{13}C n.m.r. spectroscopy. In none of the spectra was any peak observed corresponding to loss of N_2 implying the absence of any –N=N– function in the molecular structure, but all the compounds contained a prominent ion cluster at *m/e* 404, 406, and 408 for which accurate mass measurement confirmed the composition $[C_{12}H_{36}GeN_3Si_4]^+$, *i.e.* $[GeN\{N(SiMe_3)_2\}_2]^+$.

The ^{1}H and ^{13}C chemical shifts, intensities, and multiplicities for (**5**)—(**8**) are consistent with two formulations (**A**) and (**B**). The formulation (**C**) was ruled out, both by the absence of $[M - 28]^+$ peaks in the mass spectra, and by the chemical shifts of the quaternary carbon C_α: this carbon has chemical shifts ranging from δ 132.6 in (**5**) to 139.6 in (**7**), consistent with its being doubly bonded, and far outside the possible range expected in (**C**).

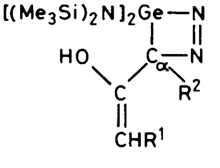


(A)

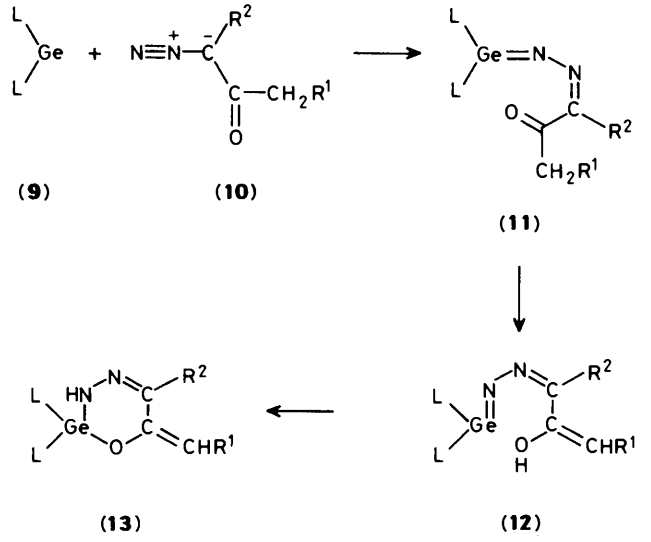


(B)

(5) $R^1 = H$ $R^2 = CO(OEt)$
(6) $R^1 = H, R^2 = SO_2C_6H_4Me\text{-}p$
(7) $R^1 = H, R^2 = COPh$
(8) $R^1, R^2 = -CMe_2CH_2C(O)-$



(C)



Scheme 1. L = NH_2

The proof of structure (**B**) was obtained using ^{15}N n.m.r spectroscopy at natural abundance. Each of (**5**)—(**8**) exhibits three ^{15}N chemical shifts, and both NOESY and DEPT sequences show the presence of NH, confirming (**B**) and excluding (**A**) and (**C**). The observation of $[GeN\{N(SiMe_3)_2\}_2]^+$ in the mass spectrum rather than $[GeNH\{N(SiMe_3)_2\}_2]^{\cdot +}$ was therefore misleading, as its formation is more indicative of (**A**) than of (**B**), although it confirmed the co-ordination of germanium by three nitrogens.

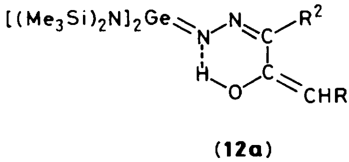
The formation of the products (**5**)—(**8**) may thus be envisaged as proceeding *via* (*i*) co-ordination of the diazo-compound to the germylene to form a Ge=N linkage, (*ii*) enolisation, and (*iii*) proton transfer from O to N forming the oxadiazagermine ring [analogous to Scheme 1 where L = $N(SiMe_3)_2$].

MNDO calculations[11] on a simple model for the reactions in Scheme 1 with L = NH_2, $R^1 = H$, $R^2 = CO(OMe)$, broadly support this reaction pathway. The calculated molecular energies are given in Table 1 for (**9**)—(**13**) (Scheme 1, L = NH_2), and show that formation of the initial Ge=N compound

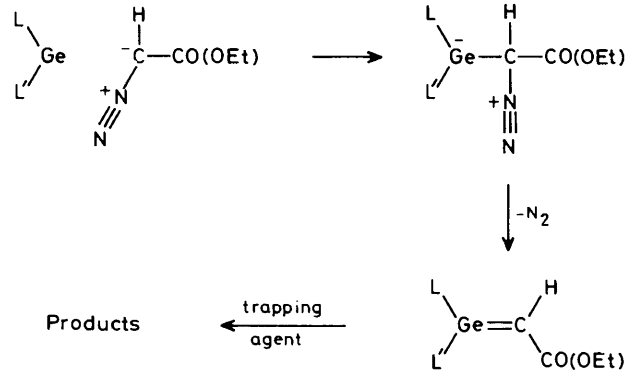
Table 1. Calculated molecular energies for compounds (9)—(13) [L = NH_2, R^1 = H, R^2 = CO(OMe)]

Compound	ΔH_f°/kJ mol^{-1}
(9)	+31.3
(10)	−265.7
(11)	−427.0*
(12)	−252.6
(13)	−439.7

* Geometries starting with either cisoid or transoid Ge=N-N=C fragments converted to cisoid structure.



(12a)

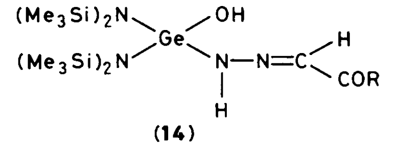


Scheme 2. L,L′ = Ph_2; Ph, Cl; or F_2 (ref. 4)

(**11**) for which only a cisoid geometry could be found is highly exothermic; enolisation is calculated to be endothermic, and the final proton shift with ring formation to be again highly exothermic. Both (**11**) and (**13**) lie below the energies calculated for [(**9**) + (**10**)]. In (**13**) the heterocyclic ring is calculated to be markedly puckered, with oxygen lying 0.46 Å above a plane defined by the ring atoms NNCC, and germanium lying 0.38 Å above the same plane. The structure having the ring constrained to planarity, however, is calculated to lie only *ca.* 1 kJ mol^{-1} higher in energy. Hence in solution the heterocyclic rings in the products (**5**)—(**8**) are expected to be very flexible. The calculated energy of (**12**), representing a barrier between (**11**) and (**13**) is almost certainly too high: MNDO is known to handle hydrogen bonding very poorly, and a structure such as (**12a**), if properly handled, would almost certainly have a lower energy than (**12**).

Reactions of $Ge[N(SiMe_3)_2]_2$ *with Ethyl Diazoacetate and Diazoacetophenone.*—The reactions of $HC(N_2)CO(OEt)$ with the simple germylenes GeF_2, GePhCl, and $GePh_2$ give[4] nitrogen-free products, and trapping experiments led to the postulate of initial attack on germanium by the carbanionic diazo-compound, with elimination of nitrogen, as in Scheme 2. By contrast, in both of the major products from the reaction of $HC(N_2)CO(OEt)$ with $Ge[N(SiMe_3)_2]_2$, all of the nitrogen is retained.

The simpler of the major products is the addition compound (**14**; R = OEt) whose composition was defined by elemental analysis and confirmed by high-resolution mass spectrometry.



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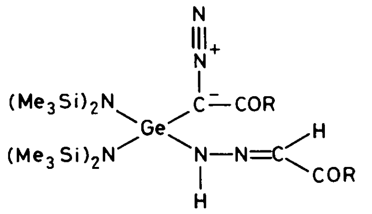


(15)

$\{GeO[N(SiMe_3)_2]_2\}_n$

(16)

The ^1H n.m.r. spectrum showed (see Experimental section) the presence of four $SiMe_3$ groups and an Et group, as well as an imine CH, and NH and OH signals. The ^{13}C spectrum confirmed the assignments of the $SiMe_3$, Et, and =CH– signals, and also showed the carbonyl group. The i.r. spectrum indicated both OH and NH, of which only the OH was exchangeable with D_2O, according to the ^1H n.m.r. spectrum.

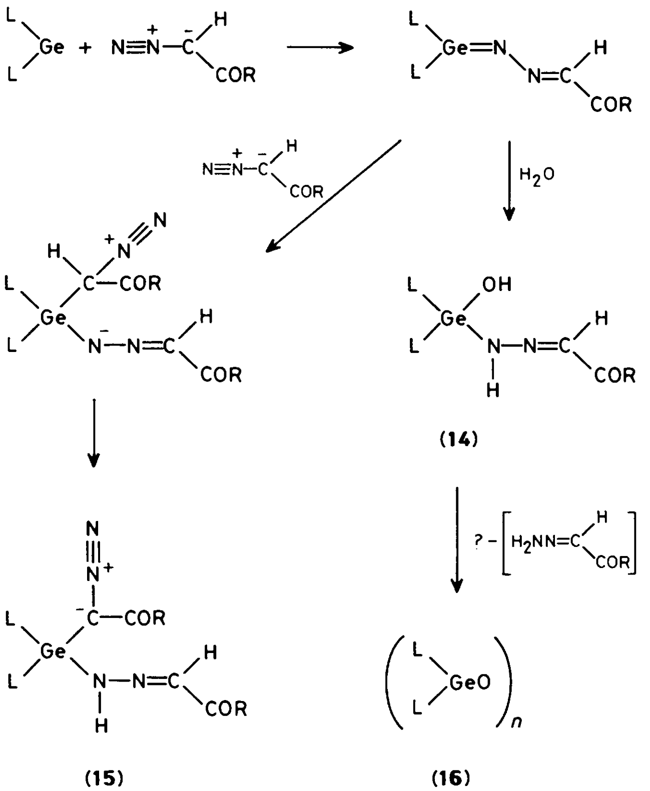
The more complex of the two major products is the 2:1 addition complex (**15**; R = OEt), whose composition was again established by elemental analysis and confirmed by high-resolution mass spectrometry. The i.r. spectrum indicated the presence both of NH and of an intact diazo-group. The ^1H and ^{13}C n.m.r. showed the presence of four equivalent $SiMe_3$ groups, of =CH–, and of two distinct Et groups: in addition the ^{13}C spectrum contained an additional singlet at δ 53.4, closely reminiscent of the chemical shift (δ 46.2) for the $HC(N_2)$ carbon in $HC(N_2)CO(OEt)$, and which was therefore assigned to a trisubstituted carbon atom bearing the intact diazo group.

A minor (4%) product isolated from this reaction was the oligomeric polygermoxane $\{GeO[N(SiMe_3)_2]_2\}_n$ (**16**): the value of *n* could not be established by mass spectrometry, but if the oligomer is cyclic then the most likely values of *n* are 3 or 4. Thus dehydration of $Ge(OH)_2Bu^t_2$ yielded[12] the cyclic trimer $(GeOBu^t_2)_3$, isostructural with both the silicon[13] and tin[14] analogues: similarly hydrolysis of $GeCl_2Ph_2$ yielded[15] the cyclic trimer $(GeOPh_2)_3$.

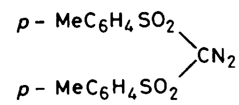
We envisage the formation of these products as depicted in Scheme 3. The initial 1:1 adduct containing a Ge=N bond is either trapped by addition across the Ge=N bond of a second mole of the diazo compound, acting as a weak acid, to give (**15**; R = OEt), or else it undergoes addition of water during chromatography to give (**14**; R = OEt).

The related weakly-acidic diazo-compound $HC(N_2)COPh$ also reacts with $Ge[N(SiMe_3)_2]_2$ to yield a 2:1 adduct (**15**; R = Ph) whose constitution follows from the analytical and spectral data.

Reactions of $Ge[N(SiMe_3)_2]_2$ *with Disubstituted Non-enolisable Diazo-compounds.*—The formation of compounds (**5**)—(**8**) above depended upon the presence of an enolisable group in the parent diazo-compound. When such a group was absent, as in the diazo-compounds (**17**)—(**19**), the reaction products were quite different. Thus, the only germanium-containing compound isolated from the reaction between (**17**) and $Ge[N(SiMe_3)_2]_2$ was the diol $Ge(OH)_2[N(SiMe_3)_2]_2$ (**20**) in 22% yield. In contrast to the fairly ready dehydration of $Ge(OH)_2Bu^t_2$ to form $(GeOBu^t_2)_3$, it was not found possible to effect the dehydration of $Ge(OH)_2[N(SiMe_3)_2]_2$ even under forcing conditions: thus refluxing in toluene or *p*-xylene for 5 or



Scheme 3. L = N(SiMe$_3$)$_2$, R = OEt or Ph



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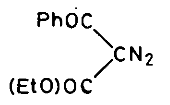

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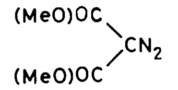

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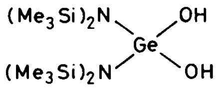


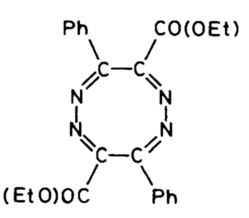
(20)

6 h, either alone or with added molecular sieves, or anhydrous calcium sulphate, or catalytic toluene-*p*-sulphonic acid, all failed to convert the diol into $\{GeO[N(SiMe_3)_2]_2\}_n$.

Chromatography of the reaction mixture from the 1:1 addition of Ge[N(SiMe$_3$)$_2$]$_2$ to the diazo-compound (**18**) similarly yielded the diol (**20**) (36%), together with the hydrazone H$_2$NN=C(COPh)CO(OEt) (42%), corresponding to the two hydrolysis products of an initial Ge=N compound, equation (3).

$$\begin{aligned}&Ge[N(SiMe_3)_2]_2 + PhCOC(N_2)CO(OEt) \longrightarrow\\ &\quad [(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COPh)CO(OEt) \xrightarrow{2H_2O}\\ &\quad Ge(OH)_2[N(SiMe_3)_2]_2 + H_2NN{=}C(COPh)CO(OEt) \quad (3)\end{aligned}$$

Although several such hydrazones have been reported previously[16] they are moderately labile, and it did not prove possible to purify and characterise the hydrazone prepared from the corresponding diazo-compound (**17**).



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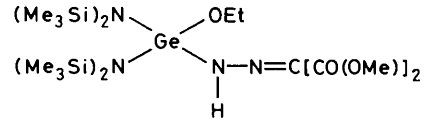

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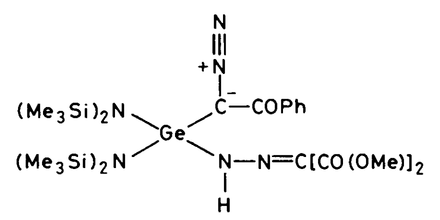


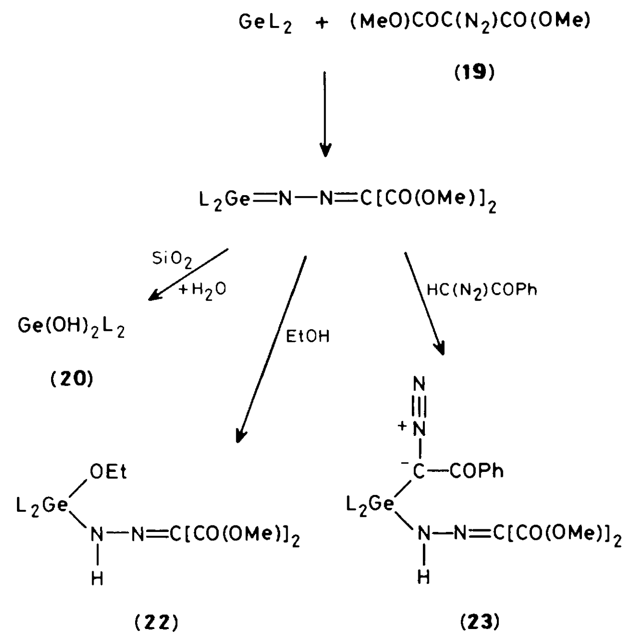
(23)

When the hydrazone H$_2$NN=C(COPh)CO(OEt) was kept at room temperature it spontaneously transformed into a different product, whose elemental analysis, and i.r. and n.m.r. spectra show it to be the tetrazocine (**21**). The ease of formation of this tetrazacyclo-octatraene system is surprising but there is ample precedent for it.[17]

The isolation of both the diol (**20**) and the hydrazone from the reaction of (**18**) with Ge[N(SiMe$_3$)$_2$]$_2$ is consistent with, but does not prove, the initial formation of a Ge=N intermediate followed by hydrolysis during chromatography. Accordingly the interception of such an intermediate was attempted using a variation on the intramolecular trapping reaction responsible for the formation of (**5**)—(**8**) (Scheme 1).

For the reaction of Ge[N(SiMe$_3$)$_2$]$_2$ with the diazo-compound (**19**), derived from dimethyl malonate, we proceeded directly to trapping reactions; this diazo-compound was selected in order to provide straightforward n.m.r. spectra. Addition of a dilute solution of ethanol in chloroform to the reaction mixture, prior to chromatography, provided after work-up a 61% yield of compound (**22**). This is the adduct of one mole of ethanol across a Ge=N bond, polarised in the sense $\overset{\delta+}{Ge}{=}\overset{\delta-}{N}$, and is a direct acyclic analogue of compounds (**5**)—(**8**): proof of structure (**22**) follows without ambiguity from the analytical and spectroscopic data. In contrast to reactions such as those of (**17**) and (**18**) in which the crude reaction mixture was chromatographed without the addition of trapping agents to give substantial yields of diol (**20**), after addition of ethanol only 8% of the diol was isolated.

When a stoicheiometric equivalent of ethanol was added after 3 h to a 1:1 mixture of (MeO)COC(N$_2$)CO(OMe) and Ge[N(SiMe$_3$)$_2$]$_2$, the ethanol adduct (**22**) was isolated in 83% yield: when the delay in adding the ethanol was increased to 21 h, the yield of (**22**) only fell to 75% indicating that the initially formed Ge=N compound [(Me$_3$Si)$_2$N]$_2$Ge=N–N=C[CO(OMe)]$_2$ has a considerable lifetime at room temperature, even in solution, although attempts to purify it by chromatography always effected complete hydrolysis to give the diol (**20**).



Scheme 4. L = $N(SiMe_3)_2$

However, treatment, at room temperature, of the ethanol adduct (**22**) with a large excess of ethanol for 3 d effected no further reaction.

If, instead of adding ethanol across the Ge=N bond in $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C[CO(OMe)]_2$, one molar equivalent of the weakly acidic diazo-compound $HC(N_2)COPh$ is added, then the adduct (**23**) can be isolated from the mixture in 42% yield.

The reactions of $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C[CO(OMe)]_2$ are summarised in Scheme 4.

In an attempt to understand the difference between the reactions of $HC(N_2)CO(OEt)$ with germylenes, in which $Ge[N(SiMe_3)_2]_2$ yielded initially a Ge=N product, wherein all the diazo-nitrogen atoms were retained, as discussed above, and those with $GePh_2$ which yielded[4] a Ge=C product, from which all the nitrogen atoms were lost, we have performed some MNDO calculations on model reactions between the diazo-compound $HC(N_2)CO(OMe)$ and the two germylenes $GePh_2$ and $Ge[N(SiH_3)_2]_2$, in the latter of which the methyl groups of the germylene used experimentally in this work were replaced by hydrogen atoms, for the sake of computational economy.

The optimised properties of the germylenes $Ge[N(SiH_3)_2]_2$ and $GePh_2$ are given in Table 2, together with experimental data[18] for $Ge[N(SiMe_3)_2]_2$ for comparison. There is no significant difference between the frontier orbitals in the two germylenes, except for a small contribution of Si(3*s*) to the lowest unoccupied molecular orbital (l.u.m.o.) of $Ge[N(SiMe_3)_2]_2$, which is presumably consequent upon the twist angle of 28°. In $HC(N_2)CO(OMe)$, for which the calculated ΔH_f° is -91.3 kJ mol^{-1}, the highest occupied molecular orbital (h.o.m.o.) is a π orbital in the CNN fragment, concentrated on the carbon and the terminal nitrogen, and the l.u.m.o. is a π antibonding orbital localised on the two nitrogen atoms. Thus any direct formation of a Ge=N bond by either germylene requires a substantial reorganisation of the frontier orbitals of the two reacting components.

In Table 3 are recorded calculated values of ΔH_f° for the species (**24**)—(**26**), where L = $N(SiH_3)_2$ or Ph, together with the sums of ΔH_f° for $HC(N_2)CO(OMe)$ and GeL_2. These ΔH_f° data show that for either substituent L, formation of (**24**) or (**25**) is substantially exothermic, and that in each case, the Ge=C species (**25**) is much more stable than the Ge=N species (**24**). Our calculations thus show that the reaction[4] between $GePh_2$ and $HC(N_2)CO(OMe)$ yielded the thermodynamically most stable product, containing a Ge=C bond, which was subsequently identified from trapping reactions. However, the corresponding reaction involving $Ge[N(SiMe_3)_2]_2$ gave the less stable Ge=N product with $HC(N_2)CO(OEt)$, and a similar product with $HC(N_2)COPh$, and it is necessary to determine why this is so.

Table 2. Optimised properties of germylenes (X = N or C)

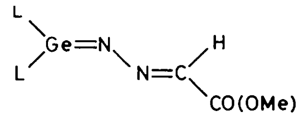
	$Ge[N(SiH_3)_2]_2$ [a]	$GePh_2$
Point group	C_2 (C_2)	C_{2v}
ΔH_f°/kJ mol^{-1}	-102.7	$+360.8$
d(Ge–X)/Å	1.832 (1.89)	1.908
X–Ge–X/°	105.6 (101)	102.0
Twist angle/° [b]	28 (90)	90
h.o.m.o.	*A*; Ge(4*p*σ)	A_1; Ge(4*p*σ)
l.u.m.o.	*B*; Ge(4*p*π) + Si(3*s*)	B_1; Ge(4*p*π)
I.p./eV [c]	7.64	7.30

[a] Experimental values[18] for $Ge[N(SiMe_3)_2]_2$ are given in parentheses. [b] Angle between XGeX plane and SiNSi or CCC planes. [c] I.p. = ionisation potential; eV ≈ 1.60×10^{-19} J.

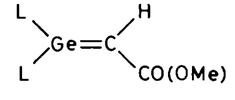
Table 3. Molecular energies (ΔH_f°/kJ mol^{-1}) for germylene adducts

L	$[GeL_2 + HC(N_2)CO(OMe)]$	(**24**)	(**25**)	(**26**)
$N(SiH_3)_2$	-194.0	-241.2	-405.4	*a*
Ph	$+269.5$	$+115.9$	-28.2	*b*

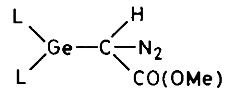
[a] Dissociates along Ge–C to yield GeL_2 + $HC(N_2)CO(OMe)$. [b] Dissociates along C–N to yield $L_2Ge{=}C(H)CO(OMe)$ + N_2.



(**24**)



(**25**)



(**26**)

It has been suggested[4] that formation of the Ge=C product (**25**; L = Ph) is preceded by attack upon germanium of the unique carbon in the diazo-compound, forming an intermediate of type (**26**). We find that calculations upon (**26**) point to the differences in behaviour of $GePh_2$ and $Ge[N(SiMe_3)_2]_2$.

Optimisation of the geometry of [**26**; L = $N(SiH_3)_2$] from any plausible starting configuration led smoothly to dissociation along the Ge–C bond, so reverting to the starting reactants. On the other hand, optimisations of (**26**; L = Ph) gave dissociation along the C–N bond to yield N_2 and (**25**; L = Ph). In further calculations on (**26**), the crucial bonds Ge–C, C–N, and N–N were fixed at 1.90, 1.30, and 1.20 Å respectively, and the bond orders were calculated for these structures. When L = $N(SiH_3)_2$, the resulting bond orders were 0.37, 1.23, and 1.99, indicative of extremely weak Ge–C bonding even at a distance of 1.90 Å: when L = Ph the bond orders were

0.80, 0.98, and 2.21 indicative of a substantial shift, as compared with L = $N(SiH_3)_2$, of bonding electron density from the C–N bond into both the Ge–C and N–N bonds.

Not only do these MNDO calculations effectively reproduce the experimental observations but they show that for the complex potential surfaces of (**24**)—(**26**), when L = Ph, the sections of the surfaces exhibit deep energy minima at reasonable bonding distances for both Ge=N and Ge=C species (1.72 and 1.73 Å respectively): when L = $N(SiH_3)_2$, while the surface corresponding to the Ge=N compound (**24**) exhibits an energy minimum at a Ge–N distance of 1.74 Å, that corresponding to (**26**) is repulsive for all values of the Ge–C distance out to at least 10 Å. If the germylene $GePh_2$ encounters $HC(N_2)CO(OR)$ in an orientation which provides a close Ge ··· $C(N_2)$ contact, the reaction will then proceed down a valley of the potential surface corresponding to formation of Ge=C with simultaneous loss of N_2. If the germylene $Ge[N(SiR_3)_2]_2$ (R = H or Me) experiences a similar collison, the collision complex breaks up along the same Ge ··· $C(N_2)$ vector, corresponding to its formation, and no net reaction occurs. The only possible reaction, exothermic with respect to the reactants, is formation of the Ge=N species (**24**). Since this is of higher energy than (**25**), it is conceivable that N_2 could under experimental conditions be extruded from preformed [**24**; L = $N(SiMe_3)_2$] to give [**25**; L = $N(SiMe_3)_2$].

The results described in this paper are all consistent with an initial addition of the terminal nitrogen of the diazo-group in a range of diazo-compounds to the germanium of the germylene $Ge[N(SiMe_3)_2]_2$: the adduct, containing a Ge=N bond, can be trapped either intramolecularly when enolisable groups are present or by addition of weakly protic species such as H_2O, EtOH, or $HC(N_2)COPh$. Furthermore the germyleneazine $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C[CO(OMe)]_2$ obtained from the diazo-compound (**19**) is obviously persistent and thermodynamically stable.

Experimental

The germylene $Ge[N(SiMe_3)_2]_2$ was prepared[19,20] from $GeCl_4$. The disubstituted diazo-compounds were all prepared using literature methods.[16,21–24] Ethyl diazoacetate was purchased from Aldrich and used as received [$\delta(^{13}C)$: 14.5 (q), 46.2 (d), 60.9 (t), and 166.9 (s); $\delta(^{1}H)$: $HC(N_2)$, 4.70]. Diazoacetophenone was prepared using a slight modification of the literature method[25] [$\delta(^{13}C)$: 54.2 (d), 126.8 (d), 128.7 (d), 132.8 (d), 136.7 (s), and 184.4 (s); $\delta(^{1}H)$: $HC(N_2)$, 5.92].

All solvents were dried and purified by conventional methods. Light petroleum had b.p. 40—60 °C. Elemental analyses were by the Microanalytical Laboratory of this Department; mass spectra, including accurate mass measurements, were recorded using an AEI MS-902 instrument. DEPT (^{13}C and ^{15}N) and NOESY (^{15}N) n.m.r. spectra were recorded using the Brüker WH-360 spectrometer of the S.E.R.C. regional n.m.r. service, Edinburgh; the relaxation agent $[Cr(acac)_3]$ (acac = acetylacetonate) was employed for natural abundance ^{15}N spectroscopy. Routine ^{13}C spectra were recorded using a Varian CFT-20 spectrometer, and ^{1}H spectra were recorded using a Brüker WP-80 instrument. ^{15}N Chemical shifts are referred to external nitromethane.

Reactions of Diazo-compounds with $Ge[N(SiMe_3)_2]_2$.—*Preparation of compound* (**5**). A solution of $MeCOC(N_2)CO(OEt)$ (1.59 g, 10.2 mmol) in benzene (15 cm^3) was added at room temperature under nitrogen to a stirred solution of $Ge[N(SiMe_3)_2]_2$ (4.0 g, 10.2 mmol) in benzene (15 cm^3), and the mixture was stirred for 3 h. After removal of solvent, chromatography on silica with diethyl ether–light petroleum (1:9 v/v) afforded the almost colourless product (**5**) (4.19 g, 75%), m.p. 148—149 °C, after recrystallisation from hexane (Found: C, 39.1; H, 8.2; N, 10.1. $C_{18}H_{44}GeN_4O_3Si_4$ requires C, 39.3; H, 8.1; N, 10.2%). N.m.r.: ^{1}H ($CDCl_3$), δ 0.28 (36 H, s, $SiMe_3$), 1.33 (3 H, t, *J* 7, CH_2CH_3), 4.28 (2 H, q, *J* 7, CH_2CH_3), 4.73 (1 H, d, *J* 0.8, $=CH_AH_B$), 5.08 (1 H, d, *J* 0.8 Hz, $=CH_AH_B$), 6.53 (1 H, s, NH; non-exchangeable with D_2O); ^{13}C ($CDCl_3$), δ 5.1 (q, $SiMe_3$), 14.3 (q, CH_2CH_3), 61.0 (t, CH_2CH_3), 100.4 (t, $=CH_2$), 132.6 (s, C=N–), 148.2 (s, $C{=}CH_2$), 163.9 [s, –CO(OEt)]; ^{15}N ($CDCl_3$), δ −24.3 [nuclear Overhauser enhancement (n.O.e.) positive, C=N–], −239.0 (n.O.e. negative, NH), −334.1 (n.O.e. positive, Si_2NGe). I.r.: ν at 3 245 (NH), 1 705 (C=O), 1 600 cm^{-1} (C=C). Mass spectrum: M^+ at *m/e* 550 (for ^{74}Ge), accurate mass found (for ^{74}Ge) 550.1739, $[C_{18}H_{44}{}^{74}GeN_4O_3Si_4]^+$ requires 550.1700; at *m/e* 408, accurate mass found 408.1184, $[C_{12}H_{36}{}^{74}GeN_3Si_4]^+$ requires 408.1196.

In a reaction similar to the above but using 2 molar equivalents of the germylene, the identical product was isolated in 68% yield.

Preparation of compound (**6**). From a reaction similar to that above, between $MeCOC(N_2)SO_2C_6H_4Me$-*p* and $Ge[N(SiMe_3)_2]_2$, the colourless product (**6**) was isolated in 56% yield, m.p. 202—203 °C, from ethyl acetate. N.m.r.: ^{1}H ($CDCl_3$), δ 0.20 (36 H, s, $SiMe_3$), 2.41 (3 H, s, $C_6H_4CH_3$), 4.73 (1 H, d, *J* 1.4, $=CH_AH_B$), 5.46 (1 H, d, *J* 1.4 Hz, $=CH_AH_B$), 7.15 (1 H, s, NH; non-exchangeable with D_2O), 7.2—7.8 (4 H, m, $C_6H_4CH_3$); ^{13}C ($CDCl_3$), δ 5.04 (q, $SiMe_3$), 21.6 (q, $C_6H_4CH_3$), 100.8 (t, $=CH_2$), 128.5 (d) and 129.3 (d) (aromatic), 137.6 (s), and 138.3 (s) (aromatic and C=N–), 145.5 (s, aromatic); ^{15}N ($CDCl_3$), δ −22.9 (n.O.e. positive, C=N–), −235.2 (n.O.e. negative, NH), −333.8 (n.O.e. positive, Si_2NGe). I.r.: ν at 3 270 (NH), 1 595 (C=C), 1 300 and 1 155 cm^{-1} (SO_2). Mass spectrum: M^+ at *m/e* 632 (for ^{74}Ge), accurate mass found (for ^{74}Ge) 632.1594, $[C_{22}H_{46}{}^{74}GeN_4O_3SSi_4]^+$ requires 632.1578; other peaks at $[M - 15]^+$, $[M - 64]^+$, and *m/e* 408.

Preparation of compound (**7**). From a reaction similar to that above, between $MeCOC(N_2)COPh$ and $Ge[N(SiMe_3)_2]_2$, the pale yellow product (**7**) was isolated in 31% yield, m.p. 134—136 °C, from hexane (Found: C, 45.6; H, 7.7; N, 9.6. $C_{22}H_{44}GeN_4O_2Si_4$ requires C, 45.4; H, 7.6; N, 9.6%). N.m.r.: ^{1}H ($CDCl_3$), δ 0.29 (36 H, s, $SiMe_3$), 4.78 (1 H, d, *J* 1.0, $=CH_AH_B$), 4.98 (1 H, d, *J* 1.0 Hz, $=CH_AH_B$), 6.44 (1 H, s, NH; non-exchangeable with D_2O), 7.4—7.8 (5 H, m, aromatic); ^{13}C ($CDCl_3$), δ 5.2 (q, $SiMe_3$), 100.5 (t, $=CH_2$), 127.9, 129.9, and 131.9 (all d, aromatic), 138.6 (s) and 139.6 (s) (aromatic and C=N–), 148.8 (s, $C{=}CH_2$), 192.0 (s, –COPh); ^{15}N ($CDCl_3$), δ −22.7 (n.O.e. positive C=N–), −240.7 (n.O.e. negative, NH), −333.5 (n.O.e. positive, Si_2NGe). I.r.: ν at 3 315 and 3 305 (NH), 1 635 (C=O), 1 600 cm^{-1} (C=C). Mass spectrum: M^+ at *m/e* 582 (for ^{74}Ge), accurate mass found (for ^{74}Ge) 582.1711, $[C_{22}H_{44}{}^{74}GeN_4O_2Si_4]^+$ requires 582.1751; other peaks at $[M - 15]^+$ and *m/e* 408.

Preparation of compound (**8**). From a reaction similar to that above, between $Me_2\overline{CCH_2C(O)N_2C(O)C}H_2$ and $Ge[N(SiMe_3)_2]_2$ the orange-yellow product (**8**) was isolated in 20% yield, m.p. 213—214 °C, from hexane (Found: C, 43.0; H, 8.4; N, 10.0. $C_{20}H_{46}GeN_4O_2Si_4$ requires C, 42.9; H, 8.3; N, 10.0%). N.m.r.: ^{1}H ($CDCl_3$), δ 0.27 (36 H, s, $SiMe_3$), 1.13 (6 H, s, CMe_2), 2.49 [2 H, s, $C(O)CH_2CMe_2$], 5.19 (1 H, s, =CH), 6.81 (1 H, s, NH; non-exchangeable with D_2O); ^{13}C ($CDCl_3$), δ 5.0 (q, $SiMe_3$), 30.5 (q, CMe_2), 32.1 (s, CMe_2), 53.7 [t, $C(O)CH_2CMe_2$], 119.8 (d, =CH), 133.7 (s, C=N–), 145.0 (s, OC=CH–), 195.5 (s, C=O); ^{15}N ($CDCl_3$), δ −25.9 (n.O.e. positive, C=N–), −237.8 (n.O.e. negative, NH), −334.0 (n.O.e. positive, Si_2NGe). I.r.: ν at 3 240 (NH), 1 680 (C=O), 1 605 cm^{-1} (C=C). Mass spectrum: M^+ at *m/e* 560 (for ^{74}G), accurate mass found (for ^{74}Ge) 560.1892, $[C_{20}H_{46}{}^{74}GeN_4O_2Si_4]^+$ requires 560.1908; other peaks at $[M - 15]^+$ and *m/e* 408.

Reaction of $\mathrm{HC(N_2)CO(OEt)}$ *with* $\mathrm{Ge[N(SiMe_3)_2]_2}$.—A solution of $\mathrm{HC(N_2)CO(OEt)}$ (0.91 g, 8.0 mmol) in benzene (5 cm^3) was added, at room temperature under nitrogen, to a solution of $\mathrm{Ge[N(SiMe_3)_2]_2}$ (3.15 g, 8.0 mmol) in benzene (10 cm^3), and the mixture was stirred for 3 h. After removal of the solvent, chromatography on silica (diethyl ether–light petroleum, initially 1:35 v/v, then 1:20 v/v) yielded the oxide $\{\mathrm{GeO[N(SiMe_3)_2]_2}\}_n$ (**16**) (130 mg, 4%), m.p. 119—121 °C, from hexane [Found: C, 35.2; H, 8.9; N, 6.8. $\mathrm{(C_{12}H_{36}GeN_2OSi_4)}_n$ requires C, 34.9; H, 8.8; N, 6.6%]. N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.34 (s, $\mathrm{SiMe_3}$); ^{13}C ($\mathrm{CDCl_3}$), δ 6.2 (q, $\mathrm{SiMe_3}$). I.r.: no assignable features. The second fraction was the 2:1 adduct (**15**; R = OEt) (770 mg, 30%) as a yellow oil (Found: C, 39.1; H, 7.9; N, 13.8. $\mathrm{C_{20}H_{48}GeN_6O_4Si_4}$ requires C, 38.7; H, 7.8; N, 13.5%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.26 (36 H, s, $\mathrm{SiMe_3}$), 1.26 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 1.28 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 4.17 (2 H, q, *J* 7, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.21 (2 H, q, *J* 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.65 (1 H, s, =CH–), 10.61 (1 H, br s, NH; non-exchangeable with $\mathrm{D_2O}$); ^{13}C ($\mathrm{CDCl_3}$), δ 5.4 (1, $\mathrm{SiMe_3}$), 14.2 (q, $\mathrm{OCH_2}C\mathrm{H_3}$), 14.6 (q, $\mathrm{OCH_2}C\mathrm{H_3}$), 53.4 (s, $\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{N}}\equiv\mathrm{N}$), 59.6 (t, $\mathrm{O}C\mathrm{H_2CH_3}$), 61.1 (t, $\mathrm{O}C\mathrm{H_2CH_3}$), 120.8 (d, =C–), 162.7 [s, –C(O)–], 167.2 [s, –C(O)–]. I.r.: ν at 3 245 (NH), 2 090 ($\mathrm{C{=}N_2}$), 1 685 cm^{-1} (C=O). Mass spectrum: no M^+: highest *m/e* 607 (for ^{74}Ge), $[M - 15]^+$, accurate mass found (for ^{74}Ge) 607.1789, $[\mathrm{C_{19}H_{45}{}^{74}GeN_6O_4Si_4}]^+$ requires 607.1837. The third fraction was the 1:1 adduct (**14**; R = OEt) (780 mg, 19%), m.p. 96—97 °C, from hexane (Found: C, 36.9; H, 8.6; N, 10.6. $\mathrm{C_{16}H_{44}GeN_4O_3Si_4}$ requires C, 36.6; H, 8.4; N, 10.7%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.25 (36 H, s, $\mathrm{SiMe_3}$), 1.28 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 2.26 (1 H, s, OH; exchangeable with $\mathrm{D_2O}$), 4.17 (2 H, q, *J* 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.65 (1 H, s, =CH–), 10.48 (1 H, br s, NH; non-exchangeable with $\mathrm{D_2O}$); ^{13}C ($\mathrm{CDCl_3}$), δ 5.1 (q, $\mathrm{SiMe_3}$), 14.2 (q, $\mathrm{OCH_2}C\mathrm{H}$), 59.8 (t, $\mathrm{O}C\mathrm{H_2CH_3}$), 121.4 (d, =CH–), 162.9 [s, –C(O)–]. I.r.: ν at 3 500 (OH), 3 245 (NH), 1 665 cm^{-1} (C=O). Mass spectrum: no M^+; highest *m/e* 511 (for ^{74}Ge), $[M - 15]^+$, accurate mass found (for ^{74}Ge) 511.1466, $[\mathrm{C_{15}H_{41}GeN_4O_3Si_4}]^+$ requires 511.1502.

Reaction of $\mathrm{HC(N_2)COPh}$ *with* $\mathrm{Ge[N(SiMe_3)_2]_2}$.—A solution of $\mathrm{HC(N_2)COPh}$ (1.4 g, 9.6 mmol) in benzene (10 cm^3) was added, at room temperature, to a solution of $\mathrm{Ge[N(SiMe_3)_2]_2}$ (3.8 g, 9.6 mmol) in benzene (15 cm^3), and the mixture was stirred for 3 h. After removal of the solvent, chromatography on silica (diethyl ether–light petroleum, 1:12 v/v) yielded unchanged $\mathrm{HC(N_2)COPh}$ (80 mg, 0.55 mmol) and the 2:1 adduct (**15**; R = Ph) (610 mg, 19.8%), m.p. 143—148 °C (decomp.), after recrystallisation from diethyl ether–hexane (Found: C, 49.2; H, 7.2; N, 12.1. $\mathrm{C_{28}H_{48}GeN_6O_2Si_4}$ requires C, 49.1; H, 7.1; N, 12.3%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.36 (s, 36 H, $\mathrm{SiMe_3}$), 7.3—7.7 and 7.9—8.1 (m, 10 H, Ph), 7.79 (s, 1 H, =CH–), 12.75 (s br, 1 H, NH); ^{13}C ($\mathrm{CDCl_3}$), δ 5.5 (q, $\mathrm{SiMe_3}$), 62.8 (s, $\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{N}}\equiv\mathrm{N}$), 125.2, 126.9, 128.1, 128.6, 131.4, 132.4, 137.8, and 138.1 (Ph and C=N–), 185.3 (s), 190.8 (s) (C=O). I.r.: ν at 3 180 (NH), 2 078 ($\mathrm{C{=}N_2}$), 1 620 cm^{-1} (C=O). Mass spectrum: $[M - 28]^+$ at *m/e* 658 (for ^{74}Ge), accurate mass found (for ^{74}Ge) 658.2092, $[\mathrm{C_{28}H_{48}GeN_4O_2Si_4}]^+$ requires 658.2064.

Reaction of p-$\mathrm{MeC_6H_4SO_2C(N_2)SO_2C_6H_4Me}$-$p$ *with* $\mathrm{Ge[N(SiMe_3)_2]_2}$.—A solution of the diazo-compound (1.1 g, 3.1 mmol) in benzene (15 cm^3) was added at room temperature under nitrogen to a solution of the germylene (2.3 g, 5.9 mmol) in benzene (15 cm^3), and the mixture stirred for 3 h. After removal of solvent, chromatography on silica (diethyl ether–light petroleum, 1:12 v/v) yielded unchanged diazo-compound (15% recovery), identical (t.l.c., i.r., ^{1}H n.m.r., m.p.) with the starting compound, preceded by the colourless diol $\mathrm{Ge(OH)_2[N(SiMe_3)_2]_2}$ (**20**) (0.54 g, 22%), m.p. 80—82 °C (Found: C, 33.9; H, 9.0; N, 6.5. $\mathrm{C_{12}H_{38}GeN_2O_2Si_4}$ requires C, 33.7; H, 9.0; N, 6.6%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.26 (36 H, s, $\mathrm{SiMe_3}$), 1.50 (2 H, s, OH; removed by $\mathrm{D_2O}$); ^{13}C ($\mathrm{CDCl_3}$), 5.01 (q). I.r.: ν at 3 605 (free OH), 3 500 cm^{-1} (br, H-bonded OH). Mass spectrum: M^+ at *m/e* 428 (for ^{74}Ge), accurate mass found (for ^{74}Ge) 428.1199, $[\mathrm{C_{12}H_{38}{}^{74}GeN_2O_2Si_4}]^+$ requires 428.1220.

Reactions of $\mathrm{PhCOC(N_2)CO(OEt)}$ *with* $\mathrm{Ge[N(SiMe_3)_2]_2}$.—A benzene solution (15 cm^3) of $\mathrm{PhCOC(N_2)CO(OEt)}$ (3.05 g, 14.0 mmol) was added to a solution of the germylene (5.80 g, 14.7 mmol) in benzene (40 cm^3) at room temperature, with stirring, under nitrogen. After stirring for 3 h, the solvent was removed, and the mixture chromatographed on silica. Elution with diethyl ether–light petroleum (initially 1:8 v/v, gradually increasing to 1:2 v/v) yielded the diol (**20**) (2.17 g, 36%), identical (t.l.c., m.p., ^{1}H n.m.r., i.r.) with that isolated previously, together with the hydrazone $\mathrm{H_2NN{=}C(COPh)CO(OEt)}$ as a yellow oil (1.29 g, 42%) (Found: C, 60.2; H, 5.8; N, 12.9. $\mathrm{C_{11}H_{12}N_2O_3}$ requires C, 60.0; H, 5.5; N, 12.7%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 1.05 (0.3 × 3 H, t, *J* 7, minor $\mathrm{OCH_2C}H_3$), 1.21 (0.7 × 3 H, t, *J* 7, major $\mathrm{OCH_2C}H_3$), 4.10 (0.3 × 2 H, q, *J* 7, minor $\mathrm{OC}H_2\mathrm{CH_3}$), 4.23 (0.7 × 2 H, q, *J* 7 Hz, major $\mathrm{OC}H_2\mathrm{CH_3}$), 7.2—7.9 (5 H, m, Ph), 9.23 and 9.38 (2 H, br, $\mathrm{NH_2}$); ^{13}C ($\mathrm{CDCl_3}$), δ 14.0 (q, $\mathrm{CH_3}$, major isomer), 25.0 (q, $\mathrm{CH_3}$, minor isomer), 60.8 (t, $\mathrm{CH_2}$, major isomer), 61.0 (t, $\mathrm{CH_2}$, minor isomer), 128.0 (d), 130.0 (d), 132.3 (d), and 137.9 (s) (aromatic), 128.7 (s, C=N–), 163.0 [s, –C(O)O–], 190.5 (s, Ph*C*O). I.r.: ν at 3 380 (NH), 3 210 (NH), 1 685 and 1 650 cm^{-1} [–C(=O)–C=N–]. Mass spectrum: *m/e* 221 $[M + 1]^+$, 220 M^+, 219 $[M - 1]^+$, 218 $[M - 2]^+$; accurate mass found for M^+ 220.0862, $[\mathrm{C_{11}H_{12}N_2O_3}]^+$ requires 220.0848.

Upon standing at room temperature during 7 d the hydrazone was converted into the tetrazocine (**21**), m.p. 195—196 °C (Found: C, 66.5; H, 5.0; N, 14.1. $\mathrm{C_{22}H_{20}N_4O_4}$ requires C, 65.3; H, 5.0; N, 13.9%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 1.35 (6 H, t, *J* 7, $\mathrm{CH_3}$), 4.43 (4 H, q, *J* 7 Hz, $\mathrm{CH_2}$), 7.4—8.0 (10 H, m, Ph). I.r.: ν at 1 705 cm^{-1} [–O–C(=O)–]. Mass spectrum: M^+ at *m/e* 404, accurate mass 404.1503, $[\mathrm{C_{22}H_{20}N_4O_4}]^+$ requires 404.1484.

In a similar reaction, between the diazo-compound (1.68 g, 7.70 mmol) and the germylene (3.05 g, 7.75 mmol), after stirring for 2 h, water (0.30 cm^3, 16.6 mmol) was added and the mixture stirred for a further 30 min. The solvent was removed, and the mixture was chromatographed on silica. Elution with diethyl ether–light petroleum (initially 1:12 v/v, gradually increasing to 3:2 v/v) yielded the diol (**20**) (2.41 g, 73%), identical (t.l.c., m.p., ^{1}H n.m.r., i.r.) to that previously isolated, together with the hydrazone $\mathrm{H_2NN{=}C(COPh)CO(OEt)}$ as a light tan solid (1.16 g, 68%), m.p. 58—59 °C, from diethyl ether–hexane (Found: C, 60.3; H, 5.5; N, 12.6. $\mathrm{C_{11}H_{12}N_2O_3}$ requires C, 60.0; H, 5.5; N, 12.7%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 1.25 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 4.26 (2 H, q, *J* 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.3—7.8 (5 H, m, Ph), 9.04 (2 H, br s, $\mathrm{NH_2}$); ^{13}C ($\mathrm{CDCl_3}$), δ 14.0 (q, $\mathrm{OCH_2}C\mathrm{H_3}$), 60.8 (t, $\mathrm{O}C\mathrm{H_2CH_3}$), 128.0 (d), 130.0 (d), 132.2 (d), and 138.0 (s) (aromatic), 128.6 (s, C=N–), 163.0 [s, –C(O)O–], 190.5 [s, –*C*(O)Ph]. I.r.: ν at 3 370 (NH), 3 200 (NH), 1 670 and 1 645 cm^{-1} [–C(=O)–C=N–]. Mass spectrum: *m/e* 221 $[M - 1]^+$, 220 M^+, 219 $[M - 1]^+$, 218 $[M - 2]^+$; accurate mass found for M^+ 220.0841, $[\mathrm{C_{11}H_{12}N_2O_3}]^+$ requires 220.0848. These spectral properties are identical (within experimental error) with those of the major isomer present in the oil previously isolated, and the ^{1}H and ^{13}C n.m.r. spectra show no trace of the peaks from the minor isomer. The ^{1}H n.m.r. spectrum of the material obtained from the mother-liquor after recrystallisation of the hydrazone shows the presence of a small amount of the minor isomer.

Reactions of $\mathrm{(MeO)COC(N_2)CO(OMe)}$ *with* $\mathrm{Ge[N(SiMe_3)_2]_2}$.—A solution of the diazo-compound (0.80 g, 5.1 mmol) in benzene (5 cm^3) was added, at room temperature under nitrogen, to a solution of $\mathrm{Ge[N(SiMe_3)_2]_2}$ (2.0 g, 5.1 mmol) in benzene (15 cm^3). After stirring for 3 h, the reaction mixture was quenched by addition of a 1% (v/v) solution of ethanol in chloroform (20 cm^3). After removal of the solvent, chromatography on silica (diethyl ether–light petroleum, initially 1:6 v/v then changing gradually to 1:1 v/v) yielded the oxide $\{GeO[N(SiMe_3)_2]_2\}_n$ (**16**) (210 mg, 10%) and the diol (**20**) (180 mg, 8%), each identical (t.l.c., ^1H n.m.r., i.r., m.p.) to samples isolated previously, together with $[(Me_3Si)_2N]_2Ge(OEt)NHNC[CO(OMe)]_2$ (**22**) as a yellow oil (1.85 g, 61%) (Found: C, 38.0, H, 8.5; N, 9.7. $C_{19}H_{48}GeN_4O_5Si_4$ requires C, 38.2; H, 8.1; N, 9.4%). N.m.r.: ^1H ($CDCl_3$), δ 0.25 (36 H, s, $SiMe_3$), 1.24 (3 H, t, *J* 7, OCH_2CH_3), 3.75 and 3.81 [2 × 3 H, 2 × s, 2 × $CO(OCH_3)$], 3.88 (2 H, q, *J* 7 Hz, OCH_2CH_3), 11.09 (1 H, s, NH); ^{13}C ($CDCl_3$), δ 5.1 (q, $SiMe_3$), 18.5 (q, OCH_2CH_3), 51.4 [q, $CO(OCH_3)$], 59.4 (t, OCH_2CH_3), 123.4 (s, C=N–), 162.7 and 164.0 [2 × s, $CO(OCH_3)$]. I.r.: ν at 3 210 (NH), 1 730, 1 680 cm^{-1} (C=O and C=N–). Mass spectrum: no M^+, highest *m/e* 395, $[C_{12}H_{37}{}^{74}GeN_2Si_2]^+$.

In a similar reaction, between $(MeO)COC(N_2)CO(OMe)$ (0.86 g, 5.4 mmol) and $Ge[N(SiMe_3)_2]_2$ (2.15 g, 5.5 mmol), after stirring for 3 h at room temperature a solution of ethanol in benzene (10%, 3.1 cm^3, 5.4 mmol EtOH) was added. After stirring for 1 h, the volatiles were removed. Chromatography on silica (diethyl ether–light petroleum, 1:15 v/v changing to 1:3 v/v) yielded $[(Me_3Si)_2N]_2Ge(OEt)NHNC[CO(OMe)]_2$ (**22**) (2.63 g, 83%), identical (i.r., t.l.c.) to the previously isolated sample. When, in an otherwise identical reaction, the initial mixture was stirred for 21 h before quenching with ethanol, the isolated yield of (**22**) was 75%, again identical (i.r., t.l.c.) to previous samples. When the adduct (**22**) (1.3 g, 2.2 mmol) was stirred for 3 d in anhydrous ethanol (25 cm^3) no further reaction occurred, and it was recovered unchanged.

In a similar reaction, between $(MeO)COC(N_2)CO(OMe)$ (1.25 g, 7.9 mmol) and $Ge[N(SiMe_3)_2]_2$ (3.10 g, 7.9 mmol), after stirring for 3 h at room temperature, a solution of $HC(N_2)COPh$ (1.15 g, 7.9 mmol) in benzene (10 cm^3) was added. After stirring for a further 1 h, the volatile products were removed, and the residue chromatographed on silica (diethyl ether–light petroleum, initially 1:20 v/v, increasing gradually to 1:3 v/v), to yield, in addition to unchanged $HC(N_2)COPh$ (390 mg, 2.7 mmol), the colourless product (**23**) (1.51 g, 42%), m.p. 139—140 °C, after recrystallisation from hexane (Found: C, 42.7; H, 6.9; N, 12.0. $C_{25}H_{48}GeN_6O_5Si_4$ requires C, 43.0; H, 6.9; N, 12.1%). N.m.r.: ^1H ($CDCl_3$), δ 0.32 (36 H, s, $SiMe_3$), 3.72 [3 H, s, $CO(OCH_3)$], 3.82 [3 H, s, $CO(OCH_3)$], 7.48 (5 H, m, Ph), 12.25 (1 H, s, NH); ^{13}C ($CDCl_3$), δ 5.4 ($SiMe_3$), 51.5 and 51.6 [2 × $CO(OCH_3)$], 62.3 ($\overset{-}{C}-\overset{+}{N}\equiv N$), 122.9, 127.0, 128.7, 131.6, and 137.8 (aromatic and C=N–), 162.6 and 163.9 [2 × $CO(OCH_3)$], 190.9 (*C*OPh). I.r.: ν at 3 220 (NH), 2 080 ($C=N_2$), 1 720, 1 685, and 1 615 (C=O and C=N–). Mass spectrum: $[M - N_2]^+$ at *m/e* 670 (for ^{74}Ge), accurate mass 670.1871, $[C_{25}H_{48}{}^{74}GeN_4O_5Si_4]^+$ requires 670.1912.

MNDO Calculations.—These were undertaken using the MOPAC system,[11,26] implemented on a VAX 11/785 computer. No assumptions were made about molecular geometries, and all independent structural parameters were simultaneously optimised. The atomic parameters used were those stored internally in the MOPAC system.

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