Reaction of an Enolisable Diazo-compound with the Electron-rich Stannylene $Sn[N(SiMe_3)_2]_2$: Preparation of a Novel Spiro[1,3,4,2-oxadiazastannine-6, 4'-pyrazole] Derivative

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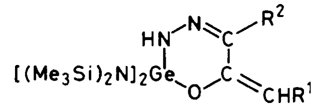
The reaction of the enolisable diazo-compound $MeCOC(N_2)CO(OEt)$ with the electron-rich stannylene $Sn[N(SiMe_3)_2]_2$ yields a 2:1 adduct {in contrast to its reaction with the analogous germylene $Ge[N(SiMe_3)_2]_2$, which gives a 1:1 adduct}, shown spectroscopically to be diethyl 3'-acetyl-2,2-di[bis(trimethylsilyl)amino]-3,6,3', 5'-tetrahydrospiro[1,3,4,2-oxadiazastannine-6,4'-pyrazole]-5,3'-dicarboxylate.

It has recently been shown[1] that the electron-rich germylene $Ge[N(SiMe_3)_2]_2$ reacts with diazo-compounds to give a wide range of products: in all of these, both nitrogen atoms of the diazo-compound are retained, and their formation can in every case be rationalised in terms of a heterodiene intermediate $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(X)Y$. When the diazo-compound is of the type $R^1CH_2COC(N_2)R^2$ [R^1, R^2 = H, CO(OEt); H, $SO_2C_6H_4Me$-*p*; H, COPh, or $-CMe_2CH_2C(O)-$], containing an enolisable group, the isolated products are the cyclic compounds (**1**) containing the novel 1,3,4,2-oxadiazagermine ring system. The compositions of (**1a**)—(**1d**) were deduced from analytical and mass spectrometric data, their constitutions from i.r. and ^1H, ^{13}C, and ^{15}N n.m.r. spectroscopy, and their structure confirmed, in the case of (**1a**), by *X*-ray crystallography.[2]

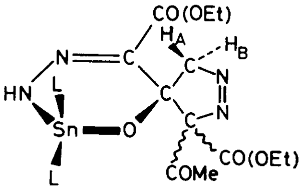
In each of (**1a**)—(**1d**) there is an exocyclic methylene function, but even in the presence of a large excess of the 1,3-dipole $R^1CH_2COC(N_2)R^2$, no further reaction was apparent.

In this paper we describe an analogous reaction between the stannylene $Sn[N(SiMe_3)_2]_2$ and $MeCOC(N_2)CO(OEt)$.

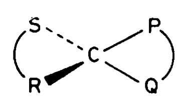


(**1**)

a; R^1 = H, R^2 = CO(OEt)
b; R^1 = H, R^2 = $SO_2C_6H_4Me$-*p*
c; R^1 = H, R^2 = COPh
d; R^1, R^2 = $-CMe_2CH_2C(O)-$



(**2**) L = $N(SiMe_3)_2$



(**I**)

Results and Discussion

Reaction of the electron-rich stannylene $Sn[N(SiMe_3)_2]_2$ with $MeCOC(N_2)CO(OEt)$ in benzene at room temperature, instead of yielding a 1:1 adduct similar to (**1a**), gave in low yield a 2:1 adduct, formulated (without implications of conformation) as the spiro compound (**2**).

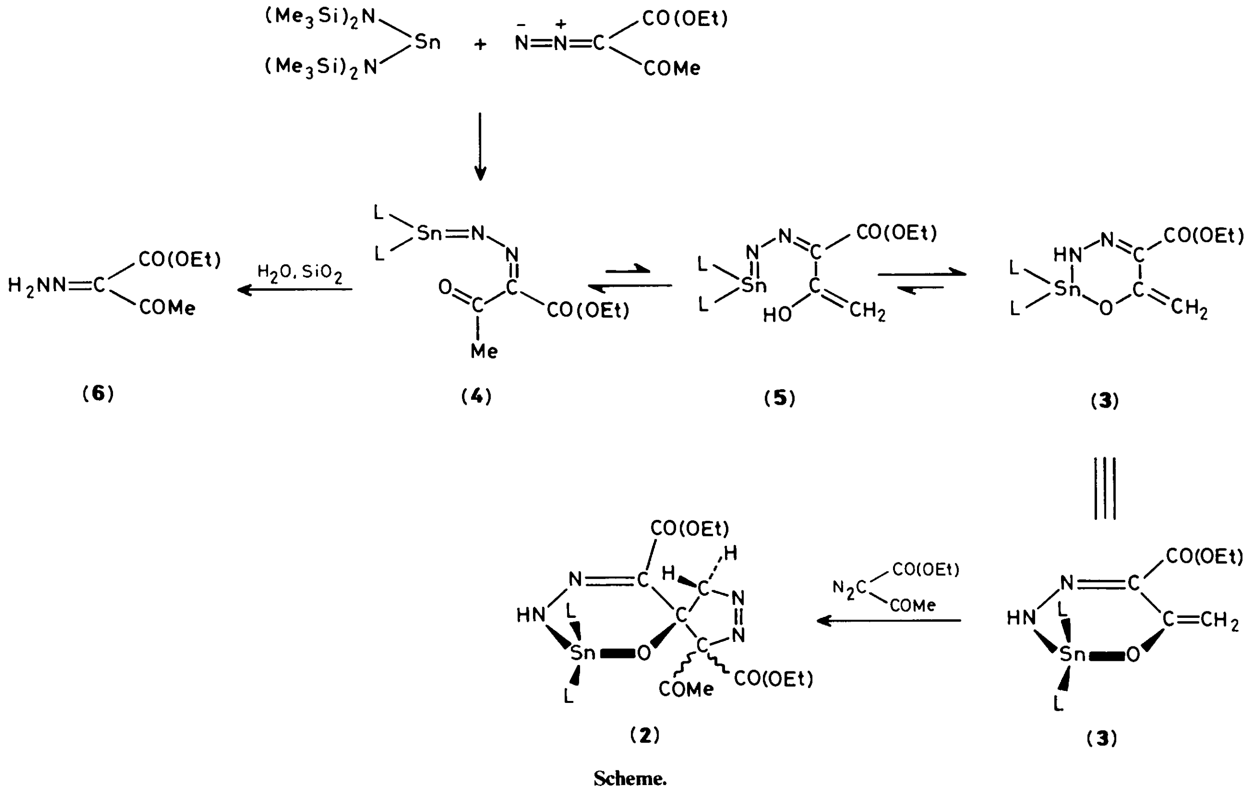
We envisage the formation of (**2**) as arising from further reaction of the diazo-compound with an initially formed 1:1 adduct (**3**) as shown in the Scheme. It has not proved possible to isolate the intermediate (**3**), analogous to the germanium species (**1a**) observed previously.[1]

The composition of (**2**) was established as a 2:1 adduct, in which all the nitrogen atoms from the diazo-compound were again retained, by microanalysis and by the observation of a strong molecular ion cluster in the mass spectrum. The ^1H and ^{13}C n.m.r. spectral data are fully in accord with a spiro structure of general type (**I**) in which the central carbon is bonded to four different groups so that for each ring the two faces of the ring are distinguishable.

The ^1H n.m.r. spectrum (see Experimental section) shows, in addition to two different ethyl groups and the methyl group of an acetyl substituent, two $SiMe_3$ signals, corresponding to the two $N(SiMe_3)_2$ substituents which are in different environments regardless of the conformation adopted by the six-membered ring, and an AB system having *J*(AB) 11.6 Hz, corresponding to the CH_2 group in the five-membered ring where the hydrogens are in different environments: there is also a single N–H resonance.

In the ^{13}C n.m.r. spectrum of (**2**) there are 14 resonances, of which five represent CH_3 groups, and three represent CH_2 groups; CH groups are absent. The five CH_3 signals comprise resonances due to the two distinct $N(SiMe_3)_2$ groups, the two distinct ethyl groups, and the CH_3 of the acetyl, while the three CH_2 signals arise from the ethyls and the methylene of the five-membered ring. The ^{13}C chemical shifts of the CH_2 groups are all very similar, in the range 60—63 p.p.m., and each represents a CH_2 adjacent to an electronegative atom: for this reason, the isomeric formulation (**2a**) is ruled out; the CH_2 of the five-membered ring would be expected to resonate at much lower frequency in this isomer.

Irradiation at the CH_AH_B proton frequency, while observing the DEPT ^{13}C spectrum, caused enhancement of the ^{13}C



Scheme.

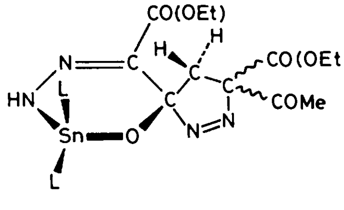
resonance at δ 61.0, which is thus assigned to the CH_2 in the five-membered ring.

Of the quaternary resonances, those at δ 177.1, 160.91, and 160.89 can be assigned respectively to the carbonyls in the acetyl substituent and in the two –CO(OEt) groups; that at 154.0 is assigned to the C=N– carbon. The remaining quaternary resonances, at δ 83.4 and 141.9 are assigned to the two saturated quaternary carbons. The quaternary carbon in the five-membered ring is directly bonded to three electronegative substituents [MeCO, (EtO)CO–, and –N=N–], each containing an α-double bond and thus the resonance at δ 141.9 is assigned to this carbon, and the resonance at δ 83.4 to the spiro carbon: this last chemical shift again allows the isomeric structure (**2a**) to be ruled out, since in (**2a**) the spiro carbon would be expected* to have δ > 100.

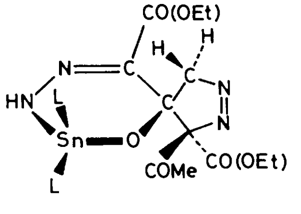
The formulation of the structure of (**2**), rather than as (**2a**) is consistent with the predictions of frontier orbital theory.[3] The 1:1 adduct (**3**) bears an electron-donating heteroatom as one substituent at the C=C double bond, whereas the diazo-compound $MeCOC(N_2)CO(OEt)$ bears two electron-withdrawing substituents at the carbon of the $C=\overset{+}{N}=\overset{-}{N}$ group: hence the 1,3-dipolar cycloaddition to form (**2**) is a dipole-LU controlled reaction[3] with the regioselectivity as deduced from the n.m.r. data.

When an attempt was made to record the ^{15}N n.m.r. spectrum at natural abundance, using a 400-mg sample of (**2**), the NH resonance was detected in a DEPT experiment, but the other resonances could not be detected even after *ca.* 5 × 10^5 scans.

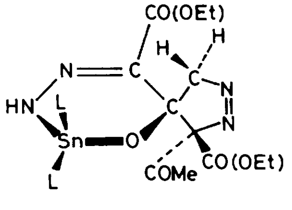
Under high resolution all the CH_2 resonances in the ^1H spectrum were found to be doubled, consistent with the presence, in approximately equal abundance, of the two diastereoisomeric forms (**2b**) and (**2c**).



(**2a**) L = $N(SiMe_3)_2$



(**2b**)



(**2c**)

In the chromatography of the reaction mixture from $Sn[N(SiMe_3)_2]_2$ and $MeCOC(N_2)CO(OEt)$, there was a fast-moving component which was however so labile that it could not be isolated. It decomposed continuously during chromatography giving rise to the hydrazone (**6**) (*cf.* Scheme). It was previously observed[1] in the reactions of $Ge[N(SiMe_3)_2]_2$ with non-enolisable diazo-compounds $N_2C(X)Y$ [X = COPh, Y = CO(OEt)] that the initially formed germyleneazine $[(Me_3Si)_2N]_2Ge=N-N=C(X)Y$ yielded in certain instances the hydrazone $H_2NN=C(X)Y$ either upon hydrolysis or during chromatography. The formation here of (**6**) may be similarly ascribed to hydrolysis during chromatography of the

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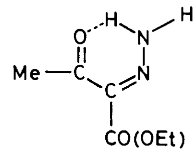
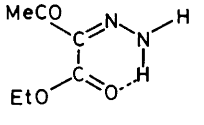
* The α substituent –N=N– effects a high frequency shift of some 25 p.p.m. (L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' John Wiley and Sons, New York, 1972).



(6a)



(6b)

equilibrium mixture composed of the stannyleneazine (**4**) and the stannacycle (**3**) [MNDO calculations suggest that the equilibrium proportion of the enol (**5**) is very low: *cf.* also ref. 1]. If the fast-moving labile product is identified with a 1:1 adduct of $\mathrm{Sn[N(SiMe_3)_2]_2}$ and $\mathrm{MeCOC(N_2)CO(OEt)}$, then its lability is readily explained provided that subsequent ring formation to give (**3**) is reversible [unlike ring formation to give the germanium analogue (**1a**)[1]]. Only when the second mole of $\mathrm{MeCOC(N_2)CO(OEt)}$ reacts to give (**2**), by formation of new C–C and C–N bonds, is the ring-opening equilibrium (**3**) $\rightleftharpoons$ (**4**) suppressed. Such lability of (**3**) would give rise to a distribution of (**6**) throughout the chromatography column, as observed.

Attempts were made to increase the isolated yield of (**2**), both by altering the initial stoicheiometric ratio of $\mathrm{MeCOC(N_2)CO(OEt)}$ to $\mathrm{Sn[N(SiMe_3)_2]_2}$ from the 2:1 which is ideal for formation of (**2**) to values such as 1:2 or 2:3, and by increasing the reaction time to as much as 50 h. The best yield of (**2**) attained in this way, using a 2:3 ratio during 50 h, was 13%: no attempt was made in this experiment to isolate and purify (**6**).

The hydrazone $\mathrm{H_2NN{=}C(COMe)CO(OEt)}$ (**6**), like the hydrazone $\mathrm{H_2NN{=}C(COPh)CO(OEt)}$ previously isolated[1] from the reaction of $\mathrm{Ge[N(SiMe_3)_2]_2}$ with $\mathrm{PhCOC(N_2)CO(OEt)}$, appears from its n.m.r. spectra to exist in two isomeric forms in solution. Their principal difference (see Experimental section) occurs in the ^{13}C chemical shift of the acetyl $\mathrm{CH_3}$ carbon and the two forms are plausibly regarded as *E* and *Z* isomers (**6a**) and (**6b**) respectively, involving different patterns of intramolecular hydrogen bonding in $\mathrm{CDCl_3}$ solution. It is possible that in the solid state the hydrogen bonding is inter- rather than intra-molecular.

Experimental

All solvents were dried and purified by conventional methods. Light petroleum used had b.p. 49—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) n.m.r. spectra were recorded using the Brüker WH-360 and WP-200SY spectrometers of the S.E.R.C. Regional N.M.R. Service, Edinburgh; the relaxation agent $\mathrm{[Cr(acac)_3]}$ (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 using a Brüker WP-80 instrument. ^{15}N Chemical shifts are referred to external nitromethane.

Literature methods[4,5] were employed for the preparation of $\mathrm{MeCOC(N_2)CO(OEt)}$ and $\mathrm{Sn[N(SiMe_3)_2]_2}$.

Preparation of Compound (**2**).—A solution of the diazo-compound $\mathrm{MeCOC(N_2)CO(OEt)}$[4] (5.7 g, 36.5 mmol) in benzene (20 $\mathrm{cm^3}$) was added to a stirred solution of the stannylene $\mathrm{Sn[N(SiMe_3)_2]_2}$[5] (8.0 g, 18.2 mmol) in benzene (50 $\mathrm{cm^3}$) at room temperature under nitrogen. The mixture was stirred for 1 h. The solvent was then evaporated and the residue chromatographed on silica. Elution with diethyl ether–light petroleum (initially 1:3 v/v, increasing gradually to pure diethyl ether) gave first the crude hydrazone $\mathrm{H_2NN{=}C(COMe)CO(OEt)}$ (620 mg) which was rechromatographed and then recrystallised twice from toluene to yield the pure product (**6**) (351 mg, 12%), m.p. 83—87 °C (lit.,[6] 85—93 °C) as an almost colourless solid (Found: C, 45.5; H, 6.2; N, 17.7. $\mathrm{C_6H_{10}N_2O_3}$ requires C, 45.6; H, 6.4; N, 17.7%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 1.36 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 2.33 (3 H, s, $\mathrm{CH_3CO}$), 4.31 (2 H, q, *J* 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), and 9.0 (2 H, s, br, NH); ^{13}C ($\mathrm{CDCl_3}$), δ 14.1 (q, $\mathrm{OCH_2}C\mathrm{H_3}$, major isomer), 14.3 (q, $\mathrm{OCH_2}C\mathrm{H_3}$, minor isomer), 26.5 (q, $C\mathrm{H_3CO}$, major isomer), 30.8 (q, $C\mathrm{H_3CO}$, minor isomer), 60.9 (t, $\mathrm{O}C\mathrm{H_2CH_3}$), 129.9 (s, C=N–), 162.9 [s, –*C*O(OEt)], and 195.2 (s, $\mathrm{CH_3}C\mathrm{O}$). I.r.: ν at 3 310, 3 160, and 3 120 (NH); 1 650 $\mathrm{cm^{-1}}$ (CO). Mass spectrum: $[M + \mathrm{H}]^+$, M^+, and $[M - \mathrm{H}]^+$ at *m/z* 159, 158, and 157; accurate mass found 158.0692, $\mathrm{[C_6H_{10}N_2O_3]^+}$ requires 158.0691. This was followed by the unchanged diazo-compound (2.9 g, 51% recovery) and then by a viscous red oil (1.51 g) containing a mixture of (**2**) and (**6**) (see text) which, having identical R_f values, were inseparable by further chromatography. Repeated fractional crystallisation from hexane yielded (**2**) (421 mg, 6%) as a beige solid, m.p. 157—158 °C after recrystallisation from hexane (Found: C, 38.5; H, 7.0; N, 11.2. $\mathrm{C_{24}H_{52}N_6O_6Si_4Sn}$ requires C, 38.4; H, 7.0; N, 11.2%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 0.18 (18 H, s) and 0.20 (18 H, s) ($\mathrm{SiMe_3}$), 1.30 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 1.34 (3 H, t, *J* 7, $\mathrm{OCH_2C}H_3$), 2.23 (3 H, s, $\mathrm{CH_3CO}$), 3.85 (1 H, d, *J* 11.6, $\mathrm{CH_AH_B}$), 3.97 (1 H, d, *J* 11.6, $\mathrm{CH_AH_B}$), 4.35 (2 H, q, *J* 7, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.45 (2 H, q, *J* 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), and 6.52 (1 H, s, br, NH); ^{13}C ($\mathrm{CDCl_3}$), δ 4.8 (q) and 5.2 (q) (2 × $\mathrm{SiMe_3}$), 13.7 (q) and 14.1 (q) (2 × $\mathrm{OCH_2}C\mathrm{H_3}$), 21.8 (q, $C\mathrm{H_3CO}$), 60.5 (t), 61.0 (t), and 62.6 (t) (3 × $\mathrm{CH_2}$), 83.4 (s, spiro C), 141.9 {s, *C*(COMe)[CO(OEt)]}, 154.0 (s, C=N), 160.89 (s), and 160.91 (s) [2 × –*C*O(OEt)], and 177.1 (s, $\mathrm{CH_3}C\mathrm{O}$); ^{15}N($\mathrm{CDCl_3}$), δ −187.0 (nuclear Overhauser enhancement negative, NH). I.r.: ν at 3 370 (NH); 1 730, 1 715 $\mathrm{cm^{-1}}$ (CO). Mass spectrum: M^+ at *m/z* 752 (for ^{120}Sn); other peaks at $[M - 14]^+$, $[M - 73]^+$, and at *m/z* 591 and 576.

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References

1 C. Glidewell, D. Lloyd, and K. W. Lumbard, preceding paper.

2 C. Glidewell, M. B. Hursthouse, D. Lloyd, K. W. Lumard, and R. L. Short, *J. Chem. Res.*, 1986, (*S*) 434; (*M*) 3501.

3 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' John Wiley and Sons, New York, 1976.

4 A. Liedhegener and M. Regitz, *Chem. Ber.*, 1966, **99**, 3128.

5 M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.

6 H. J. Bestmann and H. Kolm, *Chem. Ber.*, 1963, **96**, 1948.

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