Notes

The Unidentified Product of the Reaction of Dimethyl 2-Diazomalonate with Bis[bis(trimethylsilyl)amino]germylene

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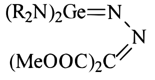
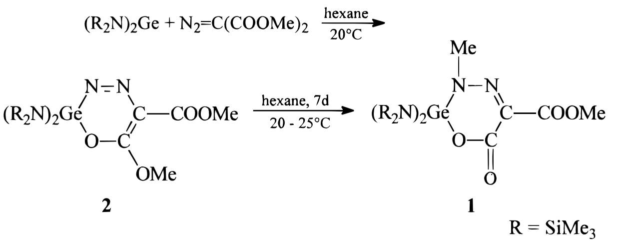
Summary: The thus far unidentified second product of the title reaction has now been characterized as methyl 3-methyl-6-oxo-2,2-bis[bis(trimethylsilyl)amino]-2H-3,6-dihydro-1,3,4,2-oxadiazagermanine-5-carboxylate.

Recently we reported about products of the reactions of dimethyl 2-diazomalonate and 2-diazoindanedione with germylenes and stannylenes.[1] At that time one of the products obtained in the title reaction and formed upon storing the 6-methoxy-2*H*-1,3,4,2-oxadiazagermanine-5-carboxylate derivative **2** at ambient temperature in a solution of hexane could not be characterized. This reaction had been studied earlier by Glidewell et al.,[2,3] and these workers had ascribed the *cisoid* structure **D** to this product. After many unsuccessful attempts to isolate this product in a pure state to enable its characterization, crystals were finally obtained which were suitable for an X-ray structure determination. It required more than the usual effort to select these crystals from the chemically uniform product. The X-ray diffraction study showed that the product **1** is an isomer of **2**, resulting from a methanide transfer from the methoxy group in position 6 to the ring nitrogen atom in position 3. The NMR data obtained for **1** are compared in Table 1 to the (incomplete) set of signals reported by Glidewell et al.[2,3] for the assumed cisoid isomer of the germaimine derivative **D** and the starting isomer **2** (labeling is in accordance with ref 1, with the exception of **1**, which is different from compound **1** in ref 1).



D



(1)

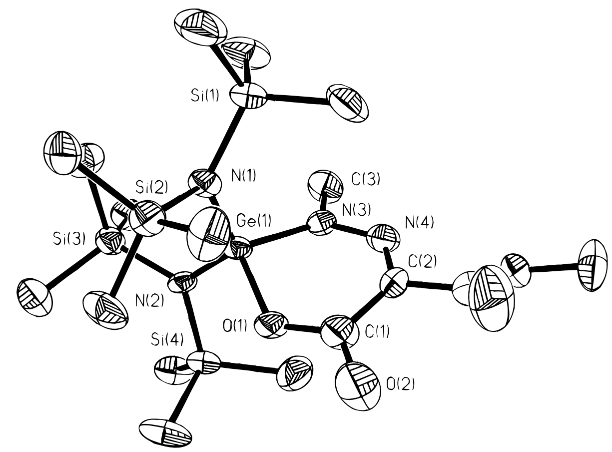


Figure 1. Crystal structure of **1** with anisotropic displacement parameters depicting 50% probability.

Table 1. ^{1}H and ^{13}C NMR Data for **D**,[2,3] **1**, and **2**[1]

	δ(^{1}H)			δ(^{13}C)					
D	0.19	3.02	3.48	4.9	43.4	52.1	123.0		
1	0.19	2.98	3.48	4.83	42.82	51.83	128.82	154.06	163.84
2	0.23	3.32	3.71	4.84	51.10	52.39	119.86	157.78	165.82

It is not clear if the transfer of the methyl substituent from the methoxy group in compound **2** to the nitrogen atom in position 3 of **1** takes place in an intra- or intermolecular process. Therefore, it is not possible to formulate an obvious mechanism for the isomerization **2** → **1**. The irreversibility of the process, however, is the result of the formation of the thermodynamically favored C=N and C=O double bonds which arise from the concerted intramolecular bond rearrangement accompanying the transfer of the methyl group.

As a consequence of the rearrangements that take place in this and several other germanium-containing molecules,[1] it appears problematic to make conclusions about the bond systems in educts from the structure of definite reaction products in such cases.

Crystal Structure

The crystal structure of **1** is shown in Figure 1. Selected bond lengths and angles are given in Table 2.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

[1] Ossig, G.; Meller, A.; Freitag, S.; Müller, O.; Gornitzka, H.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 408.

[2] Glidewell, C.; Lloyd, D.; Lumbard, K. W.; McKechnie, J. S. *Tetrahedron Lett.* **1987**, *28*, 343.

[3] Glidewell, C.; Lloyd, D.; Lumbard, K. W. *J. Chem. Soc., Dalton Trans.* **1987**, 501.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Ge(1)−N(1)	1.795(6)	Ge(1)−N(2)	1.799(6)
Ge(1)−O(1)	1.807(5)	Ge(1)−N(3)	1.855(6)
O(1)−C(1)	1.317(10)	C(1)−O(2)	1.213(9)
C(1)−C(2)	1.490(11)	C(2)−N(4)	1.309(10)
N(4)−N(3)	1.313(8)		
N(1)−Ge(1)−N(2)	121.8(3)	N(1)−Ge(1)−O(1)	105.4(2)
N(2)−Ge(1)−O(1)	106.6(2)	N(1)−Ge(1)−N(3)	112.6(3)
N(2)−Ge(1)−N(3)	110.6(3)	O(1)−Ge(1)−N(3)	96.2(2)
C(1)−O(1)−Ge(1)	124.9(5)	O(2)−C(1)−O(1)	119.6(8)
O(1)−C(1)−C(2)	118.2(7)	N(4)−C(2)−C(1)	127.5(7)
C(2)−N(4)−N(3)	123.2(7)	N(4)−N(3)−Ge(1)	123.2(5)

In comparison to structure **2**, the distance between C(1) and C(2) shows an elongation from 1.391 Å in **2** to 1.490 Å in **1** and the distance between N(3) and N(4) is elongated from 1.265 Å in **2** to 1.313 Å in **1**, while the distance between C(2) and N(4) is shortened from 1.392 Å in **2** to 1.309 Å in **1**. The distance between C(1) and O(2) is shortened from 1.315 Å in **2** to 1.213 Å in **1**. This indicates that the double bonds are now located between N(4) and C(2) and between C(1) and O(2), while the bonds C(1)−C(2) and N(3)−N(4) are now single bonds. All the other bonds are similar in **1** and **2**, with the exception of the bond Ge(1)−O(1), which is 1.863 Å in **2** and 1.807 Å in **1**.

Experimental Section

The reactions and manipulations were performed under an inert atmosphere of dry nitrogen in dry hexane saturated with nitrogen. The melting point was determined in a sealed capillary. Elemental analyses were performed by Mikroanalytisches Labor Beller, Göttingen, Germany. NMR spectra were recorded on a Bruker MSL-400 instrument. The solvent used was C_6D_6, with TMS as external standard. The mass spectrum was obtained on a Varian CH5 instrument.

A 1.81 g (2.28 mmol) portion of compound **2** (recrystallized twice from *n*-hexane at −25 °C) was dissolved in 60 mL of hexane to give a red solution. This solution was agitated slowly with a magnetic stirrer for 7 days at ambient temperature. By very slow evaporation of hexane at 20 °C, 1.13 g (2.05 mmol, 63%) of **1** separated as colorless needles, mp 131 °C, from the red mother liquor. ^{1}H NMR (C_6D_6): δ 0.19 (s, 36H, $SiMe_3$), 2.98 (s, 3H, N−Me), 3.48 (s, 3H, O−Me). ^{13}C NMR (C_6D_6): δ_C 4.83 ($SiMe_3$), 42.82 (N−Me), 51.83 (O−Me), 128.82 (C=N), 154.06, 163.84 (2 × C=O). ^{29}Si NMR (C_6D_6): δ_{Si} 8.36. IR (Nujol): 1741, 1691 (2 × C=O), 1654 (C=N) cm^{-1}. MS (EI; 70 eV): *m*/*z* (relative intensity) 552 (12) [M$^+$], 537 (66) [M − Me$^+$], 261(100). Anal. Calcd for $C_{17}H_{42}GeN_4O_4Si_4$ (551.48): C, 37.03; H, 7.68; N, 10.16. Found: C, 36.94; H, 6.85; N, 10.18.

X-ray Structure Determination of 1. Data were collected at −80 °C on a Stoe-Siemens-AED diffractometer with monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A semiempirical absorption correction was applied. The structure was solved by direct methods.[4] All non-hydrogen atoms were refined anisotropically.[5] For the hydrogen atoms the riding model was used. The structure was refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (0.0587P)^2 + 7.0708P$ with $P = (F_o^2 + 2F_c^2)/3$. The R values are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$. The group bond to C2 is disordered. Two positions are refined with distance restraints and restraints for the anisotropic displacement parameters.

Crystal data for **1**: $C_{17}H_{42}GeN_4O_4Si_4$, $M_r = 551.50$, monoclinic, space group $P2_1/n$, $a = 8.556(2)$ Å, $b = 16.494(4)$ Å, $c = 20.429(6)$ Å, $\beta = 91.19(2)°$, $V = 2882(1)$ Å^3, $Z = 4$, ρ(calcd) = 1.271 Mg/m^3, $\mu = 1.256$ mm^{-1}, $F(000) = 1168$, crystal size (mm) 0.1 × 0.1 × 0.6, 4743 reflections collected, 3750 unique reflections ($R_{int} = 0.2018$), 3746 reflections and 56 restraints used for the refinement of 314 parameters, $S = 1.018$, $R1 = 0.062$ for $I > 2\sigma(I)$, $wR2 = 0.158$ for all data, maximum/minimum residual density +0.682/−0.608 e Å^{-3}. The high value for R_{int} is caused by weak data.

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Supporting Information Available: For **1**, tables of data collection parameters, displacement parameters, non-hydrogen atomic coordinates, bond distances and angles, and hydrogen coordinates and *U* values and a figure giving the ^{13}C NMR spectrum (6 pages). Ordering information is given on any current masthead page.

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[4] Sheldrick, G. M. SHELXS-90. *Acta Crystallogr.* **1990**, *A46*, 467.

[5] Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.