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Journal of Organometallic Chemistry 604 (2000) 211-213



Reaction of trimethylsilyl azide with a digermene in the presence of water: 1,2-addition of hydrazoic acid[☆]

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Received 28 January 2000

Abstract

The sterically congested tetrakis(2,4,6-triisopropylphenyl)digermene (4) does not react with trimethylsilyl azide. However, in the presence of water hydrazoic acid is formed which adds to the Ge–Ge double bond of 4 in a 1,2-fashion to furnish the corresponding azidodigermane in high yield. The N1–N2a and N2a–N3a bond lengths of 114.6 and 113.9 pm, respectively, are nearly equal and differ markedly from those in organic azides. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Germanium; Digermene; Hydrazoic acid; 1,2-Addition

1. Introduction

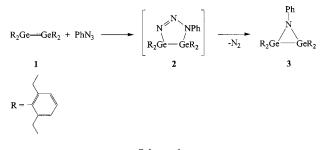
Digermenes, molecules containing a Ge–Ge double bond, are now a well established class of compounds and their chemistry has been described in several review articles [2]. One of their interesting modes of reaction is the formal [2+1] cycloaddition in which digermiranes — three-membered ring compounds made up of two germanium atoms and a heteroatom — are usually formed smoothly. Compounds of this type are formed with difficulty by other routes.

However, these cycloaddition reactions depend strongly on the spatial requirements of the substituents R at the two germanium atoms. For example, the reactions of digermenes bearing substituents of moderate size with diazomethane or aryl azides presumably proceed through a primary [2+3] cycloaddition followed by elimination of nitrogen to furnish digermiranes or azadigermiridenes (Scheme 1).

Accordingly, the 2,6-diethylphenyl-substituted compound 1 [3] reacts smoothly with diazomethane or phenyl azide to furnish the corresponding three-membered ring compounds in high yields [4,5]. On the other hand, the more highly shielded digermene 4 [6–8] reacts with diazomethane to afford the digermirane in merely 6% yield [5]. Instead, the main products of its reactions with diazomethane derivatives are the azadigermiridenes resulting in these cases from a direct [2 + 1] cycloaddition reaction [8]. We have addressed the question as to whether azides react in the same manner as the diazomethane derivatives and now report on the reactions of **4** with trimethylsilyl azide in the absence and presence of water.

2. Results and discussion

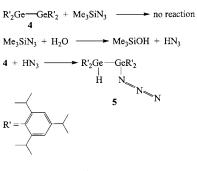
Prolonged heating of the digermene **4** with an excess of trimethylsilyl azide in an anhydrous solvent such as toluene or DME does not result in any noticeable reaction. Presumably the steric shielding of **4** prevents



Scheme 1.

[☆] See Ref. [1].

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Scheme 2.

the primary [2+3] cycloaddition to give a product of the type **2** which would furnish the three-membered ring product of type **3** by subsequent elimination of nitrogen. In contrast, when the reaction is carried out in THF containing water a 1,2-additon of hydrazoic acid occurs even at room temperature to furnish the azidodigermane **5** (Scheme 2).

Product 5 is obtained in quantitative yield as colorless, thermally stable crystals by the careful addition of water. In analogy to the corresponding reactions in organic chemistry [9], the first step of the reaction sequence should comprise the liberation of HN_3 which then undergoes a smooth 1,2-addition to the Ge–Ge double bond of 4 to form the azidodigermane 5.

An X-ray crystallographic analysis of **5** reveals that, in spite of the presence of the voluminous aryl groups, the Ge–Ge bond length is not appreciably longer than the normal single bond value of 244 pm. The azide group is disordered over two positions with occupancy factors of 0.7 and 0.3; the predominant form is shown here (Fig. 1, Table 1). Worthy of note are the almost identical N–N bond lengths in distinction to organic azides where the N–N bond lengths are markedly different [10]. These N–N bond lengths as well as the

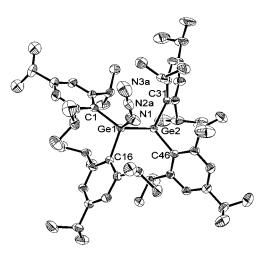


Fig. 1. Molecular structure of **5** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability.

Table 1 Selected bond lengths (pm) and angles (°) for 5

246.37(4)	Ge(1)-N(1)	189.9(3)
198.6(3)	Ge(1)-C(16)	199.7(2)
198.9(2)	Ge(2)-C(46)	198.6(3)
114.6(4)	N(2a)-N(3a)	113.9(5)
123.73(7)	C(16)-Ge(1)-Ge(2)	106.52(7)
119.55(7)	C(46)-Ge(2)-Ge(1)	112.69(7
104.92(10)	N(2a)-N(1)-Ge(1)	132.4(3)
177.6(5)		
	198.6(3) 198.9(2) 114.6(4) 123.73(7) 119.55(7) 104.92(10)	198.6(3) Ge(1)-C(16) 198.9(2) Ge(2)-C(46) 114.6(4) N(2a)-N(3a) 123.73(7) C(16)-Ge(1)-Ge(2) 119.55(7) C(46)-Ge(2)-Ge(1) 104.92(10) N(2a)-N(1)-Ge(1)

almost linear arrangement of the nitrogen atoms are reminiscent of the situation in sterically overcrowded silyl azides which exhibit similar structural parameters [11]. A recently prepared germanium(II) azide exhibits values very close to those reported here with the exception of a considerably larger Ge–N separation [12].

Although the 1,2-additions of water and alcohols to the Ge=Ge bond have been known for some time [2c], with HN_3 we have for the first time realized the corresponding addition reaction with a protic nitrogen compound.

3. Experimental

3.1. General procedure

All reactions were carried out under an atmosphere of argon. The ¹H- and ¹³C-NMR spectra were obtained on a Bruker AM 300 spectrometer using C_6D_6 as solvent. The IR spectrum was recorded on a Bruker Vector 22 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

3.2. 1-Azido-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)digermane (5)

A solution of trimethylsilyl azide (0.132 g, 1.15 mmol) and water (0.020 g, 1.1 mmol) in THF (8 ml) was added dropwise to a solution of **4** (0.200 g, 0.21 mmol) in THF (7 ml) with stirring at room temperature. The stirring was continued until after ca. 4 h the pale yellow solution was completely decolorized. The mixture was concentrated to a volume of 6 ml. Cooling to -30° C furnished 0.20 g (95% yield) colorless crystals of **5**; m.p. 219–221°C. ¹H-NMR (300 MHz, 298 K): δ 0.32–0.40 (m, 8H), 0.50 (d, 2H, ³J = 6.6 Hz), 0.73 (q, 6H), 1.04–1.30 (m, 36H), 1.37 (d, 6H, ³J = 6.6 Hz), 1.52–1.59 (m, 12H), 1.68 (d, 2H, ³J = 6.6 Hz), 2.60–2.82 (m, 4H), 3.00 (sept, 1H), 3.10–3.50 (m, 6H), 4.00

(sept, 1H), 6.14 (s, 1H, Ge*H*), 6.93 (s, 1H), 6.99 (s, 2H), 7.03 (s, 2H), 7.08 (s, 2H), 7.22 (s, 1H) ppm. ¹³C-NMR (75 MHz, 298 K): δ 22.68, 23.01, 23.30, 23.69, 23.85, 23.97, 24.01, 24.41, 24.61, 24.83, 25.75, 26.11, 26.97, 27.46, 34.45, 34.68, 35.03, 36.04, 38.12, 122.22, 122.81, 123.03, 123.46, 123.64, 123.76, 133.98, 134.44, 136.64, 137.29, 150.33, 151.17, 152.86, 153.38, 154.14, 154.42, 155.07, 155.32, 155.45 ppm. IR (Nujol, cm⁻¹) ν (NN) 2108(s), 2030(s). C₆₀H₉₃Ge₂N₃ (1001.55) Anal. Calc.: C, 71.95; H 9.36; N, 4.20. Found: C, 71.69; H, 9.51; N. 4.09%.

3.3. X-ray structure analysis of 5

Empirical formula: $C_{60}H_{93}Ge_2N_3$ (1001.55), crystal dimensions $0.75 \times 0.52 \times 0.25$ mm³, Stoe IPDS, temperature 193(2) K, monoclinic, space group $P2_1/n$, a =1525.84(5), b = 2068.76(10),c = 1846.11(6)pm, $\beta = 91.711(4)^{\circ}$, $V = 5824.8(4) \times 10^{6} \text{ pm}^{3}$, $D_{\text{calc}} = 1.142 \text{ g}$ cm⁻³, Z = 4, $2\theta_{\text{max}} = 52^{\circ}$; collected reflections 43 242; unique reflections 10 723; observed $[I > 2\sigma(I)]$ 7586; μ (Mo–K_{α}) = 1.063 mm⁻¹. The structure was solved by direct phase determination and refined by full-matrix least squares against F^2 with the SHELXL-97 program system [13]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. $R_1 = 0.0353$, wR_2 (all data) = 0.0840. GOF on $F^2 = 0.900$. The N₃ groups are disordered, occupying two positions with the occupancy factors of 0.7 and 0.3 (see text) (Section 4).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139 209. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Acknowledgements

Financial support of our work from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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