

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

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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 azidodigermene 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.

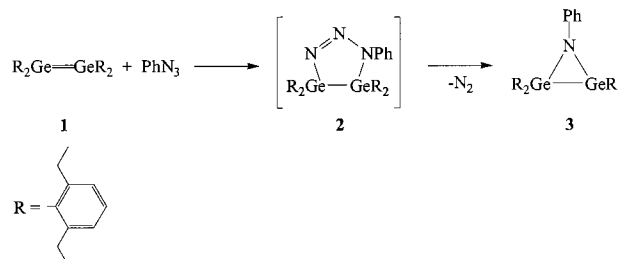
However, these cycloaddition reactions depend strongly on the spatial requirements of the substituents R at the two germanium atoms. For example, the reactions of digermenes bearing substituents of moderate size with diazomethane or aryl azides presumably proceed through a primary [2 + 3] cycloaddition followed by elimination of nitrogen to furnish digermiranes or azadigermiranes (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 azadigermiranes 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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(sept, 1H), 6.14 (s, 1H, GeH), 6.93 (s, 1H), 6.99 (s, 2H), 7.03 (s, 2H), 7.08 (s, 2H), 7.22 (s, 1H) ppm. ^{13}C -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}) $\nu(\text{NN})$ 2108(s), 2030(s). $\text{C}_{60}\text{H}_{93}\text{Ge}_2\text{N}_3$ (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: $\text{C}_{60}\text{H}_{93}\text{Ge}_2\text{N}_3$ (1001.55), crystal dimensions $0.75 \times 0.52 \times 0.25 \text{ mm}^3$, 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; $\mu(\text{Mo-K}\alpha) = 1.063 \text{ mm}^{-1}$. 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 N_3 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>).

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