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Acetylene-Linked Bis(germaethenes): The First Molecules with Conjugated Germanium−Carbon Double Bonds[1]

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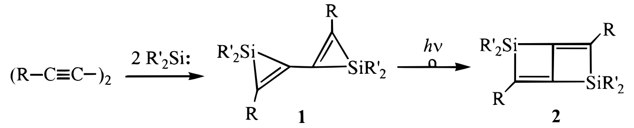
*Summary: In solution, the digermene $Ar_2Ge{=}GeAr_2$ (Ar = 2-tBu-4,5,6-Me_3C_6H) partly dissociates into two molecules of the germylene Ar_2Ge:. The reaction of this digermene with some 1,3-diynes $(RC{\equiv}C-)_2$ leads to the formation of the acetylene-linked bis(germaethenes) $Ar_2Ge{=}C(R)C{\equiv}C(R)C{=}GeAr_2$ (R = n-C_4H_9 (**6a**), C_6H_5 (**6b**)). The conjugation between the two Ge═C units is reflected by the positions of the UV/vis absorptions at longest wavelengths of 518 (**6a**) and 595 (**6b**) nm. An X-ray structure analysis of **6a** reveals a nearly linear C_4 skeleton and short Ge═C bond lengths of 1.819(2) Å.*

Since the discovery of thermally stable germaethenes (germenes) in 1987, the structures of four representatives have been unambiguously elucidated.[2−5] Common features of these compounds are the short Ge−C double bond lengths of between 1.77 and 1.84 Å and the shielding of the two participating atoms by bulky substituents that effectively prevents further reactions of the multiple-bond system.[6]

We recently investigated the reactions of some 1,3-diynes $R'C{\equiv}CC{\equiv}CR'$ with photolytically generated silylenes and found that the product pattern obtained depends strongly on the nature of the substituents R and R′.[7,8] When R is an alkyl group, the isolable bis(silirene) **1** is formed initially but undergoes rearrangement to the bicyclohexadiene derivative **2** upon longer photolysis (Scheme 1). We then addressed the question as to whether a change from silicon to germanium would lead to different products and now report on the observed unusual mode of reactivity.

Scheme 1



As the germanium component we chose the digermene **3**,[9] which partially dissociates in solution into the germylene molecules **4**.[10] The reaction of **4** with dodeca-5,7-diyne at room temperature resulted in the immediate formation of a red solution from which dark red crystals were isolated. The analytical and spectral data of this compound are indicative of a 2:1 adduct of the germylene and the diyne. The intense color and extreme air sensitivity of the compound clearly show that it is not a germanium analogue of the colorless silicon compounds **1** and **2**. The UV/vis absorption at longest wavelength of 518 nm is bathochromically shifted by about 100 nm in comparison to those of the yellow or pale orange germaethenes[2−5] and is thus rather suggestive of the molecule **6a**[11] with conjugated Ge−C double bonds. Inadequate shielding of these double bonds then would be responsible for the increased reactivity to atmospheric oxygen (Scheme 2).

An X-ray crystallographic analysis[12] (Figure 1) not only confirmed the proposed constitution of **6a** but also revealed some interesting features. The molecules of **6a** have a C_2 symmetry axis which passes through the central C−C triple bond and an almost linear C_4 skeleton with $CC{\equiv}C$ angles of 178.1(4)° each. The Ge−C

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[11] Dodeca-5,7-diyne (0.165 g, 1 mmol) was added at room temperature to a suspension of **3** (0.354 g, 0.42 mmol) in *n*-hexane (40 mL). The mixture was stirred for 5 days at room temperature, excess **3** was filtered off, and the red solution was kept at −20 °C to deposit dark red crystals of **6a**: yield 0.096 g, 23%; mp 160 °C dec. ^1H NMR (C_6D_6): δ 0.72 (m, 6 H), 0.89 (m, 4 H), 1.21 (m, 4 H), 1.41 (s, 18 H), 1.45 (s, 18 H), 1.72 (m, 4 H), 2.06 (s, 6 H), 2.09 (s, 6 H), 2.16 (s, 6 H), 2.24 (s, 6 H), 3.08 (s, 6 H), 3.26 (s, 6 H), 7.20 (s, 4 H). ^{13}C NMR (C_6D_6): δ 14.26, 16.70, 16.79, 21.18, 21.28, 22.87, 22.99, 23.99, 25.19, 25.78, 32.41, 32.85, 32.91, 35.40, 36.78, 111.34, 123.66, 133.21, 133.51, 136.77, 137.19, 138.49, 139.36, 142.40, 151.88, 152.36. UV/vis (toluene): λ_{max} 518 nm. Because of the sensitivity of **6a** in solution the ϵ value could not be determined. Anal. Calcd for $C_{64}H_{94}Ge_2$: C, 76.21; H, 9.39. Found: C, 75.79; H, 9.22.

[12] Crystal data for **6a**·C_6H_{14}: $C_{70}H_{108}Ge_2$, fw 1094.74, monoclinic, a = 26.886(1) Å, b = 9.8551(3) Å, c = 25.168(1) Å, β = 101.254(5)°, V = 6540.4(4) Å^3, space group $C2/c$, Mo Kα radiation, λ = 0.71073 Å, Z = 4, crystal dimensions 0.90 × 0.27 × 0.18 mm^3, μ = 0.956 mm^{-1}, Stoe IPDS area detector, T = 193(2) K, 24 350 reflections collected, 5982 unique reflections, 4509 observed reflections ($I > 2\sigma(I)$). The structure was solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL program system.[14] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. R1($I > 2\sigma(I)$) = 0.0350, wR2 = 0.0850, R1(all data) = 0.0519, wR2 = 0.0905 for 325 parameters, and GOF (F^2) = 0.931. The data have been deposited with the Cambridge Crystallographic Data Centre (reference no. CCDC-141 238).

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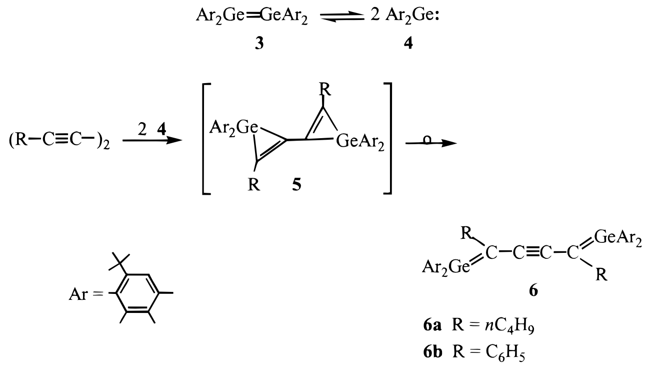
Scheme 2



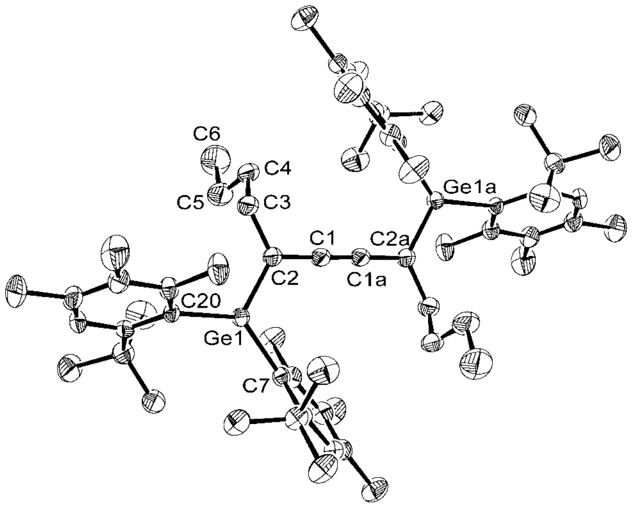


Figure 1. Molecule of **6a** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−C(2) = 1.819(2), C(1)−C(2) = 1.407(3), C(1)−C(1a) = 1.200(5), Ge(1)−C(7) = 1.991(2), Ge(1)−C(20) = 1.991(2); C(2)−C(1)−C(1a) = 178.1(4), C(7)−Ge(1)−C(20) = 130.74(9), C(7)−Ge(1)−C(2) = 113.70(9), C(20)−Ge(1)−C(2) = 115.49(9).

double-bond lengths of 1.819(2) Å are in the same range as those of the simple germenes. Although the C−C triple-bond length of 1.200(5) Å is typical for such systems, the formal C(1)−C(2) single-bond lengths of 1.407(3) Å between the sp- and the sp^2-hybridized carbon atoms are remarkably short and can be considered as further evidence in support of the conjugation between the Ge−C double bonds. The angles between the respective germanium atom and the *ipso*-C atoms of the aryl substituents of 130.74(9)° are considerably opened and are even slightly larger than the corresponding angles in digermene **3** (128.0°).[9]

The mechanism of formation of **6a** is not known with certainty. In analogy to the reactions of silylenes,[8] one possible sequence could involve the formation of the bis(germirene) **5**, which would then undergo rearrangement via the cleavage and new formation of two bonds to afford the isolated product.

To define the scope of the formation of the bis(germaethenes), we have also carried out the reaction of 1,4-diphenylbuta-1,3-diyne with germylene **4** and, after 4 days at room temperature, obtained a dark blue-violet solution from which a violet powder was isolated in 96% yield. Although we have not yet been able to grow a single crystal of this compound, its analytical and spectral data, especially its color together with the UV/vis absorption at longest wavelength at 595 nm, strongly suggest that it is the diaryl analogue **6b** of the dialkyl compound **6a**.[13] Other buta-1,3-diynes appear to react in a similar manner with the germylene **4**. However, we have not yet been able to isolate any pure compounds.

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

Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) A solution of 1,4-diphenylbuta-1,3-diyne (66 mg, 0.33 mmol) in *n*-hexane (10 mL) was added dropwise to a suspension of **3** (0.278 g, 0.33 mmol) in *n*-hexane (20 mL). The mixture was stirred for 4 days at room temperature. From the dark blue solution a violet powder of **6b** was isolated by filtration: yield 0.330 g, 96%; mp 130−135 °C dec. ^1H NMR (C_6D_6): δ 1.36 (s, 18 H), 1.38 (s, 18 H), 1.78 (s, 6 H), 1.89 (s, 6 H), 2.03 (s, 6 H), 2.10 (s, 6 H), 2.64 (s, 6 H), 3.30 (s, 6 H), 6.74 (m, 4 H), 6.85 (m, 4 H), 7.24 (m, 6 H); ^{13}C NMR (C_6D_6): δ 16.30, 16.41, 21.18, 21.40, 24.15, 32.88, 32.94, 36.54, 36.65, 107.73, 123.20, 125.87, 134.17, 134.53, 137.46, 137.74, 138.14, 140.28, 141.76, 142.53, 143.86, 151.75, 152.28, UV/vis (toluene): λ_{max} 595 nm, minor absorptions at 750 and 850 nm. Anal. Calcd for $C_{68}H_{86}Ge_2$: C, 77.89; H, 8.27. Found: C, 77.70; H, 8.08.

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