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Preliminary communication

THE ISOLATION AND X-RAY CRYSTAL STRUCTURE OF $\Delta^{1,7}$ 2,2,6,6-TETRAMETHYL-4-THIA-8,8-DIMETHYL-8-GERMABICYCLO[5.1.0]OCTENE; THE FIRST REPRESENTATIVE OF GERMIRENES

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Summary

The first representative of germirenes, $\Delta^{1,7}$ 2,2,6,6-tetramethyl-4-thia-8,8-dimethyl-8-germabicyclo[5.1.0]octene has been isolated and its X-ray crystal and molecular structure have been determined.

The silirenes and the germirenes are long sought classes of highly strained heterocycles of great interest with respect to the challenge of their synthesis and possible aromaticity [1]. The first reports dealing with the synthesis of silirenes [2] and their X-ray structure [3] were published in the 1970's. A recent report [4] demonstrated the successful synthesis of the first two germirenes, $\Delta^{1,7}$ 2,2,6,6-tetramethyl-4-thia-8,8-dimethyl- and $\Delta^{1,7}$ 2,2,6,6-tetramethyl-4-thia-8,8-diethyl-8-germabicyclo[5.1.0]octenes, (I and II), respectively, by the reaction of 7,7-dimethyl(diethyl)-1,2,3,4-tetraphenyl-7-germanorbornadiene (III) with an excess of 3,3,6,6-tetramethyl-1-thiacycloheptine-4 (IV) (benzene, 70°C)**. Germirene I has been obtained as a mixture with acetylene IV (1/1), and germirene II as a sample with ca. 95% purity. Attempts to isolate them with the help of preparative GLC failed because of the decomposition of both [4].

We report here the isolation of germirene I in a pure crystal form and the complete crystal and molecular structural analysis of the first germirene.

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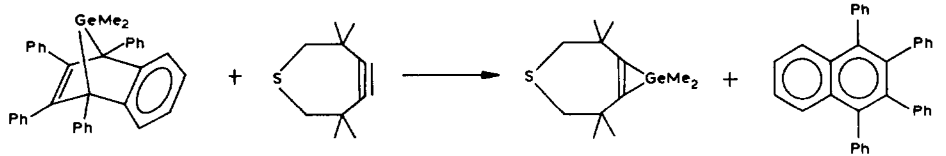
**On the contrary, the reaction of cyclic acetylene IV with $GeCl_2$·dioxane produces $\Delta^{1,7}$ 2,2,6,6-tetramethyl-4-thia-8,8,9,9-tetrachloro-8,9-digermabicyclo[5.2.0]nonene (V) [5].



(III) (IV) (I)

According to ^{1}H NMR spectral control the stoichiometric reaction of III and IV (benzene, 70°C, [III] = [IV] = 0.56 mol·l^{-1}) takes 1.5 h and results quantitatively in a single Ge product. Its spectral data are identical to the data given in ref. 4 for germirene I. These results, and especially the absence of by-products, excludes participation of free dimethylgermilene in the reaction.

We have obtained germirene I in a pure crystal form by sublimation in vacuum, m.p. 40—42°C. Compound I is very sensitive to air. The "zone melting" technique [6] was used to grow the colourless single crystal of germirene I from the melt in a vacuum sealed glass capillary ($\phi \sim 0.5$ mm). Unit cell parameters and all unique diffraction maxima were measured at −120°C with an automatic four-circle Syntex P2$_1$ diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan., $2\theta \leqslant 50°$). Of the 2750 reflections examined 2094 were chosen as having $I > 2\sigma(I)$. The structure was refined by the full-matrix least-squares technique first in isotropic and then in anisotropic approximation. All H atoms were found in the difference Fourier map and included in refinement with fixed thermal parameters B_{iso} 4.0 Å. The final R-value is equal to 0.039 (R_w = 0.059) (according to 1777 reflections with $|F| > 10\sigma$). All calculations were carried out with an Eclipse S/200 computer using the INEXTL programs [7].

Crystals I are monoclinic, at −120°C a 12.363(7), b 9.233(5), c 12.118(7) Å, β 90.24(4)°, V 1383 Å^3, d(calc) 1.30 g/cm^{-3}, Z = 4, space group $P2_1/c$. The molecular structure of I and the most important bond lengths and angles are given in Fig. 1.

The angles Ge—C(2)—C(1) and Ge—C(1)—C(2) are 70.3(4) and 69.2(4)°, respectively, the length of the double C(1)—C(2) bond is 1.331(9) Å, which happens to be close to the standard C(sp^2)=C(sp^2) bond length (1.337 Å) and results from complex intramolecular interactions in the strained molecule of I. The bond lengths Ge—C(7) (1.954(7) Å) and Ge—C(8) (1.931(7) Å) are shorter than those in Me_4Ge (1.98 Å [8]).

The bond angles C(2)—Ge—C(1) and C(7)—Ge—C(8) are 40.5(3) and 113.9(3)°, respectively (other angles are close to 120—121°). These values point to the significant deviation of the Ge atom configuration from the tetrahedral one.

An essential feature of the structure of I is that the bond lengths Ge—C(1) (1.929(6) Å) and Ge—C(2) (1.915(6) Å) are noticeably shorter, (4%), than the standard Ge—C(sp^2) bond (1.96—2.01 Å [9]). It is interesting that the difference between bond lengths C(sp^3)—C(sp^2) in cyclopropene and the acyclic ones has not been found [10]. Therefore both the decrease in the Ge—C(1) (Ge—C(2)) bond lengths (which is possible due to the increase of the bond order) and the rehybridization at the Ge atom can be considered as an argument in favour of the aromaticity of germirene. It should be noted, that Si—C(sp^2) bond lengths in silirene (VI) (1.839 Å and, especially 1.800 Å

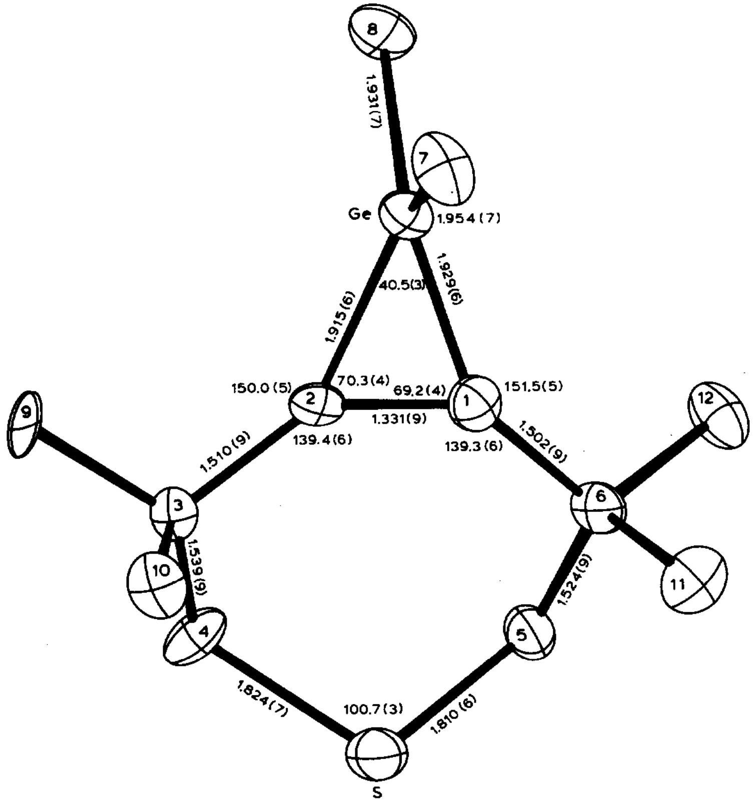
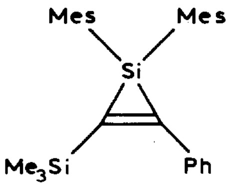
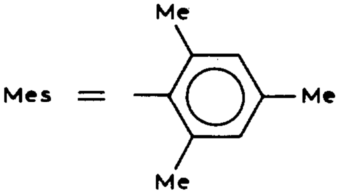


Fig. 1. Molecular structure of I with the most important bond lengths and angles.



(VI)



[3]) are shorter than the acyclic lengths (1.94 Å [11]). This is possibly the result of some aromaticity of the silirene.

Atoms C(1), C(2), C(3) and C(6) lie in one plane (with an accuracy of 0.009(6) Å). The Ge atom is displaced from this plane by 0.1107(6) Å. The structural characteristics of the 7 member 4-thiacycloheptene ring are similar to (V) [5].

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