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Preliminary communication

THE FIRST EXAMPLE OF [2+2] CYCLOADDITION OF Me_4Ge_2 TO MULTIPLE BONDS. THE SYNTHESIS OF $\Delta^{1,7}$-2,2,6,6,8,8,9,9-OCTAMETHYL-4-THIA-8,9-DIGERMABICYCLO[5.2.0]NONENE

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Summary

The first example of a [2+2] cycloaddition reaction of Me_4Ge_2 with acetylene is described. A new derivative of 1,2-digermacyclobutene, namely $\Delta^{1,7}$-2,2,6,6,-8,8,9,9-octamethyl-4-thia-8,9-digermabicyclo[5.2.0]nonene, is prepared.

It was shown recently that upon melting 7-germanorbornadiene (I) is converted into benzodigermabicyclo[2.2.2]octadiene (II) [1]. Further heating of II up to 170°C results in the extrusion of free Me_4Ge_2, and its formation was confirmed by matrix isolation [1]. Tetramethyldigermene was found to be an active dienophile, which with anthracene [1,2] and dimethylsilacyclopentadiene formed [2+4] cycloadducts. Attempts to carry out [2+2] cycloaddition of Me_4Ge_2 to diphenylacetylene and bis(trimethylgermyl)acetylene failed [2].

Here we report the first successful [2+2] cycloaddition of Me_4Ge_2 to cyclic acetylene (III), leading to the formation of the stable 1,2-digermacyclobutene: $\Delta^{1,7}$-2,2,6,6,8,8,9,9-octamethyl-4-thia-8,9-digermabicyclo[5.2.0]nonene (IV).

A mixture of I and III (molar ratio 2/1) was heated (170°C, 8 h) in an evacuated sealed glass tube. The 1,2-digermacyclobutene product (IV), m.p. 80—82°C was purified by sublimation in vacuum (yield 50%). ^1H NMR (in C_6D_6, δ, ppm): 0.62 (12H, Ge—CH_3), 1.22 (12H, C—CH_3), 2.52 (4H, CH_2); ^{13}C NMR (in C_6D_6, δ, ppm): 0.5 (Ge—CH_3), 30.9 (C—CH_3), 47.3 (CH_2), 47.8 (*C*—CH_3), 170.1 (C=C); mass spectrum (70 eV) *m/e*: 374 M^+, 359 $[M - CH_3]^+$, 318 $[M - C_4H_8]^+$, 303 $[M - C_5H_{11}]^+$, 257 $[M - GeMe_3]^+$, 206 $Me_4Ge_2^+$ (base), 119 $GeMe_3^+$.

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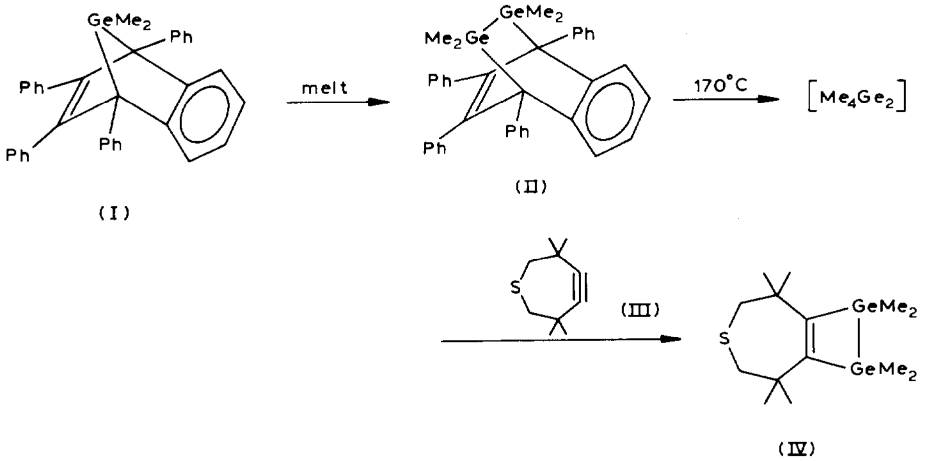
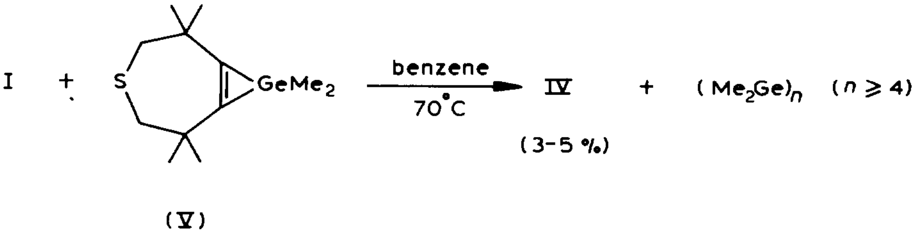


We have also studied alternative routes for the synthesis of IV: (i) by insertion of Me_2Ge: in the C—Ge bond of germacyclopropene (V) [3], and (ii) by methylation of tetrachloro-1,2-digermacyclobutene (VI) [4]. Route (i): the reaction of germacyclopropene (V) with 7-germanorbornadiene (I) used as a source of Me_2Ge: (benzene, 70°C, [I] = [V] = 0.56 mol l^{-1}, 1.5 h) results in the formation of IV in 3—5% yield. The main pathway of the reaction is apparently the formation of $(Me_2Ge)_n$, ($n \geqslant 4$).



Route (ii): the interaction of tetrachloro-1,2-digermacyclobutene (VI) with methylating agents (Me_4NBMe_4, MeMgI, 20°C) leads to extrusion of the germanium moiety with recovery of the starting acetylene (III).

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