Cycloaddition of dialkylgermoles: synthesis and structures of 2,2,3,3-tetracyano-1,4,5,6-tetraphenyl-7-germanorborn-5-enes

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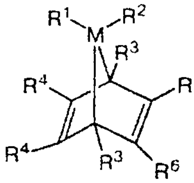
Cycloaddition reactions of 1,1-dicyclopropyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (3) with dehydrobenzene, tetracyanoethylene, cyclooctyne, or dimethyl acetylenedicarboxylate as well as of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (4) and 2,3,4,5-tetraphenyl-1-germacyclopentadiene (5) with tetracyanoethylene or cyclooctyne were studied. Diels—Alder adducts of germoles 3, 4, and 5 with tetracyanoethylene were prepared. The structures of these adducts were established by X-ray diffraction analysis and their thermal and photochemical stabilities were examined.

Key words: germoles, 7-germanorbornenes, Diels—Alder reaction, germylene precursors, structure, thermolysis, photolysis.

7-Heteronorbornadienes (**1**) (M = Si or Ge) serve as convenient sources of carbene analogs, *viz.*, silylenes and germylenes, and were studied in sufficient detail (see, for example, the reviews[1—3] and references therein). However, structurally similar 7-heteronorbornenes (**2**), which can also serve as potential sources of carbene analogs, remain poorly studied. The major publications devoted to 7-heteronorbornenes are concerned only with 7-silanorbornenes.[1] Of the other 7-heterenorbornenes, only one representative of 7-germanorbornenes[4] and one representative of 7-stannanorbornenes[5] were reported, but data on their structures and reactivities are lacking.



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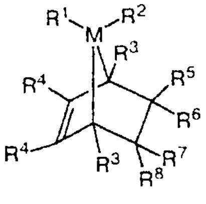

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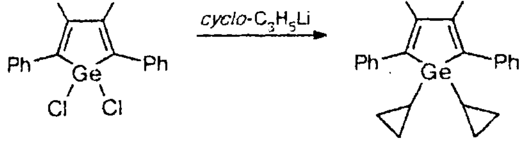
A general procedure for the preparation of heterocycles **1** and **2** involves the Diels—Alder reaction of the corresponding 1-heterocyclopenta-2,4-diene (metallole) with an active dienophile. An alternative procedure for the synthesis of 7-heteronorbornenes **2** is based on cycloaddition of carbene analogs to cyclohexa-1,3-dienes. However, the latter procedure was used only in the synthesis of 7-silanorbornenes.[6,7]

The aim of this work was to prepare new representatives of 7-germanorbornadienes and 7-germanorbornenes, to study their structures, and to examine the possibility of their use as precursors of germylenes generated either thermally or photochemically.

Results and Discussion

We studied cycloaddition of 1,1-dicyclopropyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**3**) to dehydrobenzene, tetracyanoethylene (TCE), cyclooctyne, and dimethyl acetylenecarboxylate as well as of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**4**) and 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**5**) to TCE and cyclooctyne.

Germole **3** was prepared by the reaction of 1,1-dichlorogermole **6** with cyclopropyllithium in 71% yield. Attempts to prepare germole **3** by the reaction of **6** with cyclopropylmagnesium bromide failed, due, apparently, to the lower reactivity of the latter.



6 **3**

Germole **3** is the first metallole whose heteroatom is bound to the cycloalkyl substituents. Formal Diels—

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Alder adducts of this germole with alkynes, *viz.*, 7,7-dicyclopropyl-1,2,3,4-tetraphenyl-7-germanorborna-2,5-dienes, are of particular interest. These adducts can serve as convenient precursors of cycloalkylgermylenes, which have not yet been described. Besides, by analogy with cyclopropylsilylenes,[8,9] intramolecular rearrangements would be expected to occur for dicyclopropylgermylene.

However, it appeared that germole **3** reacted neither with dehydrobenzene (it was generated *in situ* by the reaction of *o*-bromofluorobenzene with magnesium; THF; 10 °C) nor with stable cycloalkyne, *viz.*, cyclooctyne (the reaction mixture was kept at 80 °C for 10 h). We also failed to perform the reactions of cyclooctyne with sterically less shielded germoles **4** and **5**. Thus, the corresponding cycloadducts did not form in noticeable amounts (NMR control) upon keeping of equimolar mixtures of the reagents in PhH at room temperature (~20 °C) or at high temperature (60 °C) for several days. It should be noted that Diels—Alder adducts of germoles or stannoles with cyclooctyne remain unknown. Attempts to synthesize 7-germanorbornadiene by the reaction of 2,3,4,5,6,7,8,9-octaphenylspirogermole with cyclooctyne at 50 °C gave rise only to its thermolysis products.[10] However, 2,5-dipheny-, 3,4-diphenyl-, and 2,3,4,5-tetraphenylsiloles readily formed [4+2]-adducts with cyclooctyne.[11]

To elucidate the reasons for the difference in the reactivity of siloles and germoles with respect to alkynes, we carried out *ab initio* LanL2DZ quantum-chemical calculations for unsubstituted cyclopentadiene, silole, germole, stannole, and their Diels—Alder adducts with acetylene. The results of calculations given in Table 1 demonstrate that no substantial changes in the energies of the frontier orbitals of the diene systems, which are involved in cycloaddition at the triple bond of acetylene, are observed on going from cyclopentadiene to its heteroanalogs, *viz.*, silole, germole, and stannole. The exothermic effect of cycloaddition weakly increases in the series cyclopentadiene < silole < germole < stannole (Table 1). Therefore, the fact that germoles do not react with cyclooctyne cannot be explained either within the framework of the theory of frontier orbitals or by differences in the thermodynamic stability of reaction products.

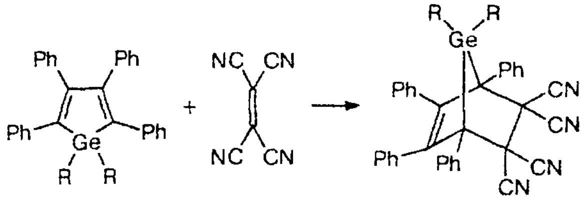
We failed to prepare a cycloadduct of germole **3** with a highly active dienophile, *viz.*, dimethyl acetylenedicarboxylate. Evidently, the corresponding 7-germanorbornadiene appears to be labile and it decomposes in the course of the reaction (like a cycloadduct of dimethyl acetylenedicarboxylate with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,5-diene (**4**)[12]).

Table 1. Energies of the highest occupied MO and the lowest unoccupied MO (E/eV) of cyclopentadiene and metalloles and the thermal effects of the Diels—Alder reactions of *cyclo*-EC_4H_6 (E = C, Si, Ge, or Sn) with acetylene (ΔE/kcal mol^{-1}) calculated by the *ab initio* LanL2DZ method

Parameter	C	Si	Ge	Sn
E(LUMO)	3.28	2.19	2.17	2.09
E(HOMO)	−8.43	−8.82	−8.83	−8.79
ΔE^a	−15.9	−24.0	−27.6	−31.8

[a] The MP2/LanL2DZ//HF/LanL2DZ calculation.

It is known[1] that 7-heteronorbornenes are more stable than 7-heteronorbornadienes. Hence, we chose TCE as a dienophile, which was expected to form a stable cycloadduct with germole **3**. Actually, germole **3** reacted with TCE (a 10% molar excess of TCE, PhH, 20 °C) to give 7-germanorbornene **7a** in quantitative yield. Germoles **4** and **5** reacted with TCE analogously.



3: R = *cyclo*-C_3H_5
4: R = Me
5: R = H

7a: R = *cyclo*-C_3H_5
7b: R = Me
7c: R = H

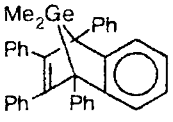
All 7-germanorbornenes **7a—c** were isolated in the crystalline state and were characterized by ^1H NMR spectroscopy and mass spectrometry, and their structures were established by X-ray diffraction analysis (see below). It should be noted that compound **7c** is the first representative of 7-heteronorbornenes which does not contain exocylcic substituents at the heteroatom (Ge).

The reversibility is a characteristic feature of the reaction of germole **5** with TCE.

$$\mathbf{5} + \mathrm{TCE} \rightleftharpoons \mathbf{7c}$$

The equilibrium is completely shifted to cycloadduct **7c** only in the presence of a 50% molar excess of TCE. Dissolution of crystalline 7-germanorbornene **7c** in benzene was accompanied by its rapid retrodecomposition to form an equilibrium mixture containing **7c** and the starting germole **5** in a ratio of 1 : 1 (^1H NMR spectral data). An increase in the temperature to 50 °C led to a further shift of the equilibrium to the starting reagents (the ratio **7c** : **5** = 1 : 3). Note that Diels—Alder retroreactions, which proceed generally upon thermolysis, are known only for adducts of 1,1-dialkyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-dienes with maleic anhydride.[13] Analogous conversions for 7-germanorbornenes have not yet been reported.

According to the data of X-ray diffraction study of 7-germanorbornenes **7a,b**, the exocyclic Ge—C bonds (Ge(1)—C(7) are 1.926(3) and 1.930(8) Å and Ge(1)—C(8) are 1.924(3) and 1.964(9) Å in **7a** and **7b**, respectively; Figs. 1 and 2; Tables 2 and 3) are noticeably shorter than the endocyclic Ge—C bonds (Ge(1)—C(1) are 2.020(3) and 2.023(6) Å and Ge(1)—C(4) are 2.038(3) and 2.016(5) Å in **7a** and **7b**, respectively). An analogous situation was observed in derivatives of 7-silanorbornene,[7,14] 7-silanorbornadiene,[10,11,15,16] and 7-germanorbornadiene,[17] which results, apparently, from electron density delocalization over the E—C endocyclic bond (E = Si or Ge) and the C=C double bond (a σ—π interaction[14,18]). It is noteworthy that the observed Ge—C bond lengths in **7b** are close to the corresponding bond lengths in 7-germanorbornadiene (**8**) (Ge(1)—C(7), 1.948(5) Å; Ge(1)—C(8), 1.938(4) Å; Ge(1)—C(1), 2.022(4) Å; and Ge(1)—C(4), 2.024(4) Å).[17] In unsubstituted 7-germanorbornene **7c** (Fig. 3, Table 4), the endocyclic bonds are equalized (1.999(2) and 1.997(2) Å). It should also be noted that the endocyclic Ge—C bond lengths decrease in the series of compounds **7a** > **7b** > **7c**, whereas the exocyclic R(1)—Ge—R(2) angle (R = *cyclo*-C_3H_5, Me, or H) increases noticeably in the reverse sequence of germoles



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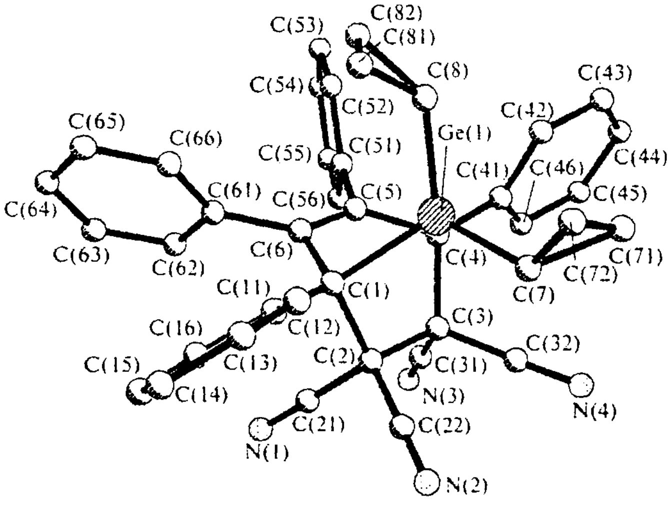


Fig. 1. Structure of compound **7a**.

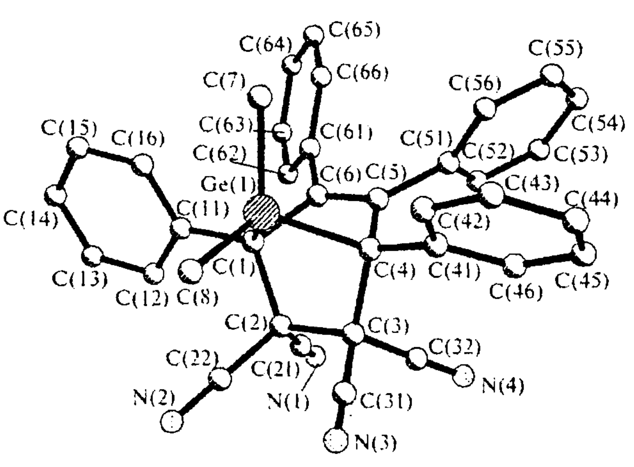


Fig. 2. Structure of compound **7b**.

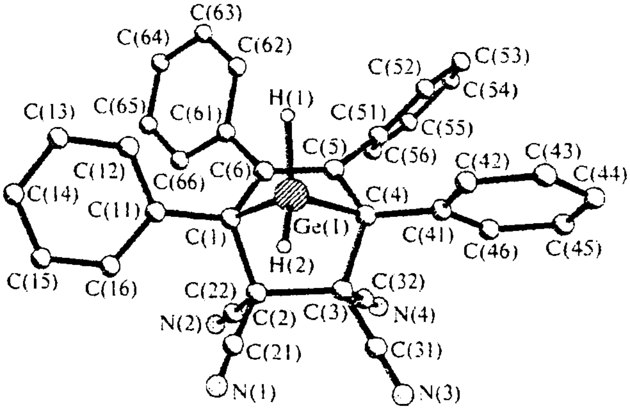


Fig. 3. Structure of compound **7c**.

Table 2. Principal bond lengths (*d*) and bond angles (ω) in compound **7a** · 2 C_6H_6

Bond	*d*/Å	Bond	*d*/Å
Ge(1)—C(8)	1.924(3)	C(2)—C(3)	1.612(5)
Ge(1)—C(7)	1.926(3)	C(3)—C(32)	1.477(4)
Ge(1)—C(1)	2.020(3)	C(3)—C(31)	1.478(4)
Ge(1)—C(4)	2.038(3)	C(3)—C(4)	1.594(4)
N(1)—C(21)	1.130(3)	C(4)—C(41)	1.507(5)
N(2)—C(22)	1.132(4)	C(4)—C(5)	1.532(4)
N(3)—C(31)	1.140(4)	C(5)—C(6)	1.346(4)
N(4)—C(32)	1.150(3)	C(5)—C(51)	1.496(4)
C(1)—C(11)	1.506(5)	C(6)—C(61)	1.486(4)
C(1)—C(6)	1.538(4)	C(7)—C(71)	1.508(5)
C(1)—C(2)	1.603(4)	C(7)—C(72)	1.513(4)
C(2)—C(22)	1.486(4)	C(8)—C(82)	1.498(4)
C(2)—C(21)	1.493(4)	C(8)—C(81)	1.504(5)

Angle	ω/deg	Angle	ω/deg
C(8)—Ge(1)—C(7)	107.34(13)	C(41)—C(4)—Ge(1)	118.3(2)
C(8)—Ge(1)—C(1)	117.52(13)	C(5)—C(4)—Ge(1)	98.6(2)
C(7)—Ge(1)—C(1)	117.57(13)	C(3)—C(4)—Ge(1)	99.5(2)
C(8)—Ge(1)—C(4)	116.80(13)	C(6)—C(5)—C(51)	125.4(3)
C(7)—Ge(1)—C(4)	117.03(13)	C(6)—C(5)—C(4)	113.8(3)
C(1)—Ge(1)—C(4)	78.86(13)	C(51)—C(5)—C(4)	120.8(3)
C(11)—C(1)—C(6)	120.1(3)	C(5)—C(6)—C(61)	125.1(3)
C(11)—C(1)—C(2)	110,8(2)	C(5)—C(6)—C(1)	113.5(3)
C(6)—C(1)—C(2)	104.6(2)	C(61)—C(6)—C(1)	121.4(3)
C(11)—C(1)—Ge(1)	120.5(2)	C(71)—C(7)—C(72)	58.5(2)
C(6)—C(1)—Ge(1)	97.9(2)	C(71)—C(7)—Ge(1)	120.9(2)
C(2)—C(1)—Ge(1)	100.1(2)	C(72)—C(7)—Ge(1)	120.6(2)
C(22)—C(2)—C(21)	105.5(2)	C(82)—C(8)—C(81)	59.7(2)
C(22)—C(2)—C(1)	110.9(2)	C(82)—C(8)—Ge(1)	128.4(2)
C(21)—C(2)—C(1)	109.2(2)	C(81)—C(8)—Ge(1)	123.1(2)
C(22)—C(2)—C(3)	112.1(2)	C(12)—C(11)—C(16)	117.1(3)
C(21)—C(2)—C(3)	110.3(3)	C(12)—C(11)—C(1)	120.8(3)
C(1)—C(2)—C(3)	108.7(2)	C(16)—C(11)—C(1)	122.0(3)
C(32)—C(3)—C(31)	106.1(3)	C(13)—C(12)—C(11)	121.7(3)
C(32)—C(3)—C(4)	109.7(2)	C(12)—C(13)—C(14)	120.6(3)
C(31)—C(3)—C(4)	114.4(2)	C(15)—C(14)—C(13)	118.8(4)
C(32)—C(3)—C(2)	111.1(2)	C(16)—C(15)—C(14)	120.9(3)
C(31)—C(3)—C(2)	109.2(2)	C(15)—C(16)—C(11)	120.8(3)
C(4)—C(3)—C(2)	106.4(2)	N(1)—C(21)—C(2)	179.5(3)
C(41)—C(4)—C(5)	118.2(2)	N(2)—C(22)—C(2)	177.6(3)
C(41)—C(4)—C(3)	113.5(3)	N(3)—C(31)—C(3)	178.2(3)
C(5)—C(4)—C(3)	106.1(2)	N(4)—C(32)—C(3)	178.9(3)

Table 3. Principal bond lengths (*d*) and bond angles (ω) in compound **7b** · C_6H_6

Bond	*d*/Å	Bond	*d*/Å
Ge(1)—C(7)	1.930(8)	C(2)—C(21)	1.492(9)
Ge(1)—C(8)	1.964(9)	C(2)—C(22)	1.472(8)
Ge(1)—C(4)	2.016(5)	C(2)—C(3)	1.621(8)
Ge(1)—C(1)	2.023(6)	C(3)—C(31)	1.462(9)
N(1)—C(21)	1.111(8)	C(3)—C(32)	1.480(8)
N(2)—C(22)	1.139(8)	C(3)—C(4)	1.610(8)
N(3)—C(31)	1.133(8)	C(4)—C(41)	1.518(7)
N(4)—C(32)	1.121(8)	C(4)—C(5)	1.528(8)
C(1)—C(11)	1.515(8)	C(5)—C(6)	1.346(8)
C(1)—C(6)	1.529(8)	C(5)—C(51)	1.506(8)
C(1)—C(2)	1.598(8)	C(6)—C(61)	1.503(8)

Angle	ω/deg	Angle	ω/deg
C(7)—Ge(1)—C(8)	110.5(4)	C(32)—C(3)—C(2)	110.4(5)
C(7)—Ge(1)—C(4)	110.7(3)	C(4)—C(3)—C(2)	107.1(4)
C(8)—Ge(1)—C(4)	120.8(4)	C(41)—C(4)—C(5)	117.5(5)
C(7)—Ge(1)—C(1)	114.5(3)	C(41)—C(4)—C(3)	114.8(4)
C(8)—Ge(1)—C(1)	118.0(4)	C(5)—C(4)—C(3)	105.0(4)
C(4)—Ge(1)—C(1)	79.3(2)	C(41)—C(4)—Ge(1)	118.6(4)
C(11)—C(1)—C(6)	116.7(5	C(5)—C(4)—Ge(1)	96.9(3)
C(11)—C(1)—C(2)	115.2(5)	C(3)—C(4)—Ge(1)	101.3(3)
C(6)—C(1)—C(2)	106.0(4)	C(6)—C(5)—C(51)	123.5(5)
C(11)—C(1)—Ge(1)	118.5(4)	C(6)—C(5)—C(4)	114.1(5)
C(6)—C(1)—Ge(1)	96.3(4)	C(51)—C(5)—C(4)	122.4(5)
C(2)—C(1)—Ge(1)	101.5(4)	C(5)—C(6)—C(61)	125.1(5)
C(21)—C(2)—C(22)	107.8(5)	C(5)—C(6)—C(1)	113.3(5)
C(21)—C(2)—C(1)	110.3(5)	C(61)—C(6)—C(1)	121.3(5)
C(22)—C(2)—C(1)	111.1(5)	C(16)—C(11)—C(12)	116.4(7)
C(21)—C(2)—C(3)	109.7(5)	C(16)—C(11)—C(1)	118.8(6)
C(22)—C(2)—C(3)	110.3(5)	C(12)—C(11)—C(1)	124.8(6)
C(1)—C(2)—C(3)	107.6(4)	N(1)—C(21)—C(2)	177.4(7)
C(31)—C(3)—C(32)	107.1(5)	N(2)—C(22)—C(2)	179.8(6)
C(31)—C(3)—C(4)	109.2(5)	N(3)—C(31)—C(3)	176.7(7)
C(32)—C(3)—C(4)	110.0(5)	N(4)—C(32)—C(3)	178.2(7)
C(31)—C(3)—C(2)	113.0(5)		

Table 4. Principal bond lengths (*d*) and bond angles (ω) in compound **7c** · C_6H_6

Bond	*d*/Å	Bond	*d*/Å
Ge(1)—C(4)	1.997(2)	C(2)—C(22)	1.477(2)
Ge(1)—C(1)	1.999(2)	C(2)—C(21)	1.487(2)
Ge(1)—H(1)	1.428(2)	C(2)—C(3)	1.628(2)
Ge(1)—H(2)	1.445(2)	C(3)—C(31)	1.480(2)
N(1)—C(21)	1.143(2)	C(3)—C(32)	1.481(2)
N(2)—C(22)	1.144(2)	C(3)—C(4)	1.597(2)
N(3)—C(31)	1.136(2)	C(4)—C(41)	1.513(2)
N(4)—C(32)	1.145(2)	C(4)—C(5)	1.534(2)
C(1)—C(11)	1.515(2)	C(5)—C(6)	1.359(2)
C(1)—C(6)	1.538(2)	C(5)—C(51)	1.487(2)
C(1)—C(2)	1.583(2)	C(6)—C(61)	1.484(2)

Angle	ω/deg	Angle	ω/deg
C(4)—Ge(1)—C(1)	79.76(6)	C(41)—C(4)—C(5)	119.64(13)
H(1)—Ge(1)—H(2)	123.3(2)	C(41)—C(4)—C(3)	113.07(12)
C(11)—C(1)—C(2)	115.42(12)	C(5)—C(4)—C(3)	103.85(12)
C(6)—C(1)—C(2)	107.53(11)	C(41)—C(4)—Ge(1)	117.87(11)
C(11)—C(1)—Ge(1)	116.31(10)	C(5)—C(4)—Ge(1)	97.74(9)
C(6)—C(1)—Ge(1)	97.78(9)	C(3)—C(4)—Ge(1)	102.02(9)
C(2)—C(1)—Ge(1)	99.42(9)	C(6)—C(5)—C(51)	125.49(14)
C(22)—C(2)—C(21)	109.91(12)	C(6)—C(5)—C(4)	113.11(13)
C(22)—C(2)—C(1)	110.83(12)	C(51)—C(5)—C(4)	121.16(13)
C(21)—C(2)—C(1)	109.77(12)	C(5)—C(6)—C(61)	125.71(14)
C(22)—C(2)—C(3)	110.91(12)	C(5)—C(6)—C(1)	113.00(13)
C(21)—C(2)—C(3)	108.29(12)	C(61)—C(6)—C(1)	121.18(12)
C(1)—C(2)—C(3)	107.06(11)	C(16)—C(11)—C(1)	123.84(13)
C(31)—C(3)—C(32)	106.40(13)	C(12)—C(11)—C(1)	117.76(13)
C(31)—C(3)—C(4)	112.10(13)	N(1)—C(21)—C(2)	175.8(2)
C(32)—C(3)—C(4)	110.97(13)	N(2)—C(22)—C(2)	176.6(2)
C(31)—C(3)—C(2)	111.80(12)	N(3)—C(31)—C(3)	178.6(2)
C(32)—C(3)—C(2)	108.74(13)	N(4)—C(32)—C(3)	178.8(2)
C(4)—C(3)—C(2)	106.84(11)	C(11)—C(1)—C(6)	117.61(12)

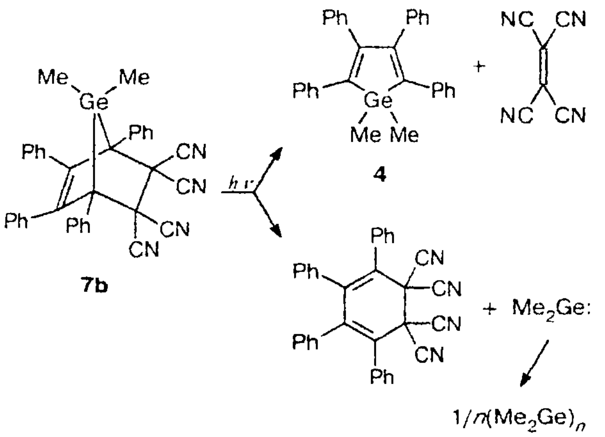
7a < **7b** < **7c** (107.3(1)°, 110.5(4)°, and 123.3(2)°, respectively). The structures of heterocycles of **7a—c** and 7-germanorbornadiene **8** are characterized by a small value of the endocyclic C(1)—Ge—C(4) angle (78.9—79.8° in **7a—c** and 78.5(5)° in **8**). The endocyclic C(1)—E—C(4) angle is somewhat smaller than those in derivatives of 7-silanorbornadiene[10,11,15,16] (79.5—82.6°) and 7-silanorbornene[14] (82.8(1)°) and is substantially smaller than that in norbornadiene (94°).[19]

The C(1)—C(2)—C(3)—C(4)—C(5)—C(6) ring in all complexes under consideration adopts a boat conformation. The angles between the C(1)—C(2)—C(3)—C(4) and C(4)—C(5)—C(6)—C(1) planes are 116.3°, 116.3°, and 116.0° in **7a—c**, respectively. The angles between the C(1)—C(4)—C(5)—C(6) and R(1)—Ge(1)—R(2) planes (R = *cyclo*-C_3H_5, Me, or H) are 89.8° (**7a**), 88.3° (**7b**), and 88.0° (**7c**). In all complexes, the plane in which the exocyclic carbon atoms are located, *viz.*, C(7)—Ge—C(8), is virtually orthogonal to the plane through the endocyclic atoms C(1)—Ge(1)—C(4) (the angles are 90° (**7a**), 92.9° (**7b**), and 88.9° (**7c**)).

It is noteworthy that the C(2)—C(3) bond lengths (1.612(5), 1.621(8), and 1.628(2) Å in **7a—c**, respectively) are noticeably larger than those in 7-silanorbornenes (1.574(5) Å).[12]

The thermal and photochemical stabilities of the synthesized cycloadducts were studied using 7-germanorbornene **7b** as an example. This heterocycle exhibits a high thermal and photochemical stability untypical of this class of compounds. Thus, heating of a solution of 7-germanorbornene **7b** in benzene to 100 °C for 4 h did not lead to its substantial decomposition. UV irradiation of compound **7b** with the full light of a medium-pressure xenon lamp (20 °C, C_6D_6, 20 min, $[7] = 0.21$ mol L^{-1}) resulted in complete decomposition to give the starting germole **4** in 50% yield and polymers $(Me_2Ge)_n$ (according to the data of ^1H NMR spectroscopy and mass spectrometry). Therefore, the photodecomposition of 7-germanorbornene **7b** took two pathways, *viz.*, it occurred as the Diels—Alder retroreaction and through elimination of a dimethylgermylene molecule.

It should be noted that unlike photodecomposition of 7-germanorbornene **7b**, photolysis of the cycloadduct of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene with maleic anhydride involved exclusively the Diels—Alder retroreaction and was not accompanied by elimination of a dimethylsilylene molecule.[13]



In conclusion, it should be noted that the analysis of the published data and the results obtained in this work suggests that the direction of thermo- and photodecomposition of the corresponding 7-heteronorbornenes can be changed by varying the nature of substituents at the heteroatom and the nature of the dienophile.

. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-200 instrument in C_6D_6. The mass spectra (electron impact, 70 eV) were measured on a Finnigan MAT INCOS instrument. Photochemical experiments were carried out using a LOT-Oriel medium-pressure Xe lamp (450 W). Germoles **4**,[20] **5**,[21] and **6**[22] were synthesized according to a known procedure.[23] The solvents were dried according to standard procedures.[24] Specimens of bromocyclopropane and TCE (both compounds were purchased from Aldrich) were used after purification (*cyclo*-C_3H_5Br and TCE were purified by distillation and sublimation).

Synthesis of 1,1-dicyclopropyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (3). A solution of bromocyclopropane (3.23 g, 26.7 mmol) in anhydrous ether (10 mL) was added with intense stirring to finely divided lithium (0.2 g, 29.4 mmol) in anhydrous ether (5 mL) under a stream of argon at −15 °C for 1 h. Then the reaction mixture was slowly warmed to 0 °C. The concentration of the resulting *cyclo*-C_3H_5Li ($6 \cdot 10^{-3}$ mol L^{-1}) was determined by double titration according to Gilman.[25] The yield was 36%. A solution of *cyclo*-C_3H_5Li (15 mL, 9.6 mmol) was added to a solution of 1,1-dichlorogermole **6** (1.6 g, 3.2 mmol) in THF (5 mL) over 30 min. Then the mixture was stirred at −20 °C for 12 h and hydrolyzed with water. 1,1-Dicyclopropylgermole **3** was extracted with benzene (3 × 5 mL), the organic layer was separated and dried over $MgSO_4$, the solution was concentrated *in vacuo*, and the reaction product was precipitated with heptane (5 mL). The yield of compound **3** was 1.15 g (71%), m.p. 154 °C. ^{1}H NMR, δ: 0.25 (m, 2 H, CH); 0.60 (m, 8 H, $C\underline{H}_2-C\underline{H}_2$); 6.80—7.35 (m, 20 H, Ph). ^{13}C NMR, δ: −4.096 (CH); 1.98 (CH_2); 125.85, 126.25, 127.26, 127.72, 128.07, 128.22, 129.25, 130.28, 134.75, 139.51, 141.06, 141.61, 152.94 (C of heterocycle, Ph). MS, *m/z*: 512 $[M]^+$, 471 $[M - C_3H_5]^+$, 356 [1,2,3,4-tetraphenylbutadiene]$^+$.

Synthesis of 5,5,6,6-tetracyano-7,7-dicyclopropyl-1,2,3,4-tetraphenyl-7-germanorborn-2-ene (7a). A solution of 1,1-dicyclopropylgermole 3 (0.2 g, 0.39 mmol) and TCE (0.055 g, 0.43 mmol) in benzene (1.5 mL) was stirred at −20 °C for 2 h. Then hexane (2 mL) was added to the solution and the white precipitate that formed was filtered off, twice washed with hexane (1-mL portions), and dried *in vacuo*. The yield of compound **7a** was 0.236 g (95%), m.p. 159 °C. ^{1}H NMR, δ: 0.25—1.00 (m, 10 H, 2 C_3H_5); 6.75—7.70 (m, 20 H, Ph). ^{13}C NMR, δ: −2.10, 5.33 (2 CH); 3.55, 4.18 (2 CH_2); 111.46, 113.85 (2 CN); 127.37, 127.65, 128.53, 128.75, 130.26, 130.73, 133.61, 134.78, 144.20, 144.00 (C of heterocycle, Ph). MS, *m/z*: 640 $[M]^+$, 614 $[M - CN]^+$, 512 [1,1-dicyclopropyl-2,3,4,5-tetraphenylgermacyclopentadiene]$^+$, 484 [5,5,6,6-tetracyano-1,2,3,4-tetraphenylcyclohexadiene]$^+$, 356 [1,2,3,4-tetraphenylbutadiene]$^+$.

Synthesis of 5,5,6,6-tetracyano-7,7-dimethyl-1,2,3,4-tetraphenyl-7-germanoborn-2-ene (7b). A solution of 1,1-dimethylgermole **4** (0.2 g, 0.44 mmol) and TCE (0.056 g, 0.440 mmol) in benzene (1.5 mL) was stirred at −20 °C for 1.5 h. Then hexane (2 mL) was added to the reaction mixture and the white precipitate that formed was filtered off and dried *in vacuo*. The yield of compound **7b** was 0.23 g (90%), m.p. 188 °C. ^{1}H NMR, δ: 0.71 (s, 3 H, CH_3); 1.12 (s, 3 H, CH_3); 6.70—7.30 (m, 20 H, Ph). MS, *m/z*: 588 $[M]^+$, 562 $[M - CN]^+$, 484 [5,5,6,6-tetracyano-1,2,3,4-tetraphenylcyclohexadiene], 460 [**4**]$^+$, 356 [1,2,3,4-tetraphenylbutadiene]$^+$.

Synthesis of 5,5,6,6-tetracyano-1,2,3,4-tetraphenyl-7-germanorborn-2-ene (7c). A solution of germole **5** (0.2 g, 0.46 mmol) and TCE (0.089 g, 0.69 mmol) in benzene (1.5 mL) was stirred at −20 °C for 1.5 h. Then hexane (2 mL) was added to the reaction mixture and the white precipitate that formed was filtered off and dried *in vacuo*. The yield of compound **7c** was 0.24 g (93.3%), m.p. 165 °C. ^{1}H NMR, δ: 4.89 (s, 1 H, GeH); 5.07 (s, 1 H, GeH); 6.61—7.40 (m, 20 H, Ph). MS, *m/z*: 484 [5,5,6,6-tetracyano-1,2,3,4-tetraphenylcyclohexadiene]$^+$, 458 [5,5,6,6-tetracyano-1,2,3,4-tetraphenylcyclohexadiene − CN]$^+$, 432 [2,3,4,5-tetraphenyl-1-germacyclopentadiene]$^+$, 356 [1,2,3,4-tetraphenylbutadiene]$^+$.

Reactions of germoles 3, 4, and 5 with cyclooctyne. The reactions were carried out in NMR tubes. Solutions of germoles **3**, **4**, or **5** (0.065, 0.058, or 0.069 mol, respectively) and cyclooctyne (0.072, 0.064, or 0.076 mol, respectively) in C_6D_6 (0.4 mL) were kept at −20 °C for 3 days and then heated at 70 °C for 7 h. According to the ^{1}H NMR spectral data, the corresponding cycloadducts did not form. The reaction of germole **3** (0.06 mol) with dimethyl acetylenedicarboxylate (0.06 mol) in C_6D_6 did not proceed at 20 °C (5 days) (NMR control). Heating of the reaction mixture to 60 °C (7 h) afforded a polymeric compound (apparently, ((*cyclo*-$C_3H_5)_2Ge)_n$) and dimethyl 3,4,5,6-tetraphenylbenzene-1,2-dicarboxylate (detected by mass spectrometry), which are products of thermolysis of 7-germanorbornadiene.

X-ray diffraction study. Single crystals of complexes **7a** · 2 C_6H_6, **7b** · C_6H_6, and **7c** · C_6H_6 were prepared by slow concentration of solutions of 7-germanorbornenes **7a—c** in benzene at −20 °C.

X-ray diffraction studies of single crystals of complexes **7a** and **7c** were performed on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 15 s, $2\theta_{max} = 60°$) using

Table 5. Crystallographic parameters of compounds **7a—c** (at 110, 293, and 110 K, respectively)

Parameter	**7a** · 2 C_6H_6	**7b** · C_6H_6	**7c** · C_6H_6
Molecular formula	$C_{52}H_{42}N_4Ge$	$C_{42}H_{32}N_4Ge$	$C_{40}H_{28}N_4Ge$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	12.4027(7)	14.192(7)	19.4125(7)
b/Å	26.3637(14)	17.358(9)	7.8669(3)
c/Å	13.0945(7)	14.247(5)	21.5607(8)
α/deg	90	90	90
β/deg	109.81(2)	100.35(4)	102.3860(10)
γ/deg	90	90	90
V/Å^3	4028.1(4)	3452.1(3)	3216.0(2)
Z	4	4	4
d_{calc}/g cm^{-3}	1.312	1.280	1.316
μ/mm^{-1}	0.803	0.922	0.987
Radiation (λ/Å)	MoKα (0.71073)	MoKα (0.71073)	MoKα (0.71073)
θ–2θ Scanning range (deg)	3—60	3—50	3—60
Number of measured reflections	24678	6357	20156
Number of reflections with $I > 2\sigma$	11111	6091	9039
R	0.0534	0.0673	0.0360
wR_2	0.0994	0.1825	0.0938

a standard procedure.[26] Semiempirical absorption corrections were applied.[27] The structures were solved by the direct method with the use of the SHELXS97 program[28] and refined anisotropically by the full-matrix least-squares method (the positions of the H atoms of the phenyl and cyclopropyl substituents were fixed with U_H = 0.08 Å^2) using the SHELXL97 program.[29] The hydrogen atoms of the GeH_2 fragment in structure **7c** were located from the difference Fourier synthesis and refined isotropically.

X-ray diffraction data for complex **7b** were collected on a four-circle automated Siemens P3/PC diffractometer (λ(Mo-Kα) radiation, graphite monochromator, θ-2θ scanning technique, 2θ < 54°). The structure was solved by direct methods, which revealed all nonhydrogen atoms. The positions of the hydrogen atoms were located from difference Fourier syntheses. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (PC version).[30] The principal bond lengths and bond angles for complexes **7a—c** are given in Tables 2—4, respectively. The crystallographic data and selected details of X-ray data collection are given in Table 5.

Quantum-chemical calculations of model cyclodienes and products of their cycloaddition with acetylene were carried out by the *ab initio* HF/LanL2DZ method with full geometry optimization. The LanL2DZ double zeta basis set was used for the H and C elements. For the heavier elements (Si, Ge, and Sn), the pseudopotential and double zeta basis sets were used for the core and valence orbitals, respectively.[31] The energies of the equilibrium structures were refined using second-order Möller—Plesset perturbation theory (MP2/LanL2DZ//HF/LanL2DZ). The thermal effects of the Diels—Alder reactions were calculated taking into account the energy contributions of zero-point vibrations. All calculations were carried out using the GAUSSIAN-94 program[32] on an SGI POWER CHALLENGE L computer at the Computer Center of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

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References

1. J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, 1990, **90**, 215.
2. O. M. Nefedov and M. P. Egorov, in *Frontiers of Organosilicon Chemistry*, Eds. A. R. Bassindale and P. P. Gaspar, The Royal Society of Chemistry, Cambridge, 1991, 145.
3. W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311.
4. N. K. Hota and C. J. Willis, *J. Organomet. Chem.*, 1969, **15**, 89.
5. C. Grugel, W. P. Neumann, and M. Schriewer, *Angew. Chem., Int. Ed.*, 1979, **18**, 543.
6. R.-J. Hwang, R. T. Conlin, and P. P. Gaspar, *J. Organomet. Chem.*, 1975, **94**, C38.
7. J. Belzner, H. Ihmels, B. O. Kneisel, R. O. Gould, and R. Herbst-Irmer, *Organometallics*, 1995, **14**, 305.
8. T. J. Barton, G. T. Burns, W. F. Goure, and W. D. Wulff, *J. Am. Chem. Soc.*, 1982, **104**, 1149.
9. W. Ando, Y. Hamada, and A. Sekiguchi, *Chem. Commun.*, 1982, 787.
10. M. Kako, M. Mori, K. Hatakenaka, S. Kakuma, Y. Nakadaira, M. Yasui, and F. Iwaşaki, *Tetrahedron*, 1997, **53**, 1265.
11. H. Appler, L. W. Gross, B. Mayer, and W. P. Neumann, *J. Organomet. Chem.*, 1985, **291**, 9.
12. J. G. Zavistoski and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1968, **90**, 6612.
13. R. Balasubramanian and M. V. George, *J. Organomet. Chem.*, 1975, **85**, 131.
14. S. I. Kirin, D. Vikic-Topic, E. Mestrovic, B. Kaitner, and M. Eckert-Maksic, *J. Organomet. Chem.*, 1998, **566**, 85.
15. H. Preut, B. Mayer, and W. P. Neumann, *Acta Crystallogr.*, 1983, **C39**, 1118.
16. A. Sekiguchi, A. S. S. Ziegler, K. J. Haller, and R. West, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 197.
17. M. P. Egorov, M. B. Ezhova, M. Yu. Antipin, and Yu. T. Struchkov, *Main Group Metal Chem.*, 1991, **14**, 19.
18. M. N. Paddon-Row, S. S. Wong, and K. D. Jordan, *J. Am. Chem. Soc.*, 1990, **112**, 1710.
19. A. Yokozeki and A. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2356.

20. N. K. Hota and C. J. Willis, *J. Organomet. Chem.*, 1968, **15**, 89.
21. H. D. Curtis, *J. Am. Chem. Soc.*, 1967, **89**, 4241.
22. H. D. Curtis, *J. Am. Chem. Soc.*, 1969, **91**, 6011.
23. L. Brandsma and H. D. Verkuijsse, *Synthesis*, 1978, 290.
24. A. J. Gordon and R. A. Ford, *The Chemist's Companion, A Handbook of Practical Data, Techniques, and References*, J. Wiley and Sons, New York, 1972.
25. H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, 1944, **66**, 1515.
26. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.
27. G. M. Sheldrick, *SADABS*, Program for Scaling and Correction of Area Detector Data, University of Göttingen, 1997 (based on the method of R. H. Blessing, *Acta Crystallogr., A*, 1995, **51**, 33).
28. G. M. Sheldrick, *SHELXS97*, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
29. G. M. Sheldrick, *SHELXL97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
30. G. M. Sheldrick, in *Crystallographic Computering 3: Data Collection, Structure Determination, Proteins, and Databases*, New York, 1985, 175.
31. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
32. *Gaussian 94, Revision D. 1*, Gaussian, Inc., Pittsburgh, PA, 1995.

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