Journal of Organometallic Chemistry, *446* (1993) 123–129

JOM 23051

A novel route to the trisilacyclobutane moiety. A possible silene–disilene reaction *

Dmitry Bravo-Zhivotovskii and Yitzhak Apeloig
Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000 (Israel)

Yuri Ovchinnikov, Vladimir Igonin and Yuri T. Struchkov
INEOS, Vavilov Str., 28, Moscow B-334, 1178133 (Russian Federation)

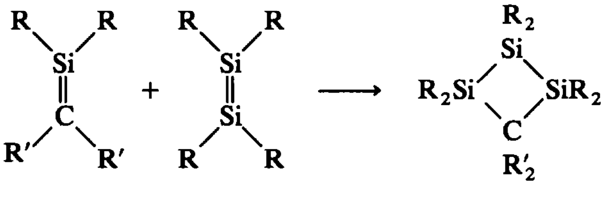
(Received May 21, 1992)

Abstract

The reaction of $(Me_3Si)_3SiC(=O)Ad$ with a two-fold excess of Et_3GeLi in THF, gives a 1:2 mixture of: 1,1,2,2-tetra-(trimethylsilyl)-3-trimethylsilyl-3-triethylgermoxy, 4-(1-adamantyl)-trisilacyclobutane (**4**) and adamantoyladamantyl-carbinol (**5**). The crystal structure of **4** is described and discussed. It is suggested that the trisilacyclobutane skeleton is formed by a cycloaddition reaction between a silene and a disilene.

1. Introduction

Exciting progress has been made in the field of multiply-bonded silicon compounds during the last decade, in particular in revealing the rich chemistry of silenes [1,2] and disilenes [1,2]. Several stable compounds with C=Si [3] and Si=Si [4] double bonds have recently been isolated, but usually these compounds are formed as highly reactive intermediates [1,2,5]. Unless they are sterically protected both silenes and disilenes undergo very facile dimerization reactions or additions to other types of double bonds [1,2,5]. However, the reaction between a silene and a disilene (eqn. (1)) is still unknown, probably because the highly reactive silenes and disilenes are usually generated in very low concentrations and because it is difficult to produce these species simultaneously in the same reaction flask.



(**1**)

(1)

In this paper we describe what we believe to be the first reported reaction of a silene with a disilene, according to eqn. (1). Furthermore, to the best of our knowledge this is also the first report of the isolation and X-ray structure determination of a derivative of a trisilacyclobutane (**1**). The only previous report on the preparation of a trisilacyclobutane derivative (*i.e.*, **1**, $R = CH_3$, $R' = H$), by Fritz and Gunert, indicated that this compound is unstable under ambient conditions [6].

2. Results and discussion

Earlier we reported [7] that reaction in tetrahydrofuran (THF) of Brook's acylsilane, **2**, with one equivalent of Et_3GeLi leads under appropriate conditions to

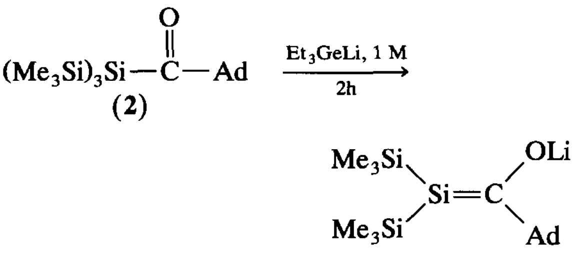
---

Correspondence to: Professor Y. Apeloig

* Dedicated to Professor Mikhail G. Voronkov, one of the founders of modern organosilicon chemistry.

0022-328X/93/$6.00

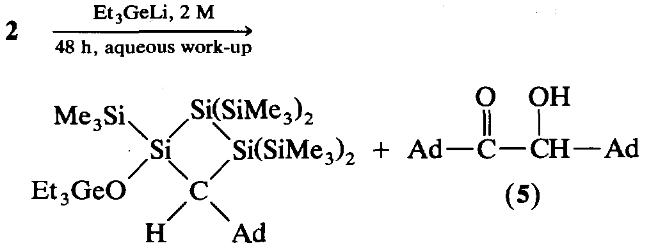
the lithium silaenolate **3** (eqn. (2)). From NMR data, it was concluded that **3** possesses a high degree of silaolefinic character [7]. The silaenolate **3** was found to be relatively unstable and it was noted that its half-life is relatively short, *ca.* 12 h [7]. However, the decomposition products resulting from **3** were not identified [7].



$$(Me_3Si)_3Si-\overset{O}{\overset{\|}{C}}-Ad \xrightarrow[2h]{Et_3GeLi,\ 1\ M}$$

(2) **(3)** (2)

In this paper we report that the reaction in THF of Brook's ketone **2** with a two-fold excess of Et$_3$GeLi gives, after 48 h at room temperature followed by aqueous work-up (eqn. (3)), a *ca.* 1:2 mixture of the trisilacyclobutane **4** and of (adamantoyl)adamantylcarbinol **5**. The structure of **4** was established by an X-ray diffraction study on suitable single crystals (see below).

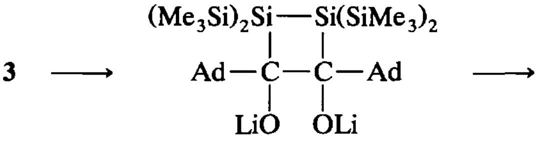


(4) **(5)**

(3)

We suggest that the formation of **4** takes place by the complex reaction sequence shown in eqns. (2) and (4)–(8).

The first step involves, as shown previously [7], the generation of the silaenolate **3** (eqn. (2)). From the number of silicon atoms in **4** it is obvious that at least three units of **3** must be involved in its production. Consequently, we suggest that in the second step two molecules of **3** dimerize to give the corresponding "head-to-head" dimer **6** (equation 4). The "head-to-head" approach is the common dimerization mode observed for sterically hindered silenes such as **3** [8,9]. In the third step, the dimer **6**, which is apparently unstable under the reaction conditions (and therefore could not be isolated), undergoes cleavage of the C–Si bonds to give the corresponding disilene **7** and the olefin **8** (eqn. (4)).



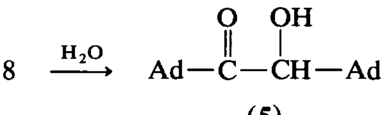
(6)

$$(Me_3Si)_2Si{=}Si(SiMe_3)_2 + Ad(LiO)C{=}C(OLi)Ad$$

(7) **(8)**

(4)

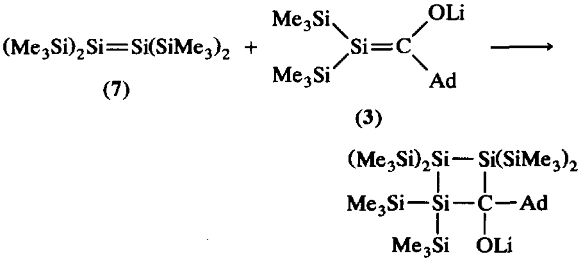
The dilithioenolate **8** yields after hydrolysis the ketocarbinol **5** (eqn. (5)), which is one of the two products isolated from reaction (3).



$$8 \xrightarrow{H_2O} Ad-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-Ad \qquad (5)$$

(5)

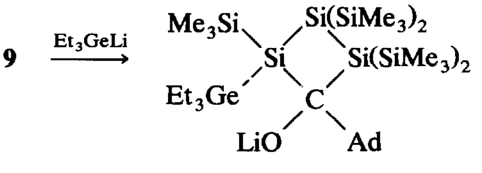
The disilene **7**, which is formed by reaction 4, is highly reactive and we propose that it is captured by the silene **3**, which is also present in the reaction mixture, to give the trisilacyclobutane **9** (eqn. (6)). This reaction, in which the trisilacyclobutane ring is formed, is the key step of the entire process. Furthermore, to the best of our knowledge this is the first claim for the occurrence of a cycloaddition reaction between a silene and a disilene.



(7) (3)

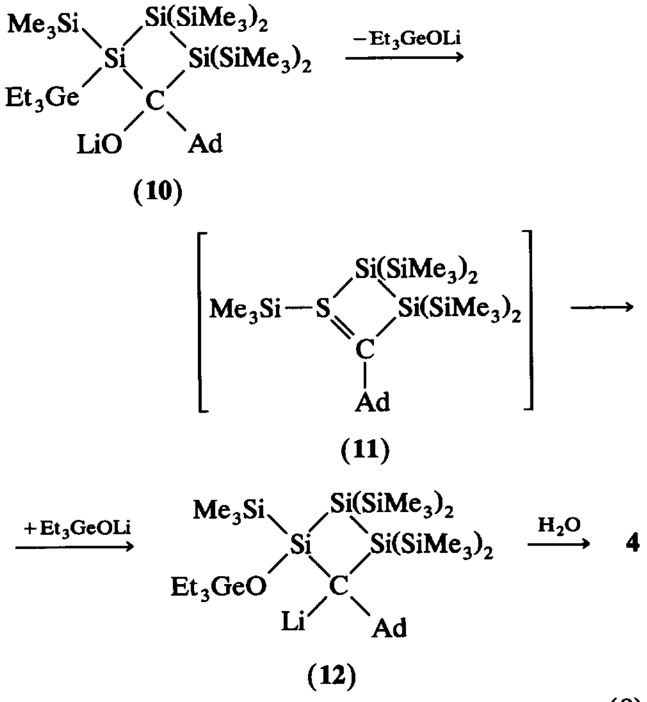
(9) (6)

Unfortunately, **9** is apparently unstable under the reaction conditions, and our attempts to stop the reaction at this stage by avoiding the use of an excess of Et$_3$GeLi led to complex product mixtures that were very difficult to separate or to analyse. We suggest that the excess of Et$_3$GeLi present in the reaction mixture makes a nucleophilic attack on one of the ring silicon atoms, leading to cleavage of one of the Si–SiMe$_3$ bonds and to formation of **10** (eqn. (7)).



(10) (7)

The cyclic lithium alkoxide **10** can then give the silene **11** *via* a Peterson-type elimination of Et_3GeOLi (eqn. (8)). We have recently observed a similar process in which Me_3SiOLi was eliminated from a lithium alkoxide to give a silene [9]. Re-addition of the triethylgermanolate to the silene **11** yields the organolithium compound **12** (eqn. (8)). Analogous elimination–addition reactions of trimethylsilaenolate have been described previously [10]. Hydrolysis of **12** during the aqueous work-up leads to **4** — the second observed product of the reaction.



(10)

(11)

(12)

(8)

We realize, of course, that the complex mechanism that we suggest above is rather speculative and it needs substantial additional support before it can be accepted. However, it is difficult to envisage a different plausible mechanism or sequence of reactions which would lead to **4**, which contains a trisilacyclobutane ring, as the major silicon-containing product of reaction (3). In particular, it appears that the most reasonable path in which the trisilacyclobutane ring can be formed is by the cycloaddition reaction between a silene and a disilene.

2.1. *The crystal structure of 4*

A PLUTO representation of the structure of **4** is shown in Fig. 1. As **4** is the first representative of the trisilacyclobutane family whose structure has been established by an X-ray study a discussion of the geometrical parameters of this molecule is of interest. Tables 1 and 2 list the most important bond lengths and bond angles, respectively, of **4**.

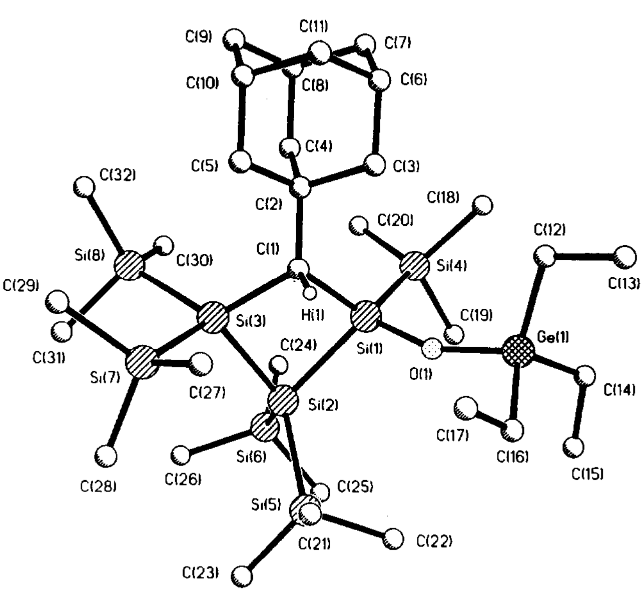


Fig. 1. Structure of the molecule 4. The hydrogen atoms of methyl and methylene groups are omitted.

The trisilacyclobutane **4** exhibits three structural features of interest: (i) the endocyclic (and some of the exocyclic) bonds are long relative to "standard values"; (ii) the trisilacyclobutane ring is only slightly puckered (*i.e.*, by 14°); (iii) the endocyclic Si–Si–Si bond angle is unusually small. These structural features are discussed in more detail below.

2.1.1. *Bond lengths*

The 4-membered ring of **4** exhibits Si–Si and Si–C bond lengths of 2.389 Å, 2.391(2) Å and 1.924 Å, 1.948(5) Å, respectively. These bond distances are considerably longer than the corresponding "standard values" of 2.34 Å [11a] and 1.89 Å [11b], or than the range

TABLE 1. Relevant bond lengths (Å) in 4

Ge(1)–O(1)	1.769(3)	Si–C(Me)	1.859–1.879(5), mean 1.871
Si(1)–Si(2)	2.389(2)		
Si(1)–Si(4)	2.363(2)	Ge–C(Et)	1.936–1.972(5), mean 1.949
Si(2)–Si(3)	2.391(2)		
Si(2)–Si(5)	2.365(2)	C–C(Ad)	1.522–1.541(5–7), mean 1.531
Si(2)–Si(6)	2.375(2)		
Si(3)–Si(7)	2.370(2)	C–C(Et)	1.495–1.544(8), mean 1.522
Si(3)–Si(8)	2.364(2)		
Si(1)–O(1)	1.648(3)		
Si(1)–C(1)	1.924(4)		
Si(3)–C(1)	1.948(5)		
C(1)–C(2)	1.551(5)		

TABLE 2. Relevant bond angles (°) in **4**

Si(2)–Si(1)–Si(4)	113.8(1)	Si(5)–Si(2)–Si(6)	103.7(1)
Si(2)–Si(1)–O(1)	113.1(1)	Si(2)–Si(3)–Si(7)	115.4(1)
Si(4)–Si(1)–O(1)	105.4(1)	Si(2)–Si(3)–Si(8)	115.2(1)
Si(2)–Si(1)–C(1)	90.4(1)	Si(7)–Si(3)–Si(8)	103.5(1)
Si(4)–Si(1)–C(1)	123.3(1)	Si(2)–Si(3)–C(1)	89.8(1)
O(1)–Si(1)–C(1)	110.6(2)	Si(7)–Si(3)–C(1)	109.8(1)
Si(1)–Si(2)–Si(3)	77.2(1)	Si(8)–Si(3)–C(1)	123.5(1)
Si(1)–Si(2)–Si(5)	110.6(1)	Ge(1)–O(1)–Si(1)	158.2(2)
Si(3)–Si(2)–Si(5)	117.6(1)	Si(1)–C(1)–Si(3)	100.8(2)
Si(1)–Si(2)–Si(6)	123.3(1)	Si(1)–C(1)–C(2)	123.0(3)
Si(3)–Si(2)–Si(6)	123.3(1)	Si(3)–C(1)–C(2)	122.3(3)
Ge–C–C	111.5–113.5(4)		
Si–Si–C–(Me)	104.2–119.0(2)		
C–(Me)–Si–C–(Me)	103.9–110.8(2)		

of bond distances found in molecules with relatively little steric congestion, where the Si–Si and Si–C bond distances are found to be in the range 2.33–2.37 Å and 1.86–1.91 Å, respectively [11,12]. *Ab initio* calculations for the parent trisilacyclobutane using a polarized basis-set predict Si–Si and Si–C bond distances of 2.364 Å and 1.914 Å, respectively [13], which are longer than the "standard values" [11] but still somewhat shorter than in **4**. This suggests that the relatively long Si–Si and C–Si bonds in **4** result from the effects of two factors: (a) the fact that these bonds are part of a strained 4-membered ring; (b) the influence of the substituents, which can affect the bond lengths either electronically or by steric congestion. As discussed below, steric repulsion between the substituents is relatively unimportant, and we therefore favour the electronic interpretation (*e.g.*, as consequence of the inductive effect of the six Me_3Si substituents).

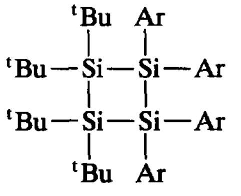
The bonds between the substituents and the endocyclic silicon atoms in **4** are also elongated (Table 1). The elongation of the exocyclic bonds is generally less than that of the endocyclic bonds, but it is still noticeable, *viz.* about 0.02 Å. For example, the Si(1)–O(1) bond is *ca.* 0.04 Å longer than the values usual for "standard" SiOSi species, although the Si(1)–O(1)–Ge(1) bond angle in **4** of 158.2° is similar to that in some siloxanes [12,14]. The Ge(1)–O(1) distance is unexceptional among known structures with SiOGe units (see *e.g.*, [15]). Similar lengthening of endo- and exo-cyclic bonds to Si were observed in other slightly puckered 4-membered silicon-containing rings (with weak inter-substituent repulsion) [16,17].

2.1.2. Bond angles

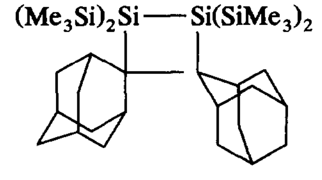
The endocyclic Si(1)–Si(2)–Si(3) bond angle of 77.2(1)° is the smallest observed for the known silacyclobutane structures [16,18]. On the other hand, the Si–C–Si bond angle is widened significantly to 100.8°. The two endocyclic Si–Si–C bond angles are close to 90°. All the observed endocyclic bond angles in **4** are close to the calculated values in the parent molecule [13], showing that the substituents cause only minor distortions of the ring bond angles.

2.1.3. Ring puckering

The trisilacyclobutane ring in **4** is slightly puckered, the dihedral angle between the Si(1)–C(1)–Si(3) and the Si(1)–Si(2)–Si(3) planes being 14.3°. The parent trisilacyclobutane is calculated to be essentially planar [13]. Similarly, symmetrically-substituted tetrasilacyclobutanes or 1,3-disilacyclobutanes are found to be planar or slightly folded [17,19–21]. On the other hand, unsymmetrically-substituted tetrasilacyclobutanes (*e.g.*, **13**) and 1,2-disilacyclobutane (*e.g.*, **14**), in which the bulky substituents around the cycle differ considerably in size, have strongly puckered cycles with torsion angles of 59° [22] and 39.6° [9], respectively. In these molecules puckering allows the large groups to get away from each other and so to minimize their steric repulsion. Thus, we suggest that the small puckering in **4** results from its nearly symmetrical substitution pattern, so that puckering does not result in considerable relief of repulsion between the large groups around the cycle and the nearly planar structure of the parent system [13] is retained. Further support for this suggestion comes from examination of the shortest intramolecular non-bonded distances such as C(3) ⋯ C(12), C(20) ⋯ C(24) and C(21) ⋯ C(27) of 3.54 Å, 3.62 Å and 3.69 Å, respectively, which are all only slightly shorter than the observed intermolecular methyl–methyl contacts (the shortest is 3.77 Å). It is therefore reasonable that these contacts do not affect the conformation of the cycle. Additional evidence for the small mutual repulsion between the methyl groups around the cycle comes from the observation that the similar contact distance of 3.60 Å between C(22) and C(25) evidently does not cause significant widening of the Si(5)–Si(2)–Si(6) bond angle beyond 103.7(1)°, although bond angles around Si atoms are usually extremely sensitive to various interactions [12], as one can be seen also from the wide range of the bond angles around the Si atoms in **4** itself (Table 2).



(**13**, Ar = 2,6-$Et_2C_6H_3$-)



(**14**)

3. Experimental details

3.1. Crystal data of 4

$C_{32}H_{76}OSi_8Ge$, triclinic, space group $P\bar{1}$ at 143 K, $a = 11.524(3)$, $b = 11.542(3)$, $c = 17.957(5)$ Å, $\alpha = 99.05(2)°$, $\beta = 90.46(2)°$, $\gamma = 105.94(2)°$ $V = 2265(2)$ Å^3, $Z = 2$, $D_{(calc)} = 1.135$ g cm^{-3}. Intensities of 5398 unique reflections were measured with Siemens P3/PC diffractometer (Mo Kα, graphite monochromomator, $\theta/2\theta$ scan, 2θ (max) = 52°). The structure was solved by direct methods and refined by block-diagonal least squares in anisotropic approximation for non-H atoms. Hydrogen atoms were located in the difference Fourier maps and refined isotropically. The final discrepancy factors are $R = 0.034$, $R_w = 0.037$ for 4335 reflections with $I > 2\sigma(I)$. All calculations were performed with IBM PC/AT computer using SHELXTL programs [23]. Atomic coordinates are given in Table 3. A table of hydrogen coordinates and a full list of bond lengths and structure factors are available from the authors.

3.2. Synthesis

NMR spectra were recorded at ambient temperatures with $CDCl_3$ or C_6D_6 solutions on Bruker EM-200 and Bruker-400 instruments. Mass spectrometric data were obtained with a Finnigan MAT TSQ 45 triple-stage quadrupole mass spectrometer.

3.3. 1,1,2,2-tetra(trimethylsilyl)-3-trimethylsilyl-3-triethylgermoxy, 4-(1-adamantyl)-trisilacyclobutane (4)

A solution of ketone **2** (2 g, 0.0048 mol) in 10 ml of THF was added at room temperature under dried Ar to 30 ml of a 0.325 M solution of Et_3GeLi [24] in THF. The mixture was stirred at room temperature for 48 h. After usual treatment with saturated aqueous ammonium chloride solution, the organic layer was separated and dried and the solvent evaporated to leave an oily product. Compound **4** was isolated by column chromatography of the product mixture on silica gel with 10 : 1 hexane/ether as eluent. The first fraction gave **4** which was further purified by recrystallization from hexane. Large colourless crystals of **4** (0.68 g, 54.0%) * separated in the cold, m.p. = 242–245°C. Anal. Found: C 48.59, H 9.81. $C_{32}H_{76}Si_8GeO$ calc: C 49.64, H 9.89%. ^1H NMR ($CDCl_3$): δ 0.21 (18H, s, $Me_3SiSiSiMe_3$), 0.24 (9H, s, Me_3Si), 0.26 (9H, s, Me_3Si), 0.28 (9H, s, Me_3Si), 0.96–1.10 (15H, br, Et_3Ge), 1.51–1.61 (16H, br, Ad + HC of cyclobutane). ^{13}C NMR ($CDCl_3$): δ 0.85, 2.43, 3.75, 4.37, 4.51 (Me_3SiSi), 8.39 (CH_2 of Et_3Ge), 9.86 (CH_3 of Et_3Ge), 29.22, 36.54, 36.73, 45.64 (C of Ad),

TABLE 3. Atom coordinates ($\times 10^4$ for C, $\times 10^5$ for Ge and Si, and $\times 10^3$ for H) and Equivalent isotropic temperature factors (Å$^2 \times 10^3$) for 4

Atom	x	y	z	U
Ge(1)	20201(4)	40352(4)	9078(3)	26(1) [a]
Si(1)	29699(9)	31776(10)	24498(6)	14(1) [a]
Si(2)	24838(9)	11143(10)	26703(6)	15(1) [a]
Si(3)	46449(9)	17213(10)	27538(6)	14(1) [a]
Si(4)	22564(10)	44908(11)	33624(6)	22(1) [a]
Si(5)	15046(10)	−2485(11)	15814(6)	21(1) [a]
Si(6)	12894(10)	4119(11)	36676(6)	21(1) [a]
Si(7)	55727(10)	5347(11)	18843(6)	21(1) [a]
Si(8)	55390(10)	16815(11)	39356(6)	20(1) [a]
O(1)	2407(3)	3308(3)	1631(2)	30(1) [a]
C(1)	4647(3)	3223(4)	2387(2)	15(1) [a]
C(2)	5691(3)	4416(4)	2598(2)	14(1) [a]
C(3)	5515(4)	5367(4)	2127(2)	22(2) [a]
C(4)	5752(4)	4967(4)	3431(2)	21(2) [a]
C(5)	6919(4)	4185(4)	2408(2)	21(2) [a]
C(6)	6536(4)	6559(4)	2307(2)	26(2) [a]
C(7)	6576(4)	7077(4)	3144(3)	29(2) [a]
C(8)	6790(4)	6154(4)	3616(2)	25(2) [a]
C(9)	7989(4)	5898(4)	3426(2)	27(2) [a]
C(10)	7954(3)	5369(4)	2587(2)	23(2) [a]
C(11)	7736(4)	6288(4)	2115(3)	31(2) [a]
C(12)	3238(5)	5555(5)	852(3)	41(2) [a]
C(13)	2932(5)	6159(5)	196(3)	51(2) [a]
C(14)	449(5)	4351(5)	1120(3)	43(2) [a]
C(15)	−568(4)	3211(5)	1087(3)	50(2) [a]
C(16)	1916(5)	2851(5)	−1(3)	39(2) [a]
C(17)	3144(5)	2740(5)	−260(3)	56(2) [a]
C(18)	2579(5)	6081(4)	3139(3)	43(2) [a]
C(19)	575(4)	3835(5)	3295(3)	39(2) [a]
C(20)	2813(4)	4628(4)	4365(3)	35(2) [a]
C(21)	2368(4)	−112(5)	714(3)	38(2) [a]
C(22)	61(4)	116(5)	1364(3)	39(2) [a]
C(23)	1119(4)	−1874(4)	1715(3)	38(2) [a]
C(24)	1312(4)	1503(5)	4558(3)	36(2) [a]
C(25)	−339(4)	−112(5)	3325(3)	40(2) [a]
C(26)	1728(5)	−917(5)	3940(3)	50(2) [a]
C(27)	56685(4)	1081(4)	955(2)	33(2) [a]
C(28)	4730(4)	−1118(4)	1769(3)	35(2) [a]
C(29)	7167(4)	649(5)	2184(3)	38(2) [a]
C(30)	4796(4)	2302(4)	4765(2)	29(2) [a]
C(31)	5347(5)	14(4)	3946(3)	38(2) [a]
C(32)	7203(4)	2457(4)	4078(3)	34(2) [a]
H(1)	466(3)	296(3)	179(2)	20(10)
H(32)	551(3)	505(3)	159(2)	20(10)
H(31)	475(3)	550(3)	224(2)	10(10)
H(42)	501(3)	510(3)	357(2)	20(10)
H(41)	587(3)	438(3)	370(2)	20(10)
H(52)	687(3)	380(3)	191(2)	10(10)
H(51)	707(4)	354(4)	269(2)	30(10)
H(61)	642(3)	707(3)	200(2)	20(10)
H(72)	586(3)	725(3)	326(2)	30(10)
H(71)	723(3)	785(3)	325(2)	20(10)
H(81)	676(3)	648(3)	413(2)	10(10)
H(92)	865(3)	666(3)	352(2)	20(10)
H(91)	817(3)	537(3)	371(2)	20(10)
H(101)	870(3)	521(3)	247(2)	10(10)
H(112)	837(3)	703(3)	220(2)	20(10)
H(111)	776(3)	597(4)	156(2)	30(10)
H(122)	397(5)	523(5)	70(3)	50(20)

---

* The calculated yield is based on the assumption that the stochiometry of eqn. (3) is as follows: 3(**2**) + $4Et_3GeLi \rightarrow$ (**4**) + 2(**5**).

TABLE 3 (continued)

Atom	*x*	*y*	*z*	*U*
H(121)	327(4)	606(5)	131(3)	50(20)
H(133)	350(4)	683(4)	20(2)	50(10)
H(132)	284(5)	561(5)	−28(3)	70(20)
H(131)	214(5)	642(5)	31(3)	70(20)
H(142)	52(4)	479(4)	164(3)	50(10)
H(141)	20(5)	477(5)	75(3)	90(20)
H(153)	−125(3)	341(3)	123(2)	20(10)
H(152)	−58(5)	270(5)	59(3)	60(20)
H(151)	−46(5)	277(5)	159(3)	90(20)
H(162)	129(4)	199(4)	14(2)	30(10)
H(161)	145(3)	309(3)	−38(2)	30(10)
H(173)	372(4)	283(4)	20(2)	40(10)
H(172)	357(4)	347(4)	−40(2)	40(10)
H(171)	308(5)	205(6)	−74(3)	110(20)
H(183)	238(5)	609(5)	264(3)	70(20)
H(182)	352(5)	647(5)	318(3)	70(20)
H(181)	229(4)	649(4)	347(3)	50(20)
H(193)	39(3)	314(4)	343(2)	30(10)
H(192)	31(4)	380(4)	283(3)	50(10)
H(191)	23(5)	423(5)	365(3)	80(20)
H(203)	227(5)	473(5)	467(3)	60(20)
H(202)	361(4)	520(4)	448(3)	50(10)
H(201)	299(6)	389(6)	449(3)	100(20)
H(213)	264(3)	58(3)	66(2)	10(10)
H(212)	308(4)	−38(4)	75(3)	50(10)
H(211)	185(5)	−52(5)	29(3)	70(20)
H(223)	24(5)	93(5)	131(3)	80(20)
H(222)	−44(5)	7(6)	171(3)	90(20)
H(221)	−27(5)	−27(5)	91(3)	90(20)
H(233)	161(3)	−210(3)	178(2)	20(10)
H(232)	72(4)	−238(4)	131(2)	40(10)
H(231)	53(5)	−203(5)	217(3)	80(20)
H(243)	205(4)	188(4)	476(2)	50(10)
H(242)	77(4)	108(4)	493(3)	50(10)
H(241)	98(4)	212(4)	446(2)	50(10)
H(253)	−67(3)	−32(3)	367(2)	20(10)
H(252)	−53(5)	−79(5)	290(3)	70(20)
H(251)	−58(5)	57(5)	321(3)	80(20)
H(263)	120(4)	−129(4)	426(3)	50(10)
H(262)	248(5)	−69(5)	415(3)	90(20)
H(261)	167(5)	−152(5)	352(3)	80(20)
H(273)	597(3)	60(3)	59(2)	20(10)
H(272)	501(4)	113(4)	77(3)	60(10)
H(271)	627(5)	180(5)	97(3)	70(20)
H(283)	510(4)	−158(4)	142(3)	50(10)
H(282)	397(5)	−130(5)	165(3)	70(20)
H(281)	476(5)	−140(5)	222(3)	80(20)
H(293)	747(3)	24(3)	186(2)	20(10)
H(292)	771(4)	150(4)	227(3)	60(10)
H(291)	719(5)	43(5)	270(3)	80(20)
H(303)	479(3)	305(3)	475(2)	20(10)
H(302)	521(4)	232(4)	521(2)	40(10)
H(301)	397(5)	185(5)	483(3)	50(20)
H(313)	558(3)	−10(3)	428(2)	20(10)
H(312)	583(4)	−30(4)	354(3)	50(10)
H(311)	447(5)	−52(5)	388(3)	80(20)
H(323)	735(3)	321(3)	413(2)	20(10)
H(322)	749(4)	231(5)	451(3)	60(20)
H(321)	765(5)	213(5)	365(3)	80(20)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

51.48 (CH of silacyclobutane). ^{29}Si NMR (C_6D_6): δ −116.86 (Si2), −75.91(S3), −10.50 (Si1), −12.47, −11.61, −8.36, −1.39 (Me_3SiSi), 18.40 (Me_3SiSiO), MS (EI): *m/z* 774 (M^+, 27), 759 (M^+-Me, 30), 701 (M^+-Me_3Si, 7), 613 (M^+-Et_3Ge, 23), 515 (M^+-Me_3Si-Et_3GeO, 100). MS/MS of 700: (M^+-Me_3Si, 100), 515 (M^+-Me_3Si-Et_3GeO, 90). MS/MS of 613: (M^+-Et_3Ge, 100), 539 (M^+-Et_3Ge-Me_3SiH, 80).

3.4. Adamantoyladamantylcarbinol (5)

This was isolated by elution of the reaction mixture on a silica gel column with a 10:1 hexane/ether mixture as eluent. The third fraction gave the keto-carbinol **5**, which was further purified by recrystallization from ether (0.92 g, 87.5%) *, m.p. 218–220°C. Anal. Found: C 80.06, H 9.98. $C_{22}H_{32}O_2$ calc: C 80.44, H 9.82%. IR ($CDCl_3$): 1698 (C=O), 3550 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.99 (1H, s, OH), 2.41 (1H, s, CHOH), 1.36–1.99 (30 H, br m, Ad). ^{13}C NMR ($CDCl_3$): δ 27.89 (CH of AdC–OH), 28.24 (CH of AdC=O), 36.51 (CH_2 of AdCOH), 37.01 (CH_2 of AdC=O), 37.91 (CH_2 of AdCOH), 38.13 (CH_2 of AdC=O), 76.18 (COH), 218.51 (C=O). MS (EI): *m/e*: 328(M^+, 8), 311 (M^+-OH, 20), 165 (M^+-AdCO, 5), 135 (Ad, 100).

Acknowledgments

At the Technion-Israel Institute of Technology this research was supported by the Wolf Fund for the Promotion of the Science and the Arts, administered by the Israel Academy of Sciences and Humanities, by the B. and G. Greenberg Research Fund (Ottawa), by the Fund for the Promotion of Research at the Technion, and by the award of a scholarship to D.B.-Z. by the Ministry of Immigrant Absorption, State of Israel.

References

1 G. Raabe and J. Michl, in S. Patai and Z. Rappoport, (Eds.), *The Chemistry of Organosilicon Compounds*, Wiley, Chichester, Chap. 17, 1989.

2 (a) R. West, *Angew. Chem., Int. Ed. Engl., 26* (1987) 20, and references therein; (b) G. Raabe and J. Michl, *Chem. Rev., 25* (1985) 419.

3 A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. M. Kallury, Y. C. Poon, Y. M. Chang and W. Wong-Ng, *J. Am. Chem. Soc., 104* (1982) 5667.

4 M. J. Fink, M. J. Michalczyk, K. S. Haller, R. West and J. Michl, *J. Chem. Soc., Chem. Commun.*, (1983) 1010.

5 L. E. Gusel'nikov and V. G. Avakyan, *Sov. Sci. Rev. B, Chem., 13* (1989) 39.

6 G. Fritz and B. Gunert, *Z. Anorg. Allg. Chem., 473* (1981) 59.

7 I. S. Biltueva, D. A. Bravo-Zhivotovskii, J. D. Kalikhman, V. Yu. Vitkovskii, S. G. Shevchenko, N. S. Vyazankin and M. G. Voronkov, *J. Organomet. Chem., 368* (1989) 163.

8 (a) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst and R. K. M. Kallury, *J. Chem. Soc., Chem. Commun.*, (1981) 191; (b) A. G. Brook, J. W. Harris, J. Lennon and M. Elsheikh, *J. Am. Chem. Soc., 101* (1979) 83.

9 D. Bravo-Zhivotovskii, V. Braude, A. Stanger, M. Kapon and Y. Apeloig, *Organometallics,* in press.

10 A. G. Brook, P. Chiu, J. McClenaghnan and A. J. Lough, *Organometallics, 10* (1991) 3292.

11 (a) G. Becker, H.-M. Hartmann, A. Munch and H. Riffel, *Z. Anorg. Allg. Chem., 530* (1985) 29; (b) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. Guy Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. II,* (1987) S1.

12 W. S. Sheldrick, in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organosilicon Compounds*, Wiley, Chichester, Chap. 3, 1989.

13 (a) R. S. Grev and J. Schaefer, *J. Am. Chem. Soc., 109* (1987) 6577; (b) C. Liang and L. C. Allen, *J. Am. Chem. Soc., 113* (1991) 1878.

14 I. L. Dubchak, V. E. Shklover, Yu. T. Struchkov, E. S. Khynku and A. A. Zhdanov, *Zh. Strukt. Khim., 22* (1981) 156.

15 H. Puff, T. R. Kok, P. Nauroth and W. Schuh, *J. Organomet. Chem., 281* (1985) 141.

16 M. Weidenbruch, B. Flintjer, S. Pohl, D. Haase and J. Martens, *J. Organomet. Chem., 338* (1988) C1.

17 K. Peters, E.-M. Peters, H.-G. von Schnering, *Z. Anorg. Allg. Chem., 502* (1983) 61.

18 A. Schafer, M. Weidenbruch and S. Pohl, *J. Organomet. Chem., 282* (1985) 305.

19 Y.-S. Chen and P. P. Gaspar, *Organometallics, 1* (1982) 1410.

20 L. Parkanayi, K. Sasvari and J. Barta, *Acta Crystallogr, Sect. B, 34* (1978) 883.

21 K. M. Baines, A. G. Brook, P. D. Lickiss and J. F. Sawyer, *Organometallics, 8* (1989) 709.

22 R. Jones, D. J. Williams, Y. Kabe and S. Masamune, *Angew. Chem., Int. Ed. Engl., 98* (1986) 176.

23 W. Robinson and G. M. Sheldrick, SHELX, in N. W. Isaacs and M. R. Taylor (eds.), *Crystallographic Computing-Techniques and New Technologies*, Oxford University Press, Oxford, 1988, p. 366.

24 E. N. Gladyshev, N. S. Vyazankin, E. A. Fedotova, L. O. Yuntila and G. A. Razuvaev, *J. Organomet. Chem., 64* (1974) 307.