14: δ 8.07 and 8.04 (overlapping d's, 2, H_8 and H_4), 7.77 (d, 1, H_5), 7.68 (t, 1, H_7), 7.48 (t, 1, H_6), 7.32 (d, 1, H_3), 3.01 (q, 2, J = 7.6 Hz, CH_2), 1.40 (t, 3, J = 7.6 Hz, CH_3); other coupling constants are J_{34} = 8.4 Hz, J_{56} = 8.0 Hz, J_{57} = 1.3 Hz, J_{67} = 6.9 Hz, J_{68} = 1.1 Hz, J_{78} = 8.5 Hz.

15: δ 6.93 (t, 1, H_7), 6.81 (d, 1, H_5), 6.54 (t, 1, H_6), 6.37 (d, 1, H_8), 6.30 (d, 1, H_4), 5.54 (d of d's, 1, H_3), 4.20 (m, 1, H_2), 1.60 (d of t's, 2, J = 7.4 Hz, J = 6.1 Hz, CH_2), 0.96 (t, 3, J = 7.5 Hz, CH_3); other coupling constants are J_{23} = 3.8 Hz, J_{24} = 1.2 Hz, J_{34} = 9.8 Hz, J_{56} = 7.4 Hz, J_{57} = 1.4 Hz, J_{67} = 6.4 Hz, J_{68} = 1.0 Hz, J_{78} = 7.9 Hz.

16: δ 8.92 (br, 1, H_2), 8.11 (resembles overlapping d's, ~2, H_5 and H_8?), 7.69 (resembles a q but perhaps is an overlapping d and t, 2, J = 7.8 Hz, H_3 and H_7?), 7.56 (t, 1, J = 7.1 Hz, H_6?), 3.13 (q, 2, J = 7.6 Hz, CH_2), 1.41 (t, ~3, J = 7.6 Hz, CH_3).

17: δ 7.01 (d, 1, H_5), 6.96 (t, 1, H_7), 6.61 (t, 1, H_6), 6.46 (d, 1, H_8), 3.32-3.22 (c, 2, H_2 and H_2'), 2.64 (m, 1, H_4), 1.90-1.50 (c, 5?, H_3 and H_3', CH_2CH_3, and NH?), 0.98 (t, 3, J = 7.4 Hz, CH_3); other coupling constants are J_{56} = 7.4 Hz, J_{57} = 1.5 Hz, J_{67} = 6.2 Hz, J_{68} = 1.2 Hz, J_{78} = 7.7 Hz.

Reactions with 2-Cyclohexen-1-one. The solutions were prepared in a glovebox. A benzene solution of EtLi was added to a vial containing a diethyl ether solution of Et_2Mg that was stirred with a magnetic stirring bar. Then a diethyl ether solution of 12-crown-4 (0.5 M), when that additive was used, was added and the resulting mixture stirred for 5 min. A diethyl ether solution (0.5 M) of cyclohexenone containing a known amount of undecane as a GC standard was added, resulting in light yellow, turbid solutions. After 4 h, the vial was removed from the glovebox, cooled in ice, and its contents hydrolyzed by addition of a saturated aqueous NH_4Cl solution (5 mL). The aqueous layer was extracted with two 5-mL portions of diethyl ether, which were combined and dried (Na_2SO_4). The "Et_2CuLi" solutions were prepared by addition of the benzene solution of EtLi to CuI in diethyl ether maintained at -15 or -60 °C; after 15 min the cyclohexenone solution was added and the procedure described above was followed. Typical retention times in the GC analyses (column A, 100 °C for 4 min, then programmed at 40 °C/min to a final temperature of 185 °C) were **18** (8.3 min), **19** (8.9), undecane (9.4), and **20** (10.6). Products **18** and **19** were identified by comparison of retention times and mass spectra (GC-MS) with those of authentic samples. Response factors relative to undecane, determined by using standard solutions prepared from authentic samples, were 1.24 for both **18** and **19**, and this factor was assumed for **20**. A sample of the 10.6-min product was collected. Its ^1H NMR spectrum ($CDCl_3$) was virtually identical with that reported above for the 1,3-diethyl-1-cyclohexanol preparation.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers. We thank Dr. Alan Freyer for obtaining some of the NMR spectra, Dr. Robert Minard for obtaining mass spectra, and James Folmer for preparing the diethylcyclohexanols.

Registry No. **1**, 28631-77-8; **2**, 536-75-4; **14**, 1613-34-9; **15**, 126422-62-6; **16**, 19020-26-9; **17**, 22494-02-6; **18**, 115834-53-2; **19**, 22461-89-8; **20**, 126422-63-7; EtLi, 811-49-4; Et_2Mg, 557-18-6; pyridine, 110-86-1; quinoline, 91-22-5; 2-cyclohexen-1-one, 930-68-7.

Preparation, Characterization, and Reactions of 3-Germabicyclo[3.2.1]octane and 2-Germabicyclo[2.2.1]heptane Derivatives

Anthony G. Sommese and Sheldon E. Cremer*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233

James A. Campbell[1] and Michael R. Thompson

Battelle Pacific Northwest Laboratories, Battelle Boulevard, P.O. Box 999,
Richland, Washington 99352

Received August 11, 1989

Ring closure of the bis-Grignard derived from *cis*-1,3-bis(bromomethyl)cyclopentane (**5**) on R_2GeCl_2 (R = Ph or Me) afforded the 3-germabicyclo[3.2.1]octane system **6** or **7**. Bromine cleavage of a phenyl group in 3,3-diphenyl-3-germabicyclo[3.2.1]octane (**6**) and subsequent nucleophilic displacement of the bromide allowed differing substitution on the germanium atom. Crystals of **6** were grown from 95% ethanol and found to crystallize in the orthorhombic space group $P_{na2}C_A2v$ (No. 33, variation) with $Z = 4$, $a = 7.921$ (2) Å, $b = 31.565$ (5) Å, $c = 6.530$ (2) Å. The refinement cycles resulted in conventional residuals of $R_1 = 0.053$ and $R_w = 0.068$ for the 1483 reflections used. The incorporation of germanium into the bicyclo[2.2.1]heptane system was achieved through a chloroplatinic acid catalyzed, intramolecular hydrogermylation reaction of di-*n*-butyl(3-cyclopentenylmethyl)germane (**14**). The physical and spectral properties of these new molecules are presented.

Introduction

As part of our ongoing studies of bicyclic systems containing heteroatoms,[2-6a] we have targeted the 3-germabicyclo[3.2.1]octane and the 2-germabicyclo[2.2.1]heptane systems for synthetic and stereochemical investigation. Incorporation of germanium into the bicyclic framework posed a synthetic challenge. The 3-germabicyclo[3.2.1]octane and 2-germabicyclo[2.2.1]heptane systems readily lend themselves to stereochemical investigations since one

---

(1) To whom questions regarding the X-ray structural analysis should be addressed.

(2) Haque, M.; Horne, W.; Cremer, S. E.; Most, J. T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1000.

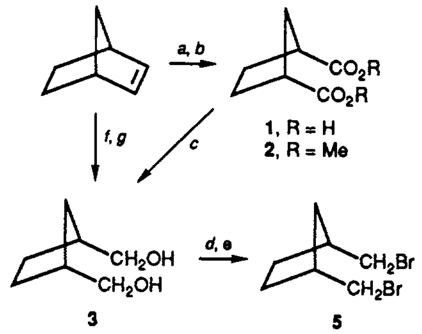
(3) (a) Haque, M.; Horne, W.; Cremer, S. E.; Kremer, P. W.; Most, J. T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1467. (b) Haque, M.; Horne, W.; Cremer, S. E. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 533.

(4) Blankenship, C.; Cremer, S. E. *Organometallics* **1986**, *5*, 1329.

(5) Blankenship, C.; Cremer, S. E. *J. Org. Chem.* **1982**, *47*, 1626.

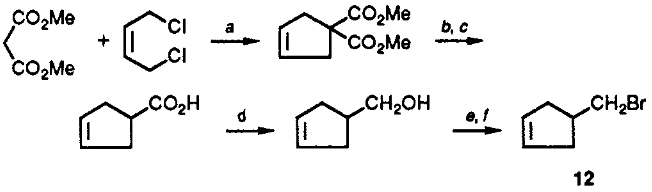
(6) (a) Borsub, L. Ph.D. Thesis, Marquette University, 1984. (b) Carleer, R.; Hosten, N.; Anteunis, M. J. O. *Soc. Chim. Belg.* **1978**, *87*, 709.

Scheme I



[a] KMnO$_4$, H$_2$O, isooctane. [b] 2,2-Dimethoxypropane, MeOH, p-TsOH (catalyst). [c] LAH, diethyl ether. [d] p-TsCl, pyridine. [e] LiBr, acetone. [f] O$_3$, MeOH. [g] NaBH$_4$.

Scheme II



[a] LiH, DMF. [b] KOH, EtOH. [c] Δ, 170 °C. [d] LAH, THF. [e] p-TsCl, pyridine. [f] LiBr, acetone.

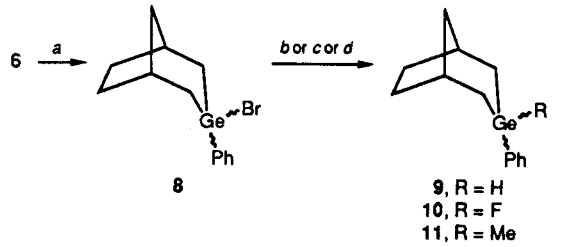
can observe the endo and exo substituents (e.g., aryl, alkyl, or halogen substituents directly bound to the germanium) and monitor their stereochemical changes during the course of a chemical reaction. In addition, the possibility of isomer interconversion, through hypervalent germanium, of the exo and endo isomers of 3-methyl-3-phenyl-3-germabicyclo[3.2.1]octane (11) by fluoride ion catalyst was of considerable interest.

Results and Discussion

Precursors of the [3.2.1] System. *cis*-1,3-Bis(bromomethyl)cyclopentane (5) was synthesized by a five-step sequence originally explored by Birch[7] and modified by Cremer and Most[8] (Scheme I). Norbornene was treated with KMnO$_4$ in a two-phase mixture of water and isooctane, under pH and temperature control, to give the diacid 1. Esterification of 1 was achieved by treatment with methanol in 2,2-dimethoxypropane. The diester 2 was reduced to the diol 3 with lithium aluminum hydride (LAH). The diol was transformed to the ditosylate 4, which was then treated with bromide ion to give the dibromide 5 in 52% overall yield. An alternative method for the preparation of 3 involved ozone cleavage of norbornene, followed by a reductive workup with NaBH$_4$ to afford the desired diol 3 in 73% yield.[6]

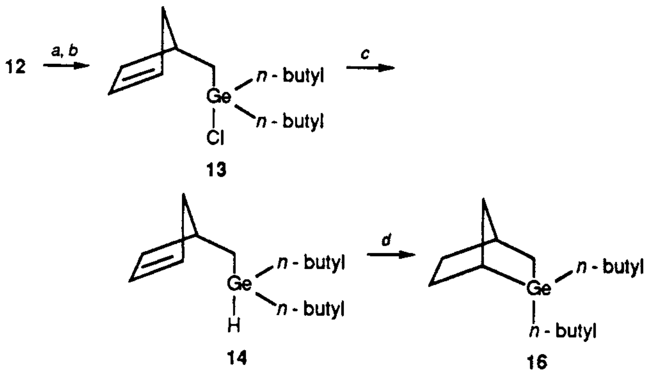
Precursors to the [2.2.1] System. The precursor 4-(bromomethyl)cyclopentene (12) was synthesized in a six-step sequence in 56% overall yield (Scheme II). The intermediate 3-cyclopentenecarboxylic acid was synthesized in three steps following the method of Greene and Depres.[9] The conversion of the carboxylic acid to the tosylate[10] and subsequent displacement by bromide ion afforded 12.

Scheme III



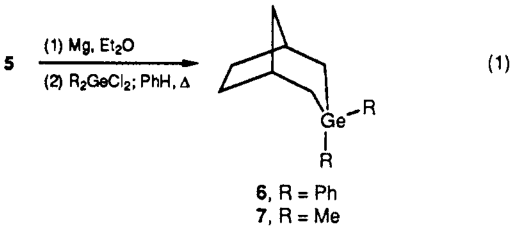
[a] Br$_2$, EtBr. [b] LAH, diethyl ether. [c] AgF, benzene. [d] MeMgBr, benzene, Δ, 60 h.

Scheme IV



[a] Mg, diethyl ether. [b] (n-Bu)$_2$GeCl$_2$, THF, −78 °C. [c] LAH, diethyl ether, Δ. [d] H$_2$PtCl$_6$/isopropyl alcohol, Δ 175–200 °C, 72 h.

Synthesis of Bicyclic Germanes. Incorporation of germanium into the bicyclo[3.2.1]octane framework was achieved through a ring closure in which the preformed bis-Grignard reagent of 5 and dichlorodiphenylgermane were added separately but simultaneously to a large volume of refluxing benzene (eq 1).[11] Slow addition and high dilution were required to avoid the intermolecular reaction of one or more germanium-containing molecules with one or more molecules of the bis-Grignard reagent. The slow addition was accomplished by the use of a "slow drop" adaptor.[12] Attempts to form the bis-Grignard reagent in situ as in the silicon analogue[4] resulted in poor yields (<7%).



The formation of derivatives in which there are two different substituents on the germanium was first accomplished by bromine cleavage[13] of 6 (Scheme III). The

---

[7] Birch, S. F.; Oldham, W. J.; Johnson, E. A. *J. Chem. Soc.* **1947**, 818.

[8] Most, J. T. M.S. Thesis, Marquette University, 1980.

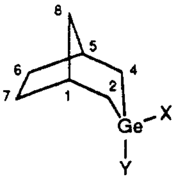
[9] Green, A. E.; Depres, J. P. *J. Org. Chem.* **1984**, *49*, 928.

[10] Johnson, C. R.; Kieser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860.

[11] Mazerolles, P.; Dubac, J.; Lesbre, M. *J. Organomet. Chem.* **1966**, *5*, 35.

[12] The "slow drop" adaptor is a simple apparatus that allows controlled addition over long periods of time. The apparatus was fabricated from a male and a female 24/40 joint, both 3–4-in. long and a 7-in. length of 8-mm glass tubing. The glass tubing was flared to the outer diameter of the male joint (20–21 mm). The female joint was prepared by making a test-tube bottom $^3/_4$ in. below the outer joint. A hole was opened and flared to 21 mm. The 8-mm flared tubing was placed inside the male joint so the flared edge rested on the outer edge of the tubing where a ring seal was made. The 8-mm tubing extended 3 in. beyond the ground male joint. This piece was joined at the ring seal to the female joint making sure the tubing was centered. The extended 8-mm tubing can then be drawn to a fine capillary of approximately 0.5 mm; the size of the opening dictated the rate of addition. A pressure-equalized addition funnel was connected to the female joint of this adaptor.

Table I. ^{13}C NMR Data[a,b] for 3-Germabicyclo[3.2.1]octane Derivatives



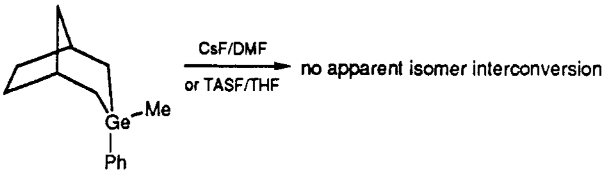
compd	C1,5	C2,4	C6,7	C8	*X*[c]	*Y*[c]
6, X = Y = Ph	34.7	23.5	32.0	41.8	133.7 128.1 127.7	133.6 127.9
7, X = Y = Me	35.2	26.1	32.2	41.4	0.6[d]	0.8[d]
8a, X = Ph, Y = Br	34.7	30.8	31.5	40.3	139.2	138.3
8b, X = Br, Y = Ph	35.2	31.2	31.9	40.8	129.7 129.5	132.3 128.2
9a, X = Ph, Y = H	34.4	21.0	31.9	41.4	133.6	134.0
9b, X = H, Y = Ph	35.0	22.1	32.3	41.8	127.9	128.4
10a, X = Ph, Y = F	34.5 (3.9)	28.2 (9.8)	32.7	41.7	132.5 130.1	132.3 130.0
10b, X = F, Y = Ph	34.1 (2.9)	28.0 (8.8)	31.8	40.9	128.4 128.2	128.3
11a, X = Ph, Y = Me	34.7	24.4	32.0	41.6	133.0 127.9 127.7	0.1
11b, X = Me, Y = Ph	34.9	25.3	32.1	41.4	−1.0	133.0 127.9 127.8

[a] Chemical shift values ($CDCl_3$, δ in ppm versus 79.0 ppm). [b] ^{13}C–^{19}F coupling constants in **10** (parentheses) are measured in hertz. [c] Aromatic chemical shift data of **6**–**10** ppm were taken on mixtures of isomers and not assigned an *X* or *Y* value. The chemical shift data for **11a** and **11b** were taken by using separated isomers. [d] Assignments may be interchanged.

bromophenylgermane **8** was produced as a 55:45 isomer mixture in 95% yield and was converted to other derivatives. For example, treatment of **8** with LAH in ether afforded a 65:35 isomer mixture of the hydridophenylgermane **9** in 95% yield. Likewise, fluorophenylgermane **10** was synthesized in 76% yield as a 61:39 isomer mixture by treatment of **8** with an excess of AgF in benzene. Methylphenylgermane **11** was synthesized by treatment of **8** with a 15-mol excess of methylmagnesium bromide in refluxing benzene for 60 h. This provided a 52:48 isomer mixture of **11** in 55% yield. The isomers of **11** were separated by preparative reverse-phase HPLC.

Incorporation of germanium into the bicyclo[2.2.1]heptane framework was achieved through a platinum-catalyzed, intramolecular hydrogermylation reaction (Scheme IV). One equivalent of the Grignard reagent derived from 4-(bromomethyl)cyclopentene (**12**) was treated with 1 equiv of di-*n*-butyldichlorogermane at −78 °C. This afforded di-*n*-butylchloro(3-cyclopentenylmethyl)germane (**13**) in 24% yield. As further proof of the formation of **13**, a small amount of the compound was subjected to treatment with 4 equiv of methylmagnesium bromide in refluxing benzene. This afforded a 46% yield of the desired di-*n*-butyl(3-cyclopentenylmethyl)methylgermane (**15**). Reduction of **13** by LAH afforded the requisite hydride di-*n*-butyl(3-cyclopentenylmethyl)germane (**14**) in 80% yield. The hydride **14** was unstable and readily decomposed in contact with air. The hydride was added to a glass screw-cap pressure tube with a catalytic amount of H_2PtCl_6, and was heated at 175–200 °C for 72 h. The ring-closure reaction afforded a complex mixture which was partially purified by GC; a high-resolution mass spectra showed the expected mass value for 2,2-di-*n*-butyl-2-germabicyclo[2.2.1]heptane (**16**). The ^{13}C NMR spectrum was entirely consistent with the assigned structure. It is likely that the high reaction temperatures and decomposition of the hydride caused the complex mixture in this reaction.

Attempted Equilibration Studies. By analogy to the silicon system,[14] we set out to equilibrate the separated endo and exo isomers of 3-methyl-3-phenyl-3-germabicyclo[3.2.1]octane (**11**) via fluoride ion. The relative amount of fluoride ion, the temperature, and the solvent, as well as the fluoride ion source were varied; no isomer interconversion was observed (eq 2). This was in contrast to the related silicon compound 3-methyl-3-phenyl-3-silabicyclo[3.2.1]octane which readily isomerized. An exo preference of the phenyl substituent (7:3 exo:endo) was observed in that system.[15a] Likewise, the tin counterpart of **11** exhibited an equilibrium value of 57:43 (exo:endo) in ether/THF solution.[15b] In **11** either a hypervalent fluoro-substituted germane intermediate was not formed under the reaction conditions or, if formed, it did not undergo intramolecular ligand rearrangement at an observable rate. One can only conjecture that substituent preference in **11** would be similar to the silicon and tin derivatives.



11

(2)

NMR Spectral Characterization of 3-Germabicyclo[3.2.1]octane. The ^{13}C NMR spectral data are presented in Table I. Peak assignments were relatively straightforward due to molecular symmetry and the similarity of this system to the silicon and tin analogues

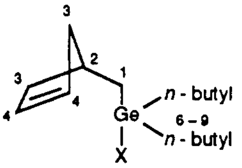
---

(13) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Wiley: London, 1971.

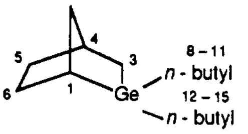
(14) Blankenship, C.; Cremer, S. E. *Tetrahedron Lett.* **1980**, 3979.

(15) (a) Blankenship, C.; Cremer, S. E. *J. Organomet. Chem.* **1989**, *371*, 19. (b) Reich, H. Phillips, N. H.; Borst, J. P., personal communication, 1989. (c) Shen, Q.; Hilderbrandt, R.; Blankenship, C.; Cremer, S. *J. Organomet. Chem.* **1981**, *214*, 155.

Table II. ^{13}C NMR Data[a] for 2-Germabicyclo[2.2.1]heptane and Precursors



compd	C1	C2	C3	C4	C6	C7[b]	C8[b]	C9	X
13, X = Cl	27.3	34.3	41.6	129.6	19.6	25.6	26.7	13.4	
14, X = H	20.2	35.7	40.8	129.9	12.2	26.0	28.5	13.6	
15, X = Me	22.3	35.3	42.2	130.0	13.7	26.5	27.4	14.5	–5.3



16

C1	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15
23.7	19.7	35.2	29.7	24.3[c]	38.9	12.4	26.9[c]	25.3[c]	12.8	10.5	27.4[c]	25.3[c]	12.8

[a] Chemical shift ($CDCl_3$, δ in ppm versus 79.0 ppm). [b] These assignments may be interchanged. [c] Assignments are uncertain.

previously reported.[4,6a] The bridging carbon C8 was identified by its relative intensity, which was roughly one-half that of the other ring carbons. The assignment of C6,7 and C1,5 was less straightforward. The bridgehead hydrogens gave a discrete resonance in the ^{1}H NMR at 2.5 ppm. A selective ^{1}H irradiation experiment of the bridgehead hydrogens allowed definitive assignment of C1,5 as the more downfield carbons. The α-carbons C2,4 showed the greatest variation in chemical shift with differing substituents at germanium. The two- and three-bond ^{13}C–^{19}F coupling constants observed for fluorogermane **10** were helpful in identifying C2,4 and confirming the assignment of C1,5. The exo and endo isomers of **11** were *tentatively* assigned by analogy to the parent hydrocarbon system.[16] In 3-methylbicyclo[3.2.1]octane the *endo*-methyl carbon absorbs downfield from the *exo*-methyl carbon. In addition C2,4 in the exo isomer are downfield from the corresponding carbons in the endo isomer. The analogy to the parent hydrocarbon system also extends to the derivatives of 3-silabicyclo[3.2.1]octane, with the notable exception of the methylphenyl derivative in which the assignment of the *endo*- and *exo*-methyl carbons is reversed. The 3-germabicyclo[3.2.1]octane derivatives are consistent with both the parent and silicon analogues with the exception of the anomalous assignment of the methylphenyl derivative in the silicon system. On this basis the chemical shifts for **11** were tentativily assigned as 0.1 ppm for the *endo*-methyl carbon and –1.0 ppm for the *exo*-methyl carbon. The assignment of the phenyl carbons was not pursued.

The 60-MHz ^{1}H NMR spectra were generally not as informative as the ^{13}C NMR spectra for structural elucidation. A typical ^{1}H NMR spectrum included a multiplet at δ 7.0–7.8 for the phenyl hydrogens, a broad multiplet centered at 2.5 ppm for the bridgehead hydrogens, and a complex multiplet from 0.8 to 2.3 ppm for the remaining ring protons. However, the ^{1}H NMR spectrum was especially useful for observing and assigning the *endo*- and *exo*-methyl hydrogens in **11**. As before the assignment was based on analogy to the silicon system; in this system unequivocal assignments of the endo and exo methyl groups were made. In the silicon system the *endo*- and *exo*-methyl groups absorbed at 0.4 and 0.1 ppm, respectively. In **11** the assigned chemical shift for the *endo*-methyl was 0.7 and 0.4 ppm for the *exo*-methyl. The anomaly noted in the ^{13}C NMR spectrum of 3-methyl-3-phenyl-3-silabicyclo[3.2.1]octane was not observed in the ^{1}H NMR spectrum.

NMR Spectral Characterization of 2-Germabicyclo[2.2.1]heptane. The ^{13}C NMR peak assignments for 2-germabicyclo[2.2.1]heptane (**16**) and precursors are shown in Table II. The peak assignments for the precursors **13** and **14** as well as the methyl derivative **15** were simplified by molecular symmetry. The α-methylene of the *n*-butyl groups in **14** and **15** absorbed at 12.2 and 13.7 ppm, respectively. These assignments were in agreement with the chemical shifts in (n-Bu)$_4$Ge[17] and were further confirmed by an off-resonance experiment. In **13**, C6 was assigned a chemical shift of 19.6 ppm due to presence of the electronegative chlorine atom. The α-methylene C1 was assigned a chemical shift in the range 20.2–27.3 ppm and showed the greatest variation in chemical shift with differing substitution on the germanium. This assignment was based on the fact that carbons directly bonded to electropositive atoms are shifted upfield, and a β-branching effect causes a downfield shift of approximately 9 ppm. The methine C2, allylic C3, and vinylic C4 all showed chemical shifts that were within the expected range for those types carbons. The α-methyl group in **15** exhibited a large upfield shift at –5.3 ppm. The methylene carbons C7,8 of the *n*-butyl groups were not uniquely assigned but were in close agreement with the analogous carbons in (n-Bu)$_4$Ge.

The carbon assignments of 2,2-di-*n*-butyl-2-germabicyclo[2.2.1]heptane (**16**) were not as straightforward as the precursor. Analogies were drawn from the parent norbornane[16] and from 2-silabicyclo[2.2.1]heptane.[5,18] An APT NMR experiment allowed assignment of the bridgehead carbons C1,4 and the methyl carbons C11,15. The α-methylene C3 was assigned by virtue of its upfield

---

(16) Lippma, E.; Pehk, T.; Belikova, N. A.; Bobleva, A. A.; Kalinchenko, A. N.; Ordubadi, M. D.; Plate, A. E. *Org. Magn. Reson.* **1976**, *8*, 74.

(17) Liepins, E.; Zicmane, I.; Lukevics, E. *Zh. Obshch. Khim.* **1982**, *56*(4), 896. ^{13}C NMR: C-1, 12.3; C-2, 27.7; C-3, 26.8; C-4, 13.8 ppm in (n-Bu)$_4$Ge.

(18) Hosomi, A.; Masashi, M.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2784.

Table III. Summary of Crystallographic Data for 6

formula	$C_{20}H_{22}Ge$
formula wt	334.52
cryst dimens, mm	0.10 × 0.17 × 0.20
cryst syst	orthorhombic
space group	$Pna2_1$-C_{2v} (No. 33)
radtn	Mo Kα (λ = 0.71073 Å)
lattice dimens	
a, Å	7.912 (2)
b, Å	31.565 (5)
c, Å	6.530 (2)
Z	4
density(calcd), g/cm^3	1.421
data coll range	
4.0°/min	3.0° < 2θ < 43.0°
3.0°/min	43.0° < 2θ < 55.0°
cryst decay	none
temp of study, °C	20
no. of data collected	2228
rejection criterion	$3.0\sigma(I)$
no. of data for refinement	1483
$\mu_{\mathrm{Mo\,K}\alpha}$, cm^{-1}	18.464
abs corr	empirical (ψ scans)

chemical shift. Since C5 was farthest removed from the germanium, it was assigned a chemical shift of 29.7 ppm, similar to C5 in norbornane. The assignment of C7 was based on its similarity to the corresponding atom in the norbornane and the silanorbornane systems.

The assignment of C6 was not trivial. Attempts to assign it by analogy met with only moderate success because of the closeness in chemical shift to the β-methylenes in the *n*-butyl groups. The methylene carbons C9,10,13,14 were tentatively assigned on the basis of the similarity to those carbons in (n-Bu)$_4$Ge.[17] The assignment of the α-methylenes C8,12 were based on analogy to the parent 2-silabicyclo[2.2.1]heptane.[5,18] In that system the *exo*-carbon absorbed 0.8–2.9 ppm downfield of the *endo*-carbon. The chemical shifts for the *exo*-methylene C8 and the *endo*-methylene C12 were tentatively assigned as 12.4 and 10.5 ppm, respectively.

The 60-MHz ^{1}H NMR spectra of the precursors 13–15 had some distinguishing features. The vinyl protons were observed as a singlet in the range 5.6–5.8 ppm. The four allylic protons were observed as a complex multiplet ranging from 2.6 to 3.5 ppm but were hard to distinguish from the complex multiplet of the remaining protons. The remaining protons were observed as a complex multiplet ranging from 0.5 to 2.8 ppm. The proton directly attached to germanium in 14 was observed as a complex multiplet centered at 3.7 ppm. The methyl protons directly bonded to the germanium in 15 absorbed as a singlet at 0.1 ppm.

The 60-MHz ^{1}H NMR spectrum for the 2,2-di-*n*-butyl-2-germabicyclo[2.2.1]heptane (16) was nondiscriminate. All of the protons absorbed as a very complex multiplet from 0.5 to 3.6 ppm.

Crystal and Molecular Structure of 6. A summary of the crystallographic refinement for the X-ray diffraction study of 6 is given in Table III. Final fractional atomic coordinates, bond lengths, and bond angles are given in Tables IV–VI, respectively. A perspective view of the structure of 6 is given in Figure 1.

The crystallographic asymmetric unit consists of one discrete general position $Ph_2Ge(C_7H_{12})$ moiety which possesses no rigorous internal symmetry. The results of structural refinement indicate that there are no particularly significant intermolecular contacts within the lattice, and with the exception of packing considerations, the structure presented in Figure 1 should be representative of the isolated molecule. There are few surprising structural features evident from the inspection of Tables III–VI. The tetrahedrally bonded Ge center possesses bonds to phenyl carbons C9,15 of 1.957 (6) and 1.941 (6) Å, respectively, and two cyclic sp^3 carbon atoms C2,4 at 1.943 (6) and 1.936 (6) Å, respectively. The two phenyl rings adopt a geometry in which they are almost perpendicular (89.3°) to each other. The phenyl and sp^2 C–Ge distances in previously published work[19] generally lie in the range

Table IV. Atomic Fractional Coordinates for Crystalline 6[a]

atom[b,c]	x	y	z	B_{eq},[d] Å^2
C1	0.193 (1)	0.0316 (3)	−0.191 (2)	4.1 (2)
C2	0.042 (1)	0.0631 (3)	−0.177 (2)	3.5 (2)
Ge3	0.0930 (1)	0.11085 (3)	0.0000 (–)	3.17 (1)
C4	0.258 (1)	0.0880 (4)	0.188 (2)	4.1 (2)
C5	0.361 (1)	0.0510 (3)	0.110 (2)	4.3 (2)
C6	0.468 (1)	0.0628 (4)	−0.079 (2)	4.8 (2)
C7	0.356 (1)	0.0550 (4)	−0.274 (2)	4.9 (3)
C8	0.245 (1)	0.0163 (3)	0.021 (2)	4.6 (2)
C9	−0.106 (1)	0.1290 (3)	0.154 (2)	3.5 (2)
C10	−0.175 (1)	0.1019 (3)	0.302 (2)	4.1 (2)
C11	−0.305 (1)	0.1150 (4)	0.427 (2)	6.0 (3)
C12	−0.370 (1)	0.1544 (5)	0.414 (2)	6.6 (3)
C13	−0.305 (2)	0.1813 (4)	0.266 (3)	6.7 (3)
C14	−0.174 (1)	0.1683 (3)	0.138 (2)	4.7 (2)
C15	0.178 (1)	0.1590 (3)	−0.153 (2)	3.4 (2)
C16	0.119 (1)	0.1690 (3)	−0.346 (2)	4.3 (2)
C17	0.178 (1)	0.2035 (3)	−0.458 (2)	5.4 (3)
C18	0.298 (1)	0.2292 (3)	−0.366 (2)	5.6 (3)
C19	0.360 (1)	0.2200 (4)	−0.185 (3)	5.9 (3)
C20	0.301 (1)	0.1852 (3)	−0.072 (2)	4.8 (2)
H1A	0.157	0.009	−0.277	5.0
H2A	0.018	0.073	−0.311	5.0
H2B	−0.054	0.049	−0.125	5.0
H4A	0.334	0.110	0.223	5.0
H4B	0.200	0.079	0.308	5.0
H5A	0.426	0.043	0.225	5.0
H6A	0.500	0.092	−0.073	5.0
H6B	0.566	0.045	−0.085	5.0
H7A	0.326	0.081	−0.336	5.0
H7B	0.414	0.038	−0.369	5.0
H8A	0.149	0.013	0.106	5.0
H8B	0.305	−0.010	0.012	5.0
H10	−0.132	0.074	0.315	5.0
H11	−0.350	0.096	0.525	5.0
H12	−0.456	0.164	0.504	5.0
H13	−0.351	0.209	0.251	5.0
H14	−0.132	0.187	0.037	5.0
H16	0.033	0.152	−0.405	5.0
H17	0.138	0.209	−0.592	5.0
H18	0.335	0.254	−0.434	5.0
H19	0.447	0.237	−0.129	5.0
H20	0.347	0.179	0.060	5.0

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit; where not given, parameter was fixed. [b] Atoms are labeled in accordance with Figure 1. [c] All hydrogen atoms were generated by using idealized geometry and held in fixed positions in cycles of least-squares refinement. [d] Equivalent isotropic thermal parameter (B_{eq}) is defined as $^4/_3$-$[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

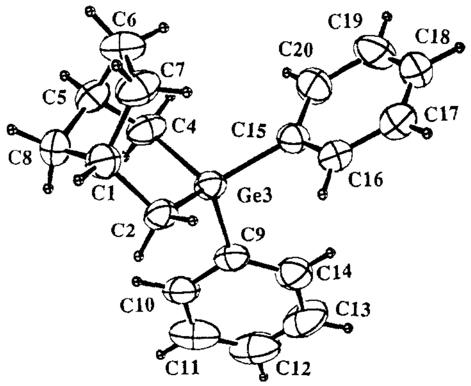


Figure 1. ORTEP drawing of 6.

Table V. Bond Lengths (Å) in Crystalline 6[a]

C1–C2	1.557 (9)	C9–C10	1.398 (8)
C1–C7	1.576 (10)	C9–C14	1.358 (8)
C1–C8	1.521 (13)	C10–C11	1.376 (9)
C1–H1	0.95	C10–H10	0.95
C2–H2A	0.95	C11–C12	1.349 (12)
C2–H2B	0.95	C11–H12	0.95
Ge3–C2	1.943 (6)	C12–C13	1.384 (13)
Ge3–C4	1.936 (6)	C12–H12	0.95
Ge3–C9	1.957 (6)	C13–C14	1.394 (10)
Ge3–C15	1.941 (6)	C13–H13	0.95
C4–C5	1.506 (9)	C14–H14	0.95
C4–H4A	0.95	C15–C16	1.380 (9)
C4–H4B	0.95	C15–C20	1.385 (8)
C5–C6	1.545 (9)	C16–C17	1.394 (9)
C5–C8	1.542 (10)	C16–H16	0.95
C5–H5	0.95	C17–C18	1.385 (10)
C6–C7	1.567 (10)	C17–H17	0.95
C6–H6A	0.95	C18–C19	1.314 (15)
C6–H6B	0.95	C18–H18	0.95
C7–H7A	0.95	C19–C20	1.404 (10)
C7–H7B	0.95	C19–H19	0.95
C8–H8A	0.95	C20–H20	0.95
C8–H8B	0.95		

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure; hydrogen atoms were not refined. Atoms are labeled in accordance with Figure 1.

Table VI. Bond Angles (deg) in Crystalline 6[a]

C2–C1–C7	110.3 (5)	C6–C7–H7B	111
C2–C1–C8	111.0 (6)	H7A–C7–H7B	110
C7–C1–C8	104.0 (5)	C1–C8–C5	106.0 (6)
C2–C1–H1	106.2	C1–C8–H8A	111
C7–C1–H1	113.2	C1–C8–H8B	111
C8–C1–H1	112.2	C5–C8–H8A	110
C1–C2–Ge3	111.7 (4)	C5–C8–H8B	110
C1–C2–H2A	109	H8A–C8–H8B	109
C1–C2–H2B	109	Ge3–C9–C10	119.3 (4)
Ge3–C2–H2A	109	Ge3–C9–C14	123.1 (5)
Ge3–C2–H2B	109	C10–C9–C14	117.3 (6)
H2A–C2–H2B	109	C10–C11–C12	121.4 (7)
C2–Ge3–C4	103.2 (2)	C10–C11–H11	119
C2–Ge3–C9	111.5 (2)	C12–C11–H11	119
C2–Ge3–C15	111.8 (2)	C11–C12–C13	118.1 (7)
C4–Ge3–C9	109.2 (2)	C11–C12–H12	121
C4–Ge3–C15	112.7 (2)	C13–C12–H12	121
C9–Ge3–C15	108.4 (2)	C12–C13–C14	120.8 (7)
Ge3–C4–C5	115.9 (4)	C12–C13–H13	120
Ge3–C4–H4A	108	C14–C13–H13	120
Ge3–C4–H4B	108	C9–C14–C13	121.1 (8)
C5–C4–H4A	108	C9–C14–H14	119
C5–C4–H4B	108	C13–C14–H14	120
H4A–C4–H4B	109	Ge3–C15–C16	122.1 (5)
C4–C5–C8	111.2 (5)	Ge3–C15–C20	120.9 (5)
C4–C5–C6	112.2 (6)	C16–C15–C20	117.0 (6)
C6–C5–C8	101.1 (7)	C15–C16–C17	122.7 (7)
C4–C5–H5	104	C15–C16–H16	119
C6–C5–H5	114	C17–C16–H16	119
C8–C5–H5	115	C16–C17–C18	118.2 (8)
Ge3–C6–C7	107.5 (5)	C16–C17–H17	121
C5–C6–H6A	110	C18–C17–H17	121
C5–C6–H6B	110	C17–C18–C19	121.1 (8)
C7–C6–H6A	110	C17–C18–H18	120
C7–C6–H6B	110	C19–C18–H18	119
H6A–C6–H6B	110	C18–C19–C20	121.5 (6)
C1–C7–C6	104.8 (6)	C18–C19–H19	119
C1–C7–H7A	111	C20–C19–H19	119
C1–C7–H7B	111	C15–C20–C19	120.0 (7)
C6–C7–H7A	111	C15–C20–H20	120

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure. Hydrogen atoms were not refined. Labeled in accordance with Figure 1.

of 1.925–1.930 Å, while cyclic sp^3 C–Ge for 5-, 6-, and 11-membered rings average approximately 1.950–1.955 Å. While the differences between carbon–germanium distances in 6 and those of previously reported germacyclanes are seemingly disparate, no special significance can be concluded since closely related structures are not available and the relative standard errors in this study are high. The distortion of the tetrahedral angles about the Ge atom is minimal; bond angles average 109.5° while the C2–Ge3–C4 angle in the ring is 103.2 (2)°.

The bicyclic ring system does show significant distortion about the germanium and carbon atoms C2,4. The three-atom plane of C2/Ge3/C4 (fold angle for the heterocyclohexane ring) makes a dihedral angle of 155.6 (4)° with the four-atom least-squares plane C1/C2/C4/C5, indicating a flattening of the chair conformation of the ring (compared to the similar angle in the parent bicyclo[3.2.1]octane hydrocarbon[15c] at 138.9°). A parallel flattening of 146.5–148.1° is also noted in 3,3-diphenyl-3-phosphoniabicyclo[3.2.1]octane bromide.[3b] The flattening in 6 is also reflected in the cyclic torsional angles that involve germanium: C1–C2–Ge3–C4 and C2–Ge3–C4–C5, 26.9 (4)° and 25.5 (4)°, respectively. These compare to computed values (MM2, MM1)[20] for the torsional angles of germacyclohexane and derivatives of 42–47°. The magnitude of flattening as compared to the molecular mechanics calculations might be ascribed to steric interactions of the *endo*-phenyl ring, but the nonbonded distances between C15, C16, and C20 and carbons C6,7 are significantly longer than the van der Waals contact distance of approximately 3.40 Å, the shortest of these being C6–C15, 3.834 (7) Å, C7–C15, 3.565 (7) Å.

Experimental Section

Unless noted, all reactions were carried out in flame-dried glassware under an inert atmosphere of nitrogen. Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR (60 MHz) spectra were recorded on a Varian EM 360L or a JEOL JNM-FX60Q spectrometer. $CDCl_3$ was the solvent, and $CHCl_3$ (7.25 ppm) was used as the internal standard. ^{13}C NMR (15 MHz) spectra were recorded on a JEOL JNM-FX60Q spectrometer; $CDCl_3$ was employed as the solvent and used as the internal standard (79.0 ppm). Ozonolysis was performed using a Welsbach ozonator Model T-408, using pure, dry oxygen (Amerigas). Analytical gas chromatography was performed on a Hewlett-Packard Model 5710A (flame ionization) with a Model 3380 A integrator. Preparative GC was performed on a Hewlett-Packard FM Model 700 or a Gow-Mac series 580. Preparative HPLC was performed using a Waters M-6000A pump equipped with a Waters variable-wavelength UV detector tuned to 254 nm. A C-18 econosphere column (250 × 10 mm) was used. GC-MS spectra were obtained by using a Hewlett-Packard Model 5970 spectrometer at 70 ev. TLC was carried out using Eastman chromagram No. 13179 silica gel sheets without an indicator and were developed with iodine. Flash chromatography was carried out using Baker silica gel 60, 60–200 mesh, or Aldrich silica gel 60, 210–400 mesh. Column dimensions for micro samples were 10 in. by $^1/_2$ in.; for larger samples a 36 in. by 1 in. column was used. Endo–exo isomer ratios were calculated from ^{13}C NMR spectra and where possible ^1H NMR spectra and analytical GC data. Tetrahydrofuran was dried by distillation from sodium/potassium/benzophenone ketyl and stored under N_2 over Linde 4-Å molecular sieves. Dry diethyl ether was obtained by distillation from methylmagnesium iodide. Benzene was obtained from the Aldrich Chemical Co. and was used without purification. Dichlorodiphenylgermane and dichlorodimethylgermane were purchased from Organometallics and used directly. Di-*n*-butyldichlorogermane was a gift from the

---

(19) (a) Lindeman, S. V.; Shklover, V. E.; Yu, T.; Vasnyova, N. A.; Sladkov, A. M. *Cryst. Struct. Commun.* **1981**, *10*, 827. (b) Ross, L.; Drager, M. *Chem. Ber.* **1982**, *115*, 615. (c) Drager, M.; Ross, L. *Z. Naturforsch, Tiel B* **1984**, *39*, 868. (d) Preut, H.; Kocher, J.; Nuemann, W. P. *Acta Crystallogr., C* **1985**, *41*, 912. (e) Faucher, A.; Mazerolles, P.; Jaud, J.; Galy, J. *Acta. Crystallogr., B* **1978**, *34*, 442.

(20) Takeuchi, Y.; Masakatsu, S.; Tanaka, K.; Tomoda, S.; Ogawa, K.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 7.

Eagle-Picher Chemical Co. and was used without purification. Elemental analyses were performed by Midwest Microlab Ltd., Indianapolis, IN, or Mic-Anal of Tucson, AZ. High-resolution mass spectrometry was performed by the Midwest center for Mass Spectrometry, an NSF regional instrumentation facility.

***cis*-Cyclopentane-1,3-dicarboxylic Acid (1).** To a 3-L three-neck flask equipped with a mechanical stirrer, two Claisen adaptors, a thermometer, and a pH combination electrode was added 1 L of distilled water and a solution of 50 g (0.53 mol) of norbornene in 200 mL of isooctane (spectroscopic grade). The mixture was stirred, and CO_2 was bubbled into the solution at a rate of 2 L/min for 5 min. With the CO_2 continuously passing through the solution, 224 g (1.42 mol) of solid, powdered $KMnO_4$ was added 1 g at a time for the first 10 g and then in 10-g increments for the remainder of the reaction. The temperature was kept at 25 °C by external cooling. The pH was monitored and adjusted to 7.0; during the $KMnO_4$ addition the solution became basic and was brought back to pH 7.0 by the CO_2. After the addition was complete, the mixture was treated with 400 g (3.85 mol) of $NaHSO_3$ in 10-g increments with stirring. The tan reaction mixture was separated by suction filtration. The filtrate was acidified with concentrated HCl to a pH of 2.0 and then continuously extracted with diethyl ether in a 3-L continuous extractor for 24 h. The ether was removed and the white product air dried. This afforded 84 g (76%) of a white solid, mp 118–120 °C (lit.[7] mp 121 °C) after recrystallization from a minimum amount of H_2O.

Dimethyl *cis*-Cyclopentane-1,3-dicarboxylate (2). To a solution of 130 mL of anhydrous methanol and 75 g (0.72 mol) of 2,2-dimethoxypropane was added 60 g (0.38 mol) of **1** and 400 mg of *p*-toluenesulfonic acid. The solution was allowed to stand for 3 days at room temperature. The appearance of the product was monitored by ^1H NMR (δ 3.8, $COOCH_3$) spectroscopy. The solvent was removed, and the product was washed with 30 mL of H_2O and then 30 mL 5% $NaHCO_3$ and then dried over Na_2SO_4. The crude product was distilled and the fraction boiling at 67–69 °C (0.1 mmHg) was collected. This afforded 65 g (95%) of **2** (lit.[7] bp 138 °C, 25 mmHg).

***cis*-1,3-Bis(hydroxymethyl)cyclopentane (3).** The diol was prepared by reduction of 0.3 mol of **2** in diethyl ether with 0.6 mol of LAH by using standard methods. Distillation gave a 72% yield of **3**, bp 100–103 °C (0.1 mmHg) (lit.[7] bp 118 °C (0.5 mmHg)).

Alternative Method for the Preparation of 3. A solution of 52.7 g (0.56 mol) of norbornene in 600 mL of absolute methanol was cooled to −78 °C. Pure oxygen was bubbled through the solution, using a gas dispersion tube, for 15 min. Ozone was bubbled through the solution at a rate of 1.2 L of oxygen/min for 6 h. The solution turned blue when the reaction was complete. Dry nitrogen was bubbled through the solution for 30 min, and the solution warmed to −35 °C. Then 35.0 g (0.92 mol) of solid $NaBH_4$ was added in portions over 3 h. The temperature was kept below 0 °C during the addition period. The mixture was stirred at room temperature for 12 h. The solution was cooled in an ice bath, and the reaction quenched by addition of 250 mL of H_2O. This was stirred at room temperature for 4 h. The solution was evaporated to near dryness and the resulting residue extracted with 5 × 50 mL of hot ethyl acetate. The ethyl acetate was evaporated to dryness, and the resulting residue distilled under vacuum to yield 55.9 g (73%) of **3**, bp 85–93 °C (0.03 mmHg) (lit.[7] bp 118 °C (0.5 mmHg)).

***cis*-1,3-Bis(((*p*-tolylsulfonyl)oxy)methyl)cyclopentane (4).** This material was prepared in 75% yield from 0.2 mol of **3** in 150 g of pyridine and 0.4 mol of tosyl chloride by using conventional methods. The crude product was air dried. One recrystallization from acetonitrile afforded 70 g (75%) of suitably pure material, mp 108–110.5 °C (lit.[7] mp 108.5–109 °C). In one instance a mixture of *cis*- and *trans*-diols was produced from the ozonolysis of norbornene. This in turn was converted to a cis–trans mixture of tosylates. The desired cis isomer was obtained by fractional recrystallization from acetonitrile to give pure product, mp 109–110 °C. The *trans*-tosylate is the more soluble isomer (mp 85–89 °C).

***cis*-1,3-Bis(bromomethyl)cyclopentane (5).** The preparation of this compound has previously been described.[3]

3,3-Diphenyl-3-germabicyclo[3.2.1]octane (6). A solution of 4.1 g (16.1 mmol) of *cis*-1,3-bis(bromomethyl)cyclopentane (**5**) in 60 mL of ether was added dropwise, over 45 min, to a solution containing 0.8 g (32.1 mmol) of magnesium in 20 mL of ether. The mixture was allowed to stir at room temperature for 4 h. Two layers formed; 20 mL of benzene was added to make the mixture homogeneous. A 1-L, three-necked flask was equipped with two Claisen adaptors, two slow-drop adaptors,[12] a reflux condenser, and mechanical stirrer. To the flask was added 300 mL of benzene. To one addition funnel, which contained 70 mL of benzene, was cannulated, under nitrogen pressure, the bis-Grignard reagent of **5**. To the other addition funnel was added 4.4 g (14.9 mmol) of dichlorodiphenylgermane and 75 mL of benzene. The two liquids were allowed to drop slowly and simultaneously into the vigorously stirred, refluxing benzene over 27 h. The mixture was allowed to stir at reflux an additional 6 h after completing the addition; a white precipitate gradually settled out of the solution. The reaction was quenched by addition of 80 mL of water and 5 g of NH_4Cl. The organic layers were separated, dried over $MgSO_4$, and concentrated first on a rotary evaporator and then in vacuo (0.05 mmHg). Crystals were observed in the residue. Recrystallization of the crude product from 95% ethanol afforded white needles, mp 57–59 °C. Flash chromatography was also used to purify the crude product, to yield 1.96 g (41%) of the desired compound **6**: TLC (pentane) R_f 0.83; ^1H NMR δ 7.1–7.6 (m, 10 H), 2.2–2.6 (m, 2 H), 1.1–1.8 (m, 10 H). Anal. Calcd for $C_{19}H_{22}Ge$: C, 70.66; H, 6.87. Found: C, 70.79; H, 6.87.

3,3-Dimethyl-3-germabicyclo[3.2.1]octane (7). The reaction of dichlorodimethylgermane with the bis-Grignard of **5** under the conditions previously described for **6** gave the desired compound in 21% yield. The sample was purified by vacuum molecular distillation (0.1 mmHg, 75–80 °C external bath). Further purification was achieved by preparative GC using a 20 × $^1/_4$ in., 5% OV 17 on chromosorb P column, with a column temperature of 117 °C, t_r 14 min. ^1H NMR δ 2.1–2.6 (m, 2 H), 0.9–1.7 (m, 10 H), 0.2 (s, 3 H), 0.05 (s, 3 H). Anal. Calcd for C_9H_{18} Ge: C, 54.37; H, 9.12. Found: C, 54.29; H, 9.31.

3-Bromo-3-phenyl-3-germabicyclo[3.2.1]octane (8). A solution containing 0.30 g (0.93 mmol) of **6** in 15 mL of ethyl bromide was cooled to −78 °C and covered to exclude light. To this was added, dropwise over 1 h, a solution of 0.20 g (1.3 mmol) of bromine in 10 mL of ethyl bromide. The mixture was allowed to warm to room temperature and stirred for 14 h; the reaction was complete upon the decoloration of the bromine solution. The solvent was removed under reduced pressure, and the resulting liquid purified by vacuum molecular distillation (0.05 mmHg, 85–90 °C external bath). This afforded 0.29 g (95%) of a 55:45 isomeric mixture of **8**: ^1H NMR δ 7.1–7.6 (m, 5 H), 2.4–2.8 (m, 2 H), 1.3–2.3 (m, 10 H). Anal. Calcd for $C_{13}H_{17}BrGe$: C, 47.93; H, 5.26. Found: C, 48.22; H, 5.37.

3-Hydrido-3-phenyl-3-germabicyclo[3.2.1]octane (9). To a solution containing 0.1 g (0.3 mmol) of **8** in 20 mL of diethyl ether was added, in one portion, 0.05 g (1.3 mmol) of lithium aluminum hydride. The mixture was allowed to stir at reflux for 14 h. The reaction was quenched by successive treatment with 0.5 mL of water, 1.5 mL of 10% NaOH, and 0.5 mL of water. This resulted in the formation of a semisolid mass, which was washed with 3 × 15 mL of diethyl ether and 15 mL of CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude liquid was purified by flash chromatography to yield 0.09 g (95%) of a 65:35 isomeric mixture of **9**: TLC (pentane) R_f 0.84; ^1H NMR δ 7.2–7.8 (m, 5 H), 4.0–4.4 (m, 3 H), 0.8–2.3 (m, 10 H). Anal. Calcd for $C_{13}H_{18}Ge$: C, 63.24; H, 7.34. Found: C, 62.96; H, 7.32.

3-Fluoro-3-phenyl-3-germabicyclo[3.2.1]octane (10). To a solution containing 0.1 g (0.3 mmol) of **8** in 15 mL of benzene was added 0.1 g (0.8 mmol) of silver fluoride. The mixture was allowed to stir at room temperature for 18 h. The black liquid was filtered and concentrated under reduced pressure. When the crude liquid was subjected to vacuum molecular distillation, it crystallized on the cold finger. Sublimation (0.3 mmHg, 50–60 °C external bath) afforded 0.06 g (76%) of a 61:39 isomeric mixture of **10**: mp 58–62 °C; ^1H NMR δ 7.2–7.8 (m, 5 H), 2.4–3.0 (m, 2 H), 1.5–2.3 (m, 10 H). Anal. Calcd for $C_{13}H_{17}FGe$: C, 58.95; H, 6.47. Found: C, 58.71; H, 6.68.

3-Methyl-3-phenyl-3-germabicyclo[3.2.1]octane (11). To a solution containing 0.15 g (0.46 mmol) of **8** in 20 mL of benzene was added, in one portion, 1 mL of a 7.6 M solution of CH_3MgBr

(7.6 mmol) in THF. The mixture was allowed to stir at reflux for 60 h. The heterogeneous solution was then filtered and concentrated under reduced pressure. The resulting liquid was purified by HPLC to yield 0.07 g (55%) of the desired compound as a 52:48 *endo*-methyl *exo*-methyl isomer mixture. The isomers were separated by using preparative reverse-phase HPLC. The liquid was dissolved in a 50:50 acetonitrile–acetone mixture. The mobile phase was 80:20 methanol–water at an 8 mL/min flow rate. Peak 1, t_r 32 min, was assigned to the *exo*-methyl isomer and peak 2, t_r 38 min, to the *endo*-methyl isomer. ^{1}H NMR (*exo*-methyl isomer) δ 7.1–7.7 (m, 5 H), 2.3–2.7 (m, 2 H), 1.0–2.1 (m, 10 H), exo-CH$_3$ 0.4 (s, 3 H); (*endo*-methyl isomer) δ 7.3–7.7 (m, 5 H), 2.5–2.9 (m, 2 H), 1.2–2.2 (m, 10 H), *endo*-CH$_3$ 0.75 (s, 3 H). Anal. Calcd for $C_{14}H_{20}Ge$: C, 64.50; H, 7.73. Found: C, 64.20; H, 7.76.

Attempted CsF Equilibration of 11. To a 5-mL flask equipped with a magnetic stirring bar and a reflux condenser was added 90 mg of the *exo*-3-methyl-3-phenyl-3-germabicyclo[3.2.1]octane, 26 mg of solid CsF, and 4 mL of dry DMF. The reaction was monitored by analytical gas chromatography using a 5% SE 30 on chromosorb W column, 6 ft × $^1/_4$ in., 80–150 °C, 8 °C/min ramp. The peak heights of the isomers were integrated at different time intervals. The retention time for the exo isomer was 16.3 min, and the endo isomer 18.1 min. After this was stirred for 120 h at room temperature, 120 h at 90 °C, or 96 h at reflux (156 °C) no isomer interconversion was evident. Varying the ratio of CsF to substrate had no effect. Changing the solvent from DMF to THF had no effect. The use of the F$^-$ source, tris(dimethylamino)sulfur trimethylsilyl difluoride (TASF) did not give isomer interconversion. Equilibration was also attempted on a 12:88 exo–endo mixture using the same conditions. This also failed to give isomer interconversion.

4-(Bromomethyl)cyclopentene (12). The compound was synthesized in a seven-step sequence following the method of Greene and Depres[9] and Johnson[10] in 50% overall yield.

Di-*n*-butylchloro(3-cyclopentenylmethyl)germane (13). A solution of 5.0 g (0.03 mol) of 12 in 25 mL of THF was added dropwise, to a flask containing 0.9 g (0.04 mol) of magnesium metal, 15 mL of THF, and 10 drops of 1,2-dibromoethane. The addition rate was varied to allow gentle reflux. The mixture was allowed to stir at reflux for 2 h after the addition. To another flask was added 7.2 g (0.03 mol) of di-*n*-butyldichlorogermane and 60 mL of THF. The preformed Grignard reagent of 12 was then cannulated, under N$_2$ pressure, to an addition funnel on this flask. The solution was cooled to −78 °C, and the Grignard reagent added dropwise over 45 min. The reaction was monitored by removing small aliquots and subjecting them to a Gilman's test.[21] After stirring for 3 h at −78 °C, the mixture was allowed to warm to room temperature and stir for 30 min. The solvent was removed by distillation (20 mm) and the crude product distilled at 90–150 °C (20 mmHg). This afforded 3.51 g (45%) of the crude chloride, which was further purified by distillation through a 6-in. Vigreux to yield 1.95 g (24%) of 13, bp 75–80 °C (0.05 mmHg). ^{1}H NMR δ 5.5–5.7 (s, 2 H), 1.7–2.8 (complex m, 4 H), 0.5–1.8 (complex m, 21 H). A HRMS was run at the Midwest Center for Mass Spectrometry. A molecular ion peak was not found using both HREI full scan and HREI peakmatch programs; however, the M − Cl peak was observed. HRMS, *m/z* (M − Cl) Calcd for $C_{14}H_{27}{}^{70}Ge$ 265.1366, found 265.1356.

Di-*n*-butyl(3-cyclopentenylmethyl)germane (14). To a solution of 0.20 g (5.1 mmol) of solid LAH in 40 mL of diethyl ether was added dropwise, over 5 min, a solution of 0.40 g (1.5 mmol) of 13 in 20 mL of diethyl ether. The mixture was allowed to reflux for 12 h. The reaction mixture was quenched by sequential addition of 0.2 mL of H$_2$O, 0.2 mL of 10% NaOH, and 0.6 mL of H$_2$O. The resulting semisolid was separated and triturated with 2 × 20 mL of CH$_2$Cl$_2$ and 20 mL of CHCl$_3$. The combined organic fractions were dried over MgSO$_4$ and concentrated first on the rotary evaporator (20 mmHg) then in vacuo (0.2 mmHg). This afforded 0.30 g (80%) of 14 with exceptional purity. An analytical sample was prepared by vacuum molecular distillation (0.2 mmHg, 100 °C). The compound decomposed on standing, and a satisfactory combustion analysis was never obtained. ^{1}H NMR δ 5.6 (s, 2 H), 3.6–3.8 (m, 1 H), 0.5–2.8 (m, 25 H). IR (neat) Ge–H γ 2000 cm^{-1}. Mass spectrum (70 eV): (M$^+$) cluster 266, 268, 269, 270, and 272; (M − 1)$^+$ cluster 265, 267, 268, 269, and 271.

Di-*n*-butyl(3-cyclopentenylmethyl)methylgermane (15). To a solution of 0.5 g (1.6 mmol) of chloride 13 in 35 mL of benzene was added, in one portion, 0.9 mL (6 mmol) of a 7.6 M solution of methylmagnesium bromide in THF. The mixture was allowed to reflux for 18 h. The white solution was quenched with 2 mL of saturated NH$_4$Cl. The solvent was removed under reduced pressure (20 mmHg), and the remaining liquid subjected to vacuum molecular distillation (0.2 mmHg, 90–100 °C). Further purification was achieved by gas chromatography. A 7 ft × $^1/_4$ in., 5% OV 101 column on chromosorb W was employed with a flow rate of 25 mL/min and an oven temperature of 160 °C. This afforded a chromatogram containing four peaks, with the desired major peak having a t_r of 13 min. Preparative chromatography afforded 0.2 g (46%) of the methyl derivative 15: ^{1}H NMR δ 5.6 (s, 2 H), 1.7–2.7 (m, 5 H), 0.6–1.6 (m, 20 H), 0.1 (s, 3 H). Anal. Calcd for $C_{15}H_{30}Ge$: C, 63.66; H, 10.69. Found: C, 63.89; H, 10.63.

2,2-Di-*n*-butyl-2-germabicyclo[2.2.1]heptane (16). To a glass pressure tube[22] equipped with a magnetic stirring bar were added 0.40 g (1.6 mmol) of 14 and 0.5 mL (1.2 × 10^{-6} M) of H$_2$PtCl$_6$ in isopropyl alcohol.[23] The mixture was heated at 175–200 °C for 72 h. The mixture turned black. The mixture was cooled and then subjected to vacuum molecular distillation (0.3 mmHg, 110–130 °C external bath). This afforded 0.3 g (69%) of a clear liquid. Preparative GC was then attempted to produce an analytical sample. A 6 ft × $^1/_4$ in., 5% SE 30 column on chromosorb W was employed with a flow rate of 25 mL/min and oven temperature of 155 °C. This afforded a chromatogram containing one peak centered at t_r 9.1 min. This peak had a shoulder high in the peak, and attempts to separate the two components failed; a satisfactory combustion analysis was never achieved. The impurity likely overlapped with the major peaks of 16 in the ^{13}C NMR spectrum and showed additional peaks at 23.4 and 25.0 ppm. ^{1}H NMR δ 0.5–3.6 (very complex multiplet, 28 H). HRMS *m/z* (M$^+$) calcd for $C_{14}H_{28}{}^{72}Ge$ 268.1408, found 268.1407. (M − C_4H_9)$^+$ calcd for $C_{10}H_{19}{}^{72}Ge$ 211.0704, found 211.0715.

Single-Crystal X-ray Structure Analysis of 6. Suitable crystals of 6 were obtained from slow evaporation from 95% ethanol. Data were collected on a Nicolet P$_4$ autodiffractometer, at room temperature using graphite monochromated Mo Kα (λ = 0.710 73 Å) radiation. Twenty high-angle reflections (2θ Mo Kα > 20°) chosen as a good sampling of reciprocal space and diffractometer settings were used to align the crystal and determine a set of lattice constants.

Intensity data were collected in the ω-scan mode with a 1° wide scan and a 1° stepoff for background accumulation. Scans were accumulated over 19 equal increments and peak intensity was computed by using 13 contiguous intervals with greatest intensity. A total of 2228 reflections were collected in two concentric shells of increasing 2θ Mo Kα 3.0–43.0° and 43.0–55.0°. Six reflections were chosen for use in empirical absorption correction (ψ-scans). Standards, systematic absences, and redundant data were removed and a $I > 3.0\sigma(I)$ rejection criteria was applied to the data. The remaining 1483 reflections were reduced to a set of relative squared amplitudes, F_o, by standard Lorentz, polarization, and absorption corrections.

The coordinates for the germanium atom were deduced from a Patterson synthesis and included in initial cycles of isotopic unit-weight full-matrix least-squares refinement.[24] These refinement cycles resulted in conventional residuals of R_1 = 0.236 (unweighted, based on F) and R_w = 0.318 (weighted, based on F) for the 1483 reflections having 3.0° < 2θ Mo Kα < 55.0° and $I > 3.0\sigma(I)$. The remaining 19 atoms contained in the asymmetric unit were located in successive difference Fourier/least-squares cycles and resulted in convergence at R_1 = 0.087 and R_w = 0.118 for the 20 isotopic non-hydrogen atoms. All 20 non-hydrogen atoms were then modeled with anisotropic temperature factors and refinement yielded R_1 = 0.062 and R_w = 0.070 for unit

---

[21] (a) Gilman, H.; Schulze, F. *J. Am. Chem. Soc.* **1925**, *47*, 2002. (b) Gilman, H.; Heck, L. L. *J. Am. Chem. Soc.* **1930**, *52*, 4949.

[22] Ace Glass Catalog No. 8648-26, 178-mm Teflon screwcap.

[23] Benkeser, R. A.; Kang, J. *J. Organomet. Chem.* **1980**, C9.

[24] Data reduction and refinement utilizing the UCLA Crystallographic package. Locally edited versions of ORFLS, ORFFE, ORTEP, and DIFFMAP.

weighing. The 22 hydrogen atoms were included in the final cycles of refinement and held at idealized geometry. Final cycles included $1/\Sigma^{25}$ weighting scheme and converged at $R_1 = 0.053$ and $R_w = 0.068$ for the 1481 reflections, with an estimated standard deviation of an observation of unit weight of 1.970. In the final cycle of least-squares refinement, no shift/error was greater than 0.07 averaging less than 0.01.

Acknowledgment. We acknowledge Louis Agnew, Dr. Laddawan Borsub, and James Most for synthetic help and also Jackie Benke, Ellie Burke, and Dr. Asirur Rahman for technical assistance. We especially thank Dr. Jane Griffen, Medical Foundation of Buffalo Inc., Research Labs, Buffalo, NY, for an X-ray data search on organogermanium compounds. .The Eagle-Picher Chemical Co. provided a generous gift of di-*n*-butyldichlorogermane. High-resolution mass spectrometry was performed by the Midwest Center for Mass Spectrometry, an NSF regional instrumentation facility. A.G.S. thanks Marquette University for a research fellowship.

Registry No. **1**, 876-05-1; **2**, 39590-04-0; **3**, 3965-56-8; **4**, 55606-07-0; **5**, 58066-43-6; **6**, 126696-64-8; **7**, 126696-65-9; **8a**, 126696-66-0; **8b**, 126696-74-0; **9a**, 126696-67-1; **9b**, 126696-75-1; **10a**, 126696-68-2; **10b**, 126696-76-2; **11a**, 126696-69-3; **11b**, 126696-77-3; **12**, 80864-33-1; **13**, 126696-70-6; **14**, 126696-71-7; **15**, 126696-72-8; **16**, 126696-73-9; norbornene, 498-66-8; *trans*-1,3-bis(((*p*-tolylsulfonyl)oxy)methyl)cyclopentane, 70723-29-4; dichlorodiphenylgermane, 1613-66-7; dichlorodimethylgermane, 1529-48-2; di-*n*-butyldichlorogermane, 4593-81-1.

Supplementary Material Available: A list of anisotropic thermal parameters for **6** (1 page); a structure factor table (13 pages). Ordering information is given on any current masthead page. A diagram of the "slow drop" adaptor is also available on direct request to the authors.

---

(25) Hahn, T. *International Tables for Crystallography*; Riedel: Dordrect, Holland, 1983; Vol. A.

Investigation of the Electrochemical Behavior and Electronic Structure of (μ-Butatriene)hexacarbonyldiiron Complexes

Domenico Osella,* Olimpia Gambino, and Roberto Gobetto

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino,
Via P. Giuria 7, 10125 Torino, Italy

Piero Zanello* and Franco Laschi

Dipartimento di Chimica, Università di Siena, Siena, Italy

Catherine E. Housecroft* and Steven M. Owen

University Chemical Laboratory, Cambridge, U.K.

Received September 11, 1989

The redox chemistry of (μ-butatriene)hexacarbonyldiiron compounds, $Fe_2(CO)_6(RR'C{=}C{=}C{=}CRR')$, has been investigated by electrochemical and spectroscopic methods and Fenske–Hall quantum-chemical calculations. The sequence of the electrode processes has been postulated on the basis of the response of different electrochemical techniques, electron spin resonance (ESR) spectroscopy, and chemical tests. The butatriene chain, interacting with the bimetallic $Fe_2(CO)_6$ framework in a multicentered σ/π fashion, is able to stabilize the electrogenerated anions.

Introduction

A number of stable (cumulene)hexacarbonyldiiron compounds have been reported.[1] These complexes show that the $Fe_2(CO)_6$ frame is able to stabilize through extensive σ/π coordination even the unsubstituted butatriene $H_2C{=}C{=}C{=}CH_2$, which is not isolable under usual conditions.[2]

The butatriene complexes can be synthesized by starting from iron carbonyls (i.e. $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) according to the following methods: (a) reaction with stable cumulene,[2] (b) zinc-assisted dehalogenation of alkynyl dihalides,[2] and (c) dehydroxylation of alkynediols.[3] Since these compounds are diamagnetic, the EAN formalism requires the interaction of all six π-electrons of the butatriene chain and the presence of an iron–iron bond.

Two X-ray structural determinations have been reported for $Fe_2(CO)_6$[μ-bis(biphenylylene)butatriene][4] and $Fe_2(CO)_5(PPh_3)$(μ-butatriene)[5] molecules. The butatriene chain assumes a nonlinear configuration twisted end by end by about 90°. This modification of the originally linear butatriene is dictated by the optimum overlap of the cumulene π MO's with the iron AO's. These structural descriptions have been corroborated by a ^1H NMR study in a nematic phase[6] and by a ^{13}C NMR investigation of a large number of such derivatives.[7] Finally, quantum-mechanical calculations within the CNDO scheme on some butatriene complexes[8] coupled with an UV-PES study have been performed.

---

(1) Nakamura, A. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1868. Nakamura, A.; Kim, P.-J.; Hagihara, N. *J. Organomet. Chem.* **1966**, *6*, 420. Joshi, K. K. *J. Chem. Soc. A* **1966**, 594. Joshi, K. K. *Ibid.* **1966**, 598. King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 2075.

(2) Nakamura, A.; Kim, P.-J.; Hagihara, N. *J. Organomet. Chem.* **1965**, *3*, 7.

(3) Victor, R. *J. Organomet. Chem.* **1977**, *127*, C25.

(4) Bright, D.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2465.

(5) Gerlach, J. N.; Wing, R. M.; Ellgen, P. C. *Inorg. Chem.* **1976**, *15*, 2959.

(6) Arumngam, S.; Kunwar, A. C.; Khetrapalm, C. C. *J. Organomet. Chem.* **1984**, *265*, 73.

(7) Victor, R.; Riugel, I. *Org. Magn. Reson.* **1978**, *11*, 31.

(8) Granozzi, G.; Casarin, M.; Aime, S.; Osella, D. *Inorg. Chem.* **1982**, *21*, 4073.

0276-7333/90/2309-1792$02.50/0 © 1990 American Chemical Society