The β-lactams were identified by mass spectral, infrared, and nmr data. Characteristic β-lactam carbonyl peaks at *ca.* 1745 cm^{-1} [9] in the infrared were obtained for all products while the nmr spectra showed no vinyl protons, but instead the expected multiplets [*ca.* τ 6.80 (2 H) and 7.1 (2 H)] associated with the methylene protons in four-membered lactam rings.[10]

We are exploring cyclopropanone ring enlargements as methods for preparing β-lactam derivatives of amino acids, and as routes toward the synthesis of substances related to penicillin.

Acknowledgment. This work was supported by Grant No. GM-07874 from the National Institutes of Health.

(9) (a) H. B. Kagan, J. J. Basselier, and J. L. Luche, *Tetrahedron Lett.*, 941 (1964); A. K. Bose, V. Sudarsanam, V. Anjaneyulu, and M. S. Manhas, *Tetrahedron*, **25**, 1191 (1969); (b) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1964.

(10) R. M. Moriarty and J. M. Kliegman, *Tetrahedron Lett.*, 891 (1966).

Harry H. Wasserman,* H. Wayne Adickes
Ofelia Espejo de Ochoa
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Received July 19, 1971

Germa- and Stannaundecaboranes

Sir:

Several examples of the insertion of representative elements other than carbon into boron hydride cages have been reported.[1-3] However, the absence of compounds containing group IVa elements below carbon has been surprising. Recently, we have found that reactions between $NaB_{10}H_{13}$ and $(CH_3)_3GeBr$ or $(CH_3)_3SnCl$ result in the formation of what appear to be the first examples of germa- and stannaundecaboranes, $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$.

In a typical preparation of $(CH_3)_2SnB_{10}H_{12}$, $NaB_{10}H_{13}$ (3.0 mmol), obtained from the NaH deprotonation of $B_{10}H_{14}$, was allowed to react under N_2 at 1 atm of pressure with $(CH_3)_3SnCl$ (7.3 mmol) in diethyl ether. After 1.5 hr at 75° the reaction mixture was evaporated to dryness and extracted with benzene. Removal of the benzene *in vacuo* followed by repeated high-vacuum sublimation of the residue at 94° yielded pure $(CH_3)_2SnB_{10}H_{12}$ (mp 123–124°, yield 18%). *Anal.* Calcd for $C_2B_{10}SnH_{18}$: B, 40.19; C, 8.93; H, 6.75. Found: B, 39.96; C, 9.07; H, 6.73. Under similar reaction and purification conditions, $NaB_{10}H_{13}$ (5.0 mmol) and $(CH_3)_3GeBr$ (6.0 mmol) react to form $(CH_3)_2GeB_{10}H_{12}$ (mp 82–83%, yield <5%). *Anal.* Calcd for $C_2B_{10}GeH_{18}$: B, 48.52; C, 10.78; H, 8.14. Found: B, 47.48; C, 10.52; H, 8.31.

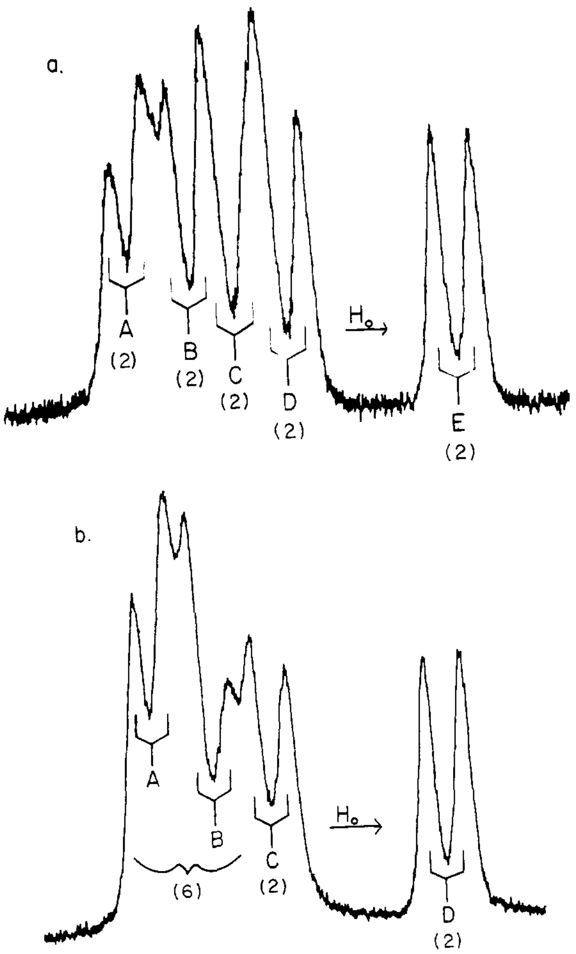


Figure 1. The 32-MHz ^{11}B nmr spectrum of (a) $(CH_3)_2GeB_{10}H_{12}$ and (b) $(CH_3)_2SnB_{10}H_{12}$ in benzene solvent. Chemical shifts (ppm relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (Hz) are, for a (A) −13.3, 145; (B) −5.5, 160; (C) +0.7, est 170; (D) +6.9, 170; and (E) 29.4, 160; and for b (A) −10.4, 148; (B) −2.4, 167; (C) 5.4, 148, and (D) 29.1, 157. Numbers in parentheses refer to relative resonance areas.

The $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$ are thermally stable and exhibit reasonable stability in air. The mass spectra of these compounds exhibit fragmentation envelopes which are entirely consistent with those expected for heteroatom-substituted decaboranes. The highest mass peaks in the low-energy (15 eV) spectra of $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$ occur at *m/e* 228 and 276, respectively, and can be assigned to the $(CH_3)_2{}^{76}Ge{}^{11}B_{10}H_{12}^+$ and $(CH_3)_2{}^{124}Sn{}^{11}B_{10}H_{12}^+$ molecular ions. Absorption peaks in the infrared spectrum of $(CH_3)_2GeB_{10}H_{12}$ at 2950, 2590, and 1970 cm^{-1} and in the spectrum of $(CH_3)_2SnB_{10}H_{12}$ at 2900, 2550, and 1910 cm^{-1} suggest the presence of B–H,[4-6] C–H,[4] and B–H–B[5,6] groups. The lack of absorptions in the 2060–2100- and 1820–1870-cm^{-1} regions[4,7] indicates the absence of Ge–H or Sn–H bonded units, respectively.

The 32.1-MHz ^{11}B nmr spectra of the new compounds are shown in Figure 1, and spectral parameters are given in the figure legend. From ^{11}B-[^1H] double-resonance experiments and examination of the 70.6-MHz high-field spectra, the spectra appear to consist of doublet resonances only, suggesting that each boron atom is terminally bonded to a single hydrogen atom. The presence of an area 2 doublet in the region of the

---

(1) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

(2) J. L. Little, J. T. Moran, and L. S. Todd, *J. Amer. Chem. Soc.*, **89**, 5495 (1967).

(3) J. L. Little and A. C. Wong, *ibid.*, **93**, 522 (1971).

(4) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(5) J. J. Miller and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **81**, 4501 (1959).

(6) W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

(7) W. P. Neumann, "The Organic Chemistry of Tin," Interscience, New York, N. Y., 1970, and references cited therein.

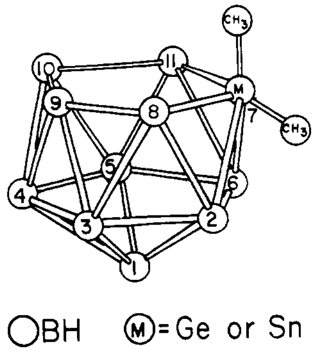


Figure 2. A possible structure for $(CH_3)_2MB_{10}H_{12}$.

2,4 borons of $B_{10}H_{14}$ (and derivatives)[8] suggests that the $(CH_3)_2Ge$ or $(CH_3)_2Sn$ group occupies a cage position such that a plane of symmetry and the equivalence of the 2,4 borons is maintained. The 60.0- and 100-MHz ^1H nmr spectra exhibit broadly spaced peaks due to terminal hydrogens on boron (area 10) and a broad singlet (area 2) at δ 5.4 ppm[9] due to bridge protons. In addition, two sharp singlet peaks of area 3 each at δ −0.46 and −0.27 ppm for $(CH_3)_2GeB_{10}H_{12}$ and δ +0.13 and −0.17 ppm for $(CH_3)_2SnB_{10}H_{12}$ are seen. In the latter case, the tin satellite peaks expected for the $(CH_3)_2Sn$ moiety are present, demonstrating conclusively that the methyl groups are bonded to the tin and not to cage boron atoms.

A possible structure for the new germa- and stannaundecaboranes inferred from the above data is shown in Figure 2. Assuming a rearrangement of the boron cage does not occur in the reaction, it seems plausible to describe the compounds as 7-substituted $(CH_3)_2Ge$ or $(CH_3)_2Sn$ undecaboranes. The methyl groups on the group IV element lie on a plane of symmetry in positions exo and endo relative to the open face of the nido 11-atom fragment. Data which allow assignment of the positions of the two bridging hydrogens are not yet available; however, they may reside in 8-9 and 10-11 positions analogous to that suggested for $B_{10}H_{12}$-transition metal complexes.[10,11]

Preliminary reactions of $(CH_3)_2SnB_{10}H_{12}$ have been carried out which support the structure postulated above. Reaction with HCl yields $(CH_3)_2SnCl_2$ and $B_{10}H_{14}$ in >95% yield.

$$(CH_3)_2SnB_{10}H_{12} + 2HCl \longrightarrow (CH_3)_2SnCl_2 + B_{10}H_{14}$$

An analogous reaction using DCl yields μ-$B_{10}H_{12}D_2$. Attempts to deprotonate $(CH_3)_2SnB_{10}H_{12}$ to form the conjugate base anions have so far been unsuccessful. Treatment with aqueous $(CH_3)_4NOH$ solutions results in the formation of mixtures of $(CH_3)_4NB_{10}H_{13}$ and $(CH_3)_4NB_{10}H_{15}$.

Further studies of the mechanism by which the CH_3 group is cleaved from $(CH_3)_3Ge$– and $(CH_3)_3Sn$– moieties in the formation reactions are in progress. The chemistry of the new group IV substituted boranes and other reactions in which they might form are being investigated and will be reported later.

Acknowledgment. This work was supported by Grant No. GP-23575 from the National Science Foundation. Our appreciation to Professor Riley Schaeffer and Mr. Richard Reitz of Indiana University for obtaining the high-field magnetic resonance data is gratefully expressed.

Robert E. Loffredo, Arlan D. Norman*
Department of Chemistry, University of Colorado
Boulder, Colorado 80302
Received June 28, 1971

---

[8] A. D. Norman and S. L. Rosell, *Inorg. Chem.*, **8**, 2818 (1969), and references cited therein.

[9] Proton resonance positions were measured relative to benzene solvent but are reported relative to $(CH_3)_4Si$.

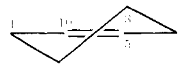
[10] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **7**, 2072 (1968).

[11] N. N. Greenwood and D. N. Sharrocks, *J. Chem. Soc. A*, 2334 (1969).

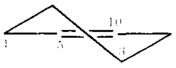
The Crystal Structure of a 5(10)-Unsaturated 3-Keto Steroid. The Conformation of Ring A[1]

Sir:

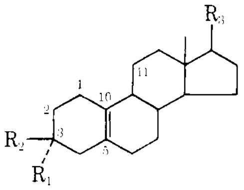
The half-chair cyclohexene[2] conformation **1** has been proposed[3] as the low-energy form of ring A in 5(10)-unsaturated steroids in order to account for (a) the stereoselective LiAl(*O-tert*-Bu)$_3$H reduction of the 3-ketone **3** leading to the 3α- and 3β-alcohols **6** and **7** in 7:1 molar ratio and (b) the nmr spectral characteristics of the epimeric 3-alcohols and 3-azides in the respective C-3 proton regions.[4] On the other hand, similar experiments[5] starting with the estra-5(10),9(11)-dien-3-one (**8**) have led to the conclusion that conformational preference in ring A of this system is very weak, though in the same direction. These results have recently provided a testing ground for semiempirical calculations of equilibrium geometry employing advanced computer methods.[6] It was calculated that ketone **3** should exist in the half-chair form **1**, favored by 0.9 kcal/mol over the alternative half-chair **2**. Ketone **8** was predicted to favor conformer **2**, but by only 0.3 kcal/mol. We have now found that the conformation of the 5(10)-unsaturated 3-ketone **4** *in the crystalline state* entails not a half-chair but a *semiplanar*[2] form of



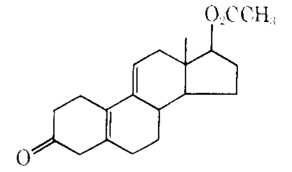
1



2



3, $R_1 = R_2 = O$; $R_3 = O_2CC_2H_5$
4, $R_1 = R_2 = O$; $R_3 = O_2CCH_2I$
5, $R_1 = R_2 = O$; $R_3 = OH$
6, $R_1 = OH$; $R_2 = H$; $R_3 = O_2CC_2H_5$
7, $R_1 = H$; $R_2 = OH$; $R_3 = O_2CC_2H_5$



8

---

[1] This work was supported by the U. S. Public Health Service under Grant No. AM09279.

[2] For a resumé of the current status of conformational analysis of cyclohexene and its derivatives, see: F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, **91**, 5774 (1969).

[3] (a) S. G. Levine, N. H. Eudy, and E. C. Farthing, *Tetrahedron Lett.*, 1517 (1963); (b) S. G. Levine, N. H. Eudy, and C. F. Leffer, *J. Org. Chem.*, **31**, 3995 (1966).

[4] Additional evidence for the preferred half-chair **1** was obtained in a study of 5(10)-estrene-2,3-*cis*-diols: S. G. Levine, D. M. Feigl, and N. H. Eudy, *Tetrahedron Lett.*, 4615 (1967).

[5] S. G. Levine and N. H. Eudy, *J. Org. Chem.*, **35**, 549 (1970).

[6] N. C. Cohen, *Tetrahedron*, **27**, 789 (1971).