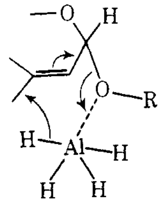
Table I. Preparation of 3-Deoxy Glycals from Some Hex-2-enopyranosides Using Different Solvents[a]

Re-act-ant	Reagent[b]	Solvent Ether	 Tetrahydro-furan	 Dioxane
1	LAH	10 hr,	4 hr	0.5 hr
	LAD	3 days		5 hr
6	LAH	14 days, incomplete	8 days	20 hr
	LAD			2 days
4	LAH	3 days	17 hr	2.5 hr

[a] The solutions were 0.135 *M* in both reactant and reagent except in the case of **4**, where the reagent was in threefold excess. The solutions were refluxed. [b] The more sluggish reaction of LAD is a phenomenon which has also been observed by Eliel.[1d]

cordingly, the β-D olefin **6** gave **21**, while the α-D anomer **1** gave **22**, as the only deuterated cyclic ether in each case.[16,17]



20

Brown has rationalized the course of LAH–AlCl$_3$ hydrogenolysis of acetals on the basis of a stable oxocarbonium intermediate.[2] It is conceivable that in complex **20** there exists considerable carbonium-ion character in the -O—C$_1$—C$_2$=C$_3$– array. In this connection it should be noted that the carbon-4 methoxy of compound **7** is available for formation of a complex (akin to **20**) which would deliver the hydride ion at carbon-2 and give the olefin at carbon-3. The complete absence of such a product in spite of the formation of **15** and **16** is in complete accord with a carbonium-ion-like intermediate.

Acknowledgments. Generous financial help from the National Research Council of Canada and Bristol Laboratories is gratefully acknowledged.

[16] The stereochemistry at carbon-3 can be determined by comparing the spacing for J_{23} with the corresponding value in the iodide **18**[9,10] (2.0 Hz) or its 3-epimer **19**[9,11] (5.2 Hz).

[17] The observed values for J_{12} and J_{23} are:[16] in **21**, 7.0 and 1.7 Hz; in **22**, 7.0 and 6.0 Hz, respectively.

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Reaction of (3)-1,2-$B_9C_2H_{13}$ with Aluminum Trialkyls. Synthesis of 1,2-$B_9C_2H_{12}AlR_2$ and 1,2-$B_9C_2H_{11}AlR$ Complexes, with Crystallographic Characterization of 1,2-$B_9C_2H_{11}Al(C_2H_5)$

Sir:

The (3)-1,2-dicarbollide ion, $B_9C_2H_{11}^{2-}$, has previously been shown capable of accepting a variety of transition metal ions[1] and main group species through insertion reactions.[2] The acidic carborane (3)-1,2-$B_9C_2H_{13}$ has been employed in an analogous insertion reaction in only one reported case, the synthesis of 1-trimethylamino-1-beryl-2,3-dicarba-*closo*-dodecaborane(12), $B_9C_2H_{11}BeN(CH_3)_3$.[3]

We wish to report the results of extending this latter synthetic route to trialkylaluminum derivatives and the structural characterization of one of the products.

The slow addition of an equimolar benzene solution of triethylaluminum to a benzene solution of (3)-1,2-$B_9C_2H_{13}$[4] under dry nitrogen, followed by heating to 50° for 1 hr, led to the release of 1 mol equiv of ethane and the initial formation of 1,2-$B_9C_2H_{12}Al(C_2H_5)_2$ (I). Removal of solvent gave a quantitative yield of crude microcrystalline product which was purified by recrystallization from cold, dry *n*-hexane: yield 79% of clear large crystals, mp 34.5–35.5° (uncor) in a sealed capillary.

Upon heating I in benzene at 77° for 25 hr, a second mole equivalent of ethane was released. Removal of solvent left a quantitative yield of crude microcrystalline 1,2-$B_9C_2H_{11}Al(C_2H_5)$ (II). Recrystallization from benzene-*n*-hexane solution gave medium-sized clear crystals of pure product: yield 72%, mp 97–99° (uncor) in a sealed capillary.

Trimethylaluminum was found to give completely analogous derivatives, 1,2-$B_9C_2H_{12}Al(CH_3)_2$ (III) and 1,2-$B_9C_2H_{11}Al(CH_3)$ (IV). In this case, however, higher temperatures and longer reaction times were necessary.

During the course of these investigations the synthesis of an ethyl-substituted aluminocarborane–tetrahydrofuran (THF) adduct, 1,2-$B_9C_2H_{11}Al(C_2H_5)\cdot 2THF$, prepared from (3)-1,2-$B_9C_2H_{11}^{2-}$ and $Al(C_2H_5)Cl_2$ in THF, was reported.[5] It was alleged by these authors from microanalysis and melting-point data that the complex contained the aluminum atom incorporated in such a manner as to form an icosahedral carborane skeleton solvated with 2 molecules of THF.

We have repeated and confirm this synthesis. Moreover, when II was dissolved in THF and excess solvent pumped off, the identical product, 1,2-$B_9C_2H_{11}Al(C_2H_5)\cdot 2THF$, was obtained. That II forms a THF adduct is not surprising, since trialkylaluminum–THF adducts have been reported previously[6,7] and the possibility of opening the icosahedral structure by THF complexation exists.

Both I and II appear to be monomeric in solution, their proton nmr spectra remaining unchanged, except for viscosity broadening, in toluene solution to −95°. Under these conditions the bridging and terminal alkyl resonances of trialkylaluminum dimers have been resolved.[8]

Both I and II were slowly hydroyzed by diffusion exposure to air and subsequently dissolved in water (they both violently enflame on contact with water). The product recovered from the aqueous solution,

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[1] M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[2] R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351 (1970).

[3] 3-Trimethylamino-3-beryl-1,2-dicarba-*closo*-dodecaborane(12), using the nomenclature system of the present communication: G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968).

[4] R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964).

[5] B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **5**, 1153 (1968).

[6] W. R. Kroll, *Chem. Commun.*, 1969, 844.

[7] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed, Methuen, London, 1967, p 305.

[8] K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *J. Phys. Chem.*, **69**, 3418 (1965).

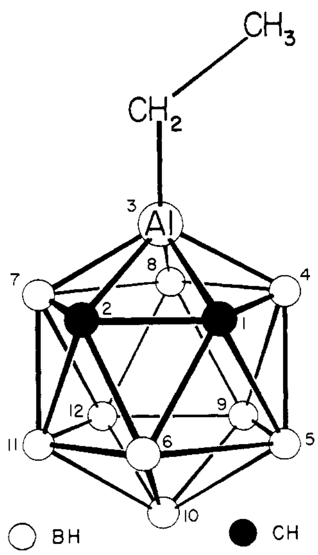

Figure 1. Structure of (3)-1,2-$B_9C_2H_{11}Al(C_2H_5)$ in schematic form.

upon precipitation with trimethylammonium chloride, proved to be (3)-1,2-$B_9C_2H_{12}^{-}NH(CH_3)_3^{+}$.[9]

Treatment of II with anhydrous HCl regenerated (3)-1,2-$B_9C_2H_{13}$ in quantitative yield.

Addition of either I or II to $TiCl_4$ in heptane produced dark red solutions similar to those described by Ziegler using trialkylaluminums.[10] Subsequent exposure of these solutions to ethylene gas catalytically produced high-molecular-weight polyethylene at ambient temperature and pressure.

Finally, it was possible to thermally rearrange II by subliming the compound through a glass-wool-filled hot tube. Only starting material was recovered at 350°, but at 410° an 85% yield of pure 1,7-$B_9C_2H_{11}$-$Al(C_2H_5)$ (V) was obtained, mp 100–102° (uncor) in a sealed capillary. Slow hydrolysis of V and precipitation with trimethylammonium chloride gave (3)-1,7-$B_9C_2H_{12}^{-}NH(CH_3)_3^{+}$.[9]

Compound II crystallizes in the centrosymmetric orthorhombic space group *Pnma* (D_{2h}^{16}; No. 62) with $a = 16.304$, $b = 7.533$, $c = 9.398$ Å, $\rho_{\text{calcd}} = 1.084$ g cm^{-3} for mol wt 188.45 and $Z = 4$.[11] X-Ray diffraction data to $\sin\theta = 0.95$ (Cu Kα radiation, $\bar{\lambda}$ 1.5418 Å) were collected on a PAILRED diffractometer using a stationary-background, ω scan, stationary-background counting sequence and equiinclination Weissenberg geometry. All data were corrected for absorption ($\mu = 10.18$ cm^{-1}). The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for nonhydrogen atoms and (fixed) isotropic thermal parameters for icosahedral hydrogen atoms, the final discrepancy index was $R_F = 8.42\%$ for the 499 independent nonzero reflections.

The molecule (II) is bisected by a crystallographic mirror plane which passes through the aluminum atom and the carbon of the methylene group. The terminal carbon of the ethyl group is disordered about the crystallographic mirror plane.[12] As shown in Figure 1, the aluminum atom is bonded to the C_2B_3 face of the $B_9C_2H_{11}^{2-}$ ion, mean distances being Al–B = 2.137 ± 0.008 and Al–C = 2.173 ± 0.007 Å. The aluminum–ethyl σ-bond length is 1.930 ± 0.006 Å. Mean distances within the B_9C_2 icosahedron are: B–B = 1.777 ± 0.012, B–C = 1.697 ± 0.011, and C–C = 1.561 ± 0.009 Å. Boron–hydrogen distances range from 1.09 ± 0.07 to 1.33 ± 0.09, averaging 1.20 ± 0.08 Å; the (icosahedral carbon)–hydrogen bond is 0.80 ± 0.08 Å in length.[13]

Having demonstrated the structure of II and the most likely analogous structures of IV and V (1,7 carbon atoms in V) two interesting points remain; the structure of I (and III, by analogy) and the nature of the THF adduct of II reported earlier.[5] These problems are currently under investigation.

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[9] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 862 (1968).

[10] K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, 67, 541 (1955).

[11] Because of the great air sensitivity of the complex, the density was not measured.

[12] Thermal parameters of all atoms in the structure are reasonable, thus militating against a possible redesignation of the molecule to the noncentrosymmetric space group *Pna*2$_1$. A plot of the distribution of X-ray intensities as a function of $\sin\theta$ does not allow us to distinguish satisfactorily between the centrosymmetric or noncentrosymmetric alternatives; see E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, 3, 210 (1950).

[13] X-Ray diffraction experiments typically give abnormally low values to (light atom)–hydrogen bonds.

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[15] Alfred P. Sloan Research Fellow, 1968–1970.

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Reactions of Optically Active Heterohelicenes. Synthesis of an Optically Active Undecaheterohelicene

Sir:

The synthesis, resolution, and racemization of a number of heterohelicenes has recently been described.[1] We now wish to report the synthesis of an optically active undecaheterohelicene, starting from the partially resolved heptaheterohelicene I as outlined in Scheme I.[2] The compound I (15 mg, $[\alpha]^{25}_{436}$ +550° ($CHCl_3$), optical purity *ca.* 7.5%) was converted into the aldehyde II, which was coupled with the phosphonium salt III. The resulting alkene IV (8 mg, $[\alpha]^{25}_{578}$ +140° ($CHCl_3$)) was irradiated for 3 hr in 120 ml of benzene in the presence of a trace of iodine using a Hanovia S 81 lamp. Evaporation of the solvent and column chromatography of the residue furnished 1.12 mg of the optically active undecaheterohelicene bis(naphtho[2,1-*b*]thieno)[1,2-*e*:1′,2′-*e*′]benzo[1,2-*b*:-4,3-*b*′]bis-[1]benzothiopene (V),[3] $[\alpha]^{25}_{578}$ +214° ($CHCl_3$). The

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[1] (a) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, 90, 5339 (1968); (b) H. Wynberg and M. B. Groen, *Chem. Commun.*, 964 (1969).

[2] This reaction sequence was successfully carried out first with racemic I on a larger scale. Correct elemental analyses (C, H, and S) were obtained for the racemic forms of all products.