Journal of Organometallic Chemistry, 85 (1975) 287—296

THE CONDENSATION REACTIONS OF BIS(*B*-HYDROXY)DICARBA-*closo*-UNDECABORANE(11)*

DANIEL GLADKOWSKI and FRED R. SCHOLER*

Department of Chemistry, Cornell University, Ithaca, New York 14850 (U.S.A.)

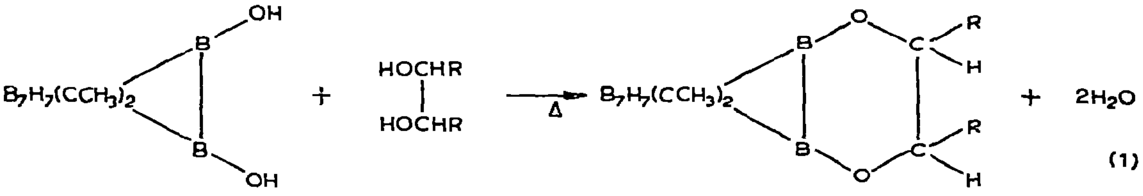
(Received August 21st, 1974)

Summary

The title compound, 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$ (11), reacts cleanly with various glycols to yield exocyclic ring systems. The glycol fragment is fused to the carborane polyhedra through two boron—oxygen—carbon bonds. The use of ^{18}O enriched ethylene glycol indicates the hydroxyl groups on the carborane polyhedra are displaced during the condensation reaction. The reaction of optically active glycols with the title compound also indicates the hydroxyl groups on the glycol must adopt a *cis* conformation during the condensation reaction.

Introduction

The synthesis and characterization of 4,7-$(OH)_2$-2,3-$(CH_3C)_2B_9H_7$ (I) and 4-(OH)-2,3-$(CH_3C)_2B_9H_8$ (II) have been reported [1, 2]. Both *B*-hydroxy derivatives are moderately stable in acid, but rapidly degrade in a basic solution. The stability is increased markedly if the boron—oxygen vertex is bonded to an organic group rather than a hydrogen atom. Unlike vicinal organic diols or the *B*-hydroxy-1,2-dicarba-*closo*-dodecaborane [3], the *B*-hydroxy-dicarba-*closo*-undecaboranes do not undergo nucleophilic substitution reactions with silylating agents, i.e. $(CH_3)_3SiCl$, alkyl halides or diazomethane, to produce the oxygen-substituted systems. However, I readily condenses with glycols to yield exocyclic ethers enhancing the stability of the oxygen-substituted carborane. Although a variety of *B*-substituted-1,2-dicarba-*closo*-dodecaborane derivatives



(1)

---

* Presented in part at the 167th ACS National Meeting.

TABLE 1

CONDENSATION PRODUCTS OF BIS(*B*-HYDROXY)CARBORANE (I)

Organic diol	Condensation product	Mass spec M^+	Isomers	^{1}H NMR spectra ppm (−δ) Carborane *C*-CH_3	^{1}H NMR spectra ppm (−δ) Organic radical	Character[a]
(—)-2,3-Butanediol	*trans*-[4,7-$(OCH(CH_3)CH(CH_3)O)$-2,3-$(CH_3C)_2B_9H_7$], III	248	1	1.94 (6)	1.16 (6 Hz) 1.10 (6 Hz) 3.6-4.6	D(6) M(2)
meso,dl-2,3-Butanediol	*trans*- and *cis*-[4,7-$(OCH(CH_3)CH(CH_3)O)$-2,3-$(CH_3C)_2B_9H_7$], IV	248	2	2.02 (6)	1.03 (6 Hz) 1.22 (6 Hz) 1.25 (6 Hz) 3.6-4.6	D(6) M(2)
Catechol	4,7-(OC_6H_4O)-2,3-$(CH_3C)_2B_9H_7$, V	268	1	2.56 (6)	7.13	D(4)
3-Chlorocatechol	4,7-(OC_6H_3ClO)-2,3-$(CH_3C)_2B_9H_7$, VI	302	1	2.30 (6)[b]	6.65-6.85	M(3)
Ethylene glycol	4,7-(OCH_2CH_2O)-2,3-$(CH_3C)_2B_9H_7$, VII	220	1	2.08 (6)	3.65-4.7	M(4)
1,2-*cis*-Cyclopentanediol	*syn, anti*-[4,7-(OC_5H_8O)-2,3-$(CH_3C)_2B_9H_7$], VIII	260	2	2.02 (6)[b]	1.3-2.0 4.3-4.9	M(6) M(2)
1,3-Propanediol	4,7-(OC_3H_6O)-2,3-$(CH_3C)_2B_9H_7$, IX	234	1	2.00 (6)	4.1-4.6	M(4)
1,3-Butanediol	4,7-(OC_4H_8)-2,3-$(CH_3C)_2B_9H_7$, X	248	1	2.00 (6)	1.26 (6 Hz)	D(3)
2,4-Pentanediol (isomeric mixture)	*cis*- and *trans*-[4,7-$(OC_5H_{10}O)$-2,3-$(CH_3C)_2B_9H_7$], XI	262	2	2.20 (6)	1.28 (6 Hz) 1.30 (6 Hz) 1.48-1.8 4.3-4.9	D(6) M(2) M(2)
1,5-Pentanediol	4,7-$(OC_5H_{10}O)$-2,3-$(CH_3C)_2B_9H_7$, XIII	262	1			
2,3-Dihydroxytetrahydrofuran	4,7-$(O_3C_3H_6)$-2,3-$(CH_3C)_2B_9H_7$, XIII	262	1	2.05 (6)	3.5-4.2 4.55-4.95	M(4) M(2)

---

[a] D = doublet, M = multiplet; relative intensities in parentheses. [b] FT NMR spectrum.

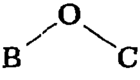
are known [3, 4], the products from the condensation reactions are the only known *B*-substituted-dicarba-*closo*-undecaboranes (eqn. 1). We report here the mechanism and scope of the condensation reaction.

Results and discussion

The stoichiometry of the reaction between I and glycols of the general formula RCH(OH)CH(OH)R is given by eqn. 1. Table 1 contains a partial list of condensation reactions attempted in this study. The structural features of the *B*-substituted-dicarba-*closo*-undecaborane products from the condensation reactions are shown in Fig. 1*.

Previous investigations [1, 2] have shown that in the condensation reaction the carborane unit remains intact as a *closo*-octadecahedron, in which the organic moiety is bonded to the octadecahedron via oxygen bridging atoms at the B(4, 7) positions. The structural features shown in Fig. 1 are supported by ^{11}B NMR data (Table 2) and ^{1}H NMR data (Table 1). The ^{11}B NMR spectrum of 4,7-[3,4-tetrahydrofurandiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane (11), (XIII), shown in Fig. 2, is an example.

The 70 MHz ^{11}B NMR of XIII consists of a series of doublets of relative intensity 1/2/1/2/1 in agreement with the molecular symmetry of the carborane indicated in Fig. 1. The lowest field singlet of intensity two and the highest field doublet of intensity one have been assigned to the B(4,7) and B(11) positions, respectively [1, 2]. The ^{11}B NMR data in Table 2 indicates the B(4,7;11) positions are most sensitive to changes in the exopolyhedral substituent. Both show a maximum change of approximately 4.5 ppm for the range of compounds studied. Whereas the ^{11}B NMR data indicates the molecular symmetry of the carborane unit, the ^{1}H NMR is useful in determining the environment of the organic radical and the number of different isomers formed. The ^{1}H NMR data will, therefore, be most useful in determining a possible condensation mechanism (vide infra).

Referring to the organic moiety of the *B*-substituted-*closo*-octadecahedron shown in Fig. 1 there are a number of different isomers, both optical and geometric, which can result from the condensation reaction. This study involves only configurational isomers, where the R-groups may differ in spatial arrangement around the asymmetric carbon atoms. In the *trans* isomer, one R-substituent herein referred to as being *syn*, is uppermost (as seen by an observer looking at the carborane polyhedra from atop the B(1) position and the second, the *anti* isomer, is lowermost. In the *cis* isomer both R groups are either *syn* or *anti* and we can expect two different *cis* isomers. Each configurational isomer may also have two different *cis* isomers. Each configurational isomer may also have two different conformations about the  $\mathrm{B}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{C}$ bond. Referring to

---

[*] The numbers accompanying formulas refer to the positions of the atoms in the *closo*-octadecahedron and to the locants on the divalent radial exopolyhedral substituents. The divalent radicals bonded to the carborane, i.e. —OCH_2CH_2O— are indicated by the suffix diylbis(oxy) with locants for the radical position numbered as low as possible. Previous publications [1, 2] have used the alternative nomenclature scheme for the octadecahedron (see ref. 4), which has not been approved by IUPAC Inorganic Nomenclature Committee (see ref. 5).

TABLE 2

70.56 MHz ^{11}B NMR SPECTRA

Condensation product	Chemical shift (ppm relative to $BF_3 \cdot OEt_2$)
III	−15.77 (−17.57)(2)^a, +1.16(1), +3.92(2), +12.46(1), +23.05(2), +24.12(1)
V	−14.90(2)^a, +0.12(1), +4.48(2), +10.72(1), +21.70(2), +21.70(1)
VII	−16.26(2)^a, +1.80(1), +4.20(2), +11.64(1), +23.10(2), +23.10(1)
XI	−19.58(2)^a, +0.54(1), +3.16(2), +11.84(1), +22.96(2), 26.2(1)
XIII	−16.84(2)^a, +1.14(1), +3.40(2), +13.16(1), +23.04(2), +24.20(1)

[a] Singlet.

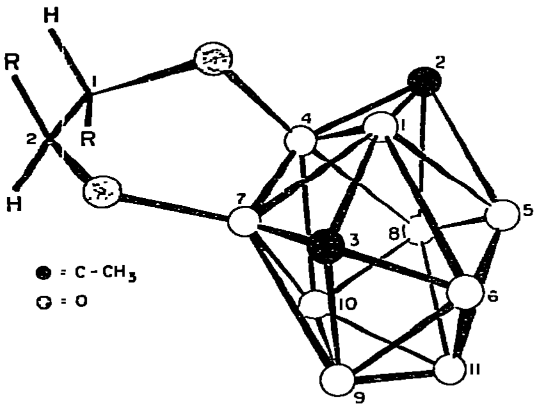


Fig. 1. Numbering system and proposed structure for the 4,7-[1,2-RCH(O)CH(O)R]-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$ (11).

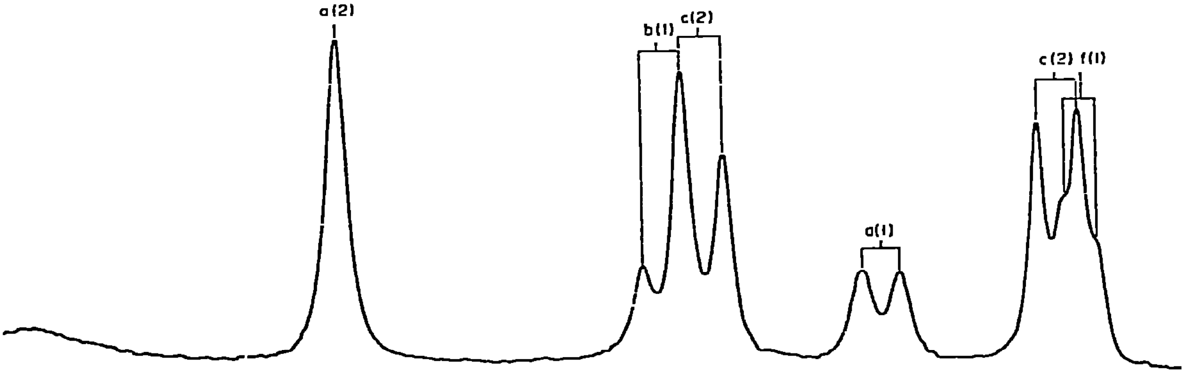


Fig. 2. The 70.56 MHz ^{11}B NMR of 4,7-[3,4-tetrahydrofurandiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), XIII. Chemical shifts relative to boron trifluoride etherate (coupling constants, Hz): (a) −16.84 ppm, (b) +1.14 ppm (161), (c) +3.40 ppm (158), (d) +13.16 ppm (149), (e) + 23.04 (161), (f) +24.20 ppm (140).

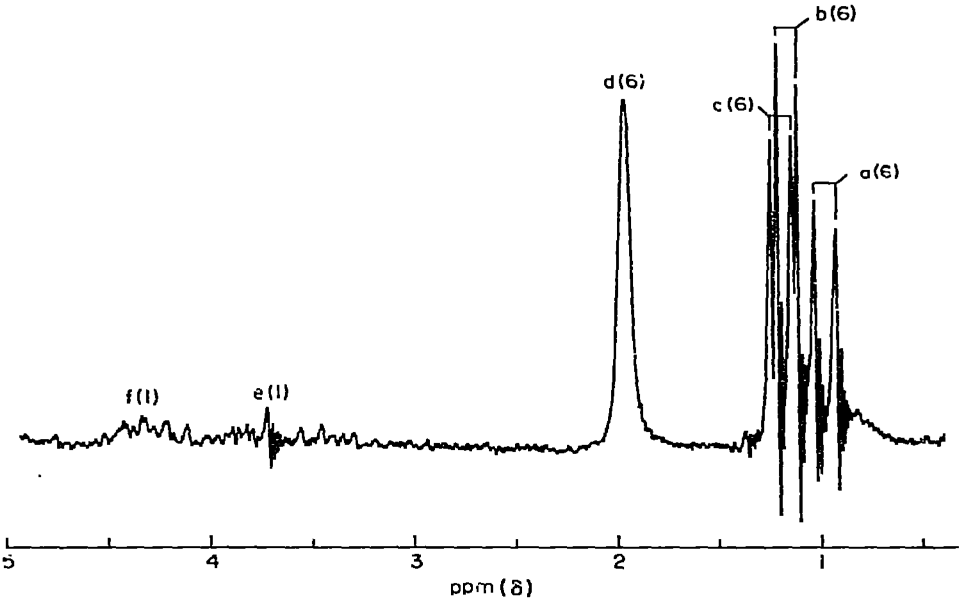


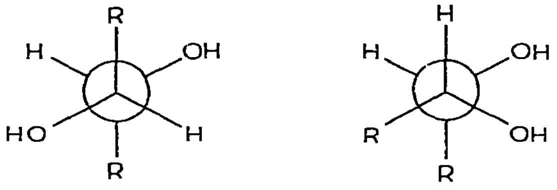
Fig. 3. The 60 MHz ^1H NMR spectrum in CD_2Cl_2 of the isomeric mixture of 4,7-[1,2-dimethyl-1,2-ethanediylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), IV. Relative areas in figure are given in parentheses. Chemical shifts are relative to TMS (coupling constants, Hz): (a) —1.03(6), (b) —1.22(6), (c) —1.25(6), (d) —1.95(6), (c) —3.67 (complex), (f) —4.34 (complex).

Fig. 1 the organic ligand may be bent toward or away from the uppermost face of the octadecahedron. A mechanism of the condensation reaction is suggested by analyzing the distribution of isomers produced by the reaction of the bis(hydroxy)carborane (I) with optically active glycols.

Reaction of 2,3-butanediol, which is 87% *meso* and 13% *dl*, with I gives both the *cis* and *trans* configurational isomers. Evidence for the two isomers appears in both the ^1H and ^{11}B NMR. The ^1H NMR of the isomeric mixture is shown in Fig. 3. The two overlapping doublets at —1.22 ppm ($J = 6$ Hz) and —1.25 ppm ($J = 6$ Hz) are assigned to the two different methyl groups of the *trans* isomer. The doublet at —1.03 ppm ($J = 6$ Hz) is assigned to the equivalent methyl groups of the *cis* isomer. The ^1H NMR indicates only one *cis* isomer is formed. Model systems indicate the *syn* isomer is favored. The ^{11}B NMR of the mixture indicates two different singlets at low field, —15.27 ppm and —17.57 ppm relative to $BF_3 \cdot OEt_2$, in a ratio of 2/1. The ^1H NMR indicates the relative amounts of *trans* to *cis* isomer is approximately 2.2/1.

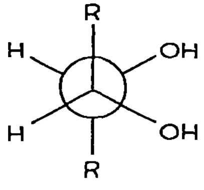
The pure *trans* isomer can be isolated by multiple sublimations of the reaction mixture or by direct reaction of I with the optically active isomer (—)-2,3-butanediol. The ^1H NMR assignments are indicated in Table 1 and the spectrum has been published elsewhere [1].

With reference to the Newmann projections shown below for the glycol series, RCH(OH)CH(OH)R, in order to obtain the *trans* isomer in the reaction between I and (—)-2,3-butanediol the hydroxyl groups must approach the *cis* conformation. If the hydroxyl groups in the glycol are in the *cis* conformation during the condensation, the *meso* isomer would yield the *cis* product. In the *meso* form, when R = phenyl or t-butyl, the only conformation present is the *anti* isomer, where the hydroxyl groups are *trans* [6]. Reaction of ether with I yields no condensation products emphasizing the necessity of the hydroxyl group to adopt the *cis* conformation. Reactions where R is a combination of H and CH_3 are most successful. In those cases where the condensation reaction is not possible the only product isolated is 1,3-$(CH_3C)_2B_7H_{11}$, indicating the two B(OH) vertices are removed.



anti *gauche*

meso form



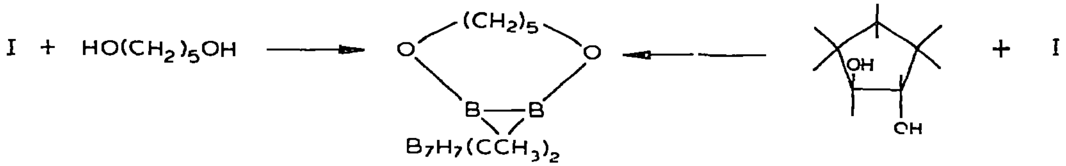
dl form

For the glycol series RCH(OH)CH_2CH(OH)R, R = H, CH_3, C_6H_5, t-butyl, the condensation reaction is successful only for R = H, CH_3. The configurational interaction of the t-butyl or phenyl groups in the *meso* form should be small allowing the hydroxyl groups to approach the *cis* conformation. Phenylethanediol, which has no substantial steric restriction on rotation about the carbon—carbon bond, also fails to condense with I. The phenyl substituent may inhibit the reaction via an inductive effect or there may be a steric interaction with the *C*-methyl groups on the carborane I.

For acyclic glycols the reduction of the valency angle between the carbon—oxygen bonds to assume near *cis* conformation is dependent on the freedom of rotation about the carbon—carbon bond. For cyclic vicinal diols the reduction of the valency angle is related to the flexibility of the ring. *cis*-1,2-Cyclopentanediol reacts with I to give two condensation isomers in relative yields of 95/5 based on GLC analysis. The *syn* isomer is favored over the *anti*. The ^{11}B NMR and ^{1}H NMR data are consistent with the proposed structure for the bicyclo-4,7-[1,2-cyclopentanediylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), (VII).

The valency angle of 120° in the *trans* isomer [6] as well as a difference of over 3000 in the rate of tetraacetate cleavage of the *cis* and *trans* cyclopentanediols [7] would seem not to favor the condensation reaction of *trans*-1,2-cyclopentanediol and I. Although the major product is the 1,3-$(CH_3C)_2B_7H_{11}$, at least two other products derived from condensation are indicated by gas chromatography-mass spectrometry analysis. One configurational isomer is formed in approximately 3% yield. The mass spectrum has a parent ion at *m/e* 260 corresponding to the $^{11}B_9{}^{12}C_9{}^{1}H_{21}{}^{16}O_2{}^{+}$ ion. The only major fragment observed is the $C_5H_8O_2^{+}$ ion. The ^{11}B NMR and ^{1}H NMR also support a direct condensation product.

The second product indicated by GCMS analysis is formed in less than 1% yield and has a parent ion at *m/e* 262 corresponding to $^{11}B_9{}^{12}C_9{}^{1}H_{23}{}^{16}O_2{}^{+}$ ion. The intensities of the parent ion envelope is nearly identical to the configurational isomer mentioned previously. Due to the low yield of this product direct identification by spectroscopy has not been possible. However, the condensation product can be synthesized by an alternative procedure. Reaction of I and 1,5-pentanediol gives a product identical to the compound having an *m/e* 262 based on comparison of their GCMS data. Isolation of identical products indicates



a novel scission of the carbon—carbon bond at the C(1)—C(2) position of the exocyclic ring. The proposed scission would convert the condensation product having two rings fused at the C(1)—C(2) atoms to one having an exopolyhedral cyclononane ring. The strain across the $\mathrm{B}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{C}$ bond in the bicyclo product may initiate the ring scission. The ^{11}B NMR and the ^{1}H NMR of the product is in agreement with the cyclononane structure, i.e. the relative intensities of the $-(CH_2)_5-$ in the ^{1}H NMR and the carborane methyl groups is 10/6.

In contrast to the cyclopentanediol condensation reactions, in which degradation to $1,3\text{-}(CH_3C)_2B_7H_{11}$ is vastly favored over condensation, 3,4-dihydroxytetrahydrofuran reacts cleanly with I in 50% yield to give two condensation products. The mass spectrum of the first, which is the predominant product, has a cut-off at *m/e* 262 corresponding to $^{11}B_9{}^{12}C_8{}^{1}H_{19}{}^{16}O_3$. The ^{11}B NMR (Fig. 2) and the ^{1}H NMR data support the proposed structure and formula. At the present we have no rationale as to why the *cis*-3,4-dihydroxytetrahydrofuran condenses so readily with I as compared to *cis*-1,2-cyclopentanediol. A second product identified by its mass spectrum, but formed in extremely low yields, is a proposed crown ether analogue, $[(CH_3C)_2B_9H_7\cdot O_3C_4H_4]_2$. The mass spectrum has a cut-off at *m/e* 524 corresponding to $^{11}B_{18}{}^{12}C_{16}{}^{1}H_{38}{}^{16}O_6$ as well as an abundant fragment at *m/e* 262 indicating homolytic cleavage of the crown ether analogue. The organic chemistry of these two products is currently being pursued in our laboratory.

Oxygen displacement

The reaction of $CH_2(^{18}OH)CH_2OH$ with I gave a condensation product containing 95% of the expected ^{18}O based on the stoichiometry of the reaction and the 2.5% ^{18}O enrichment of the ethylene glycol. This requires a displacement of the terminal OH groups from the B(4,7) boron atoms and may be viewed as a frontal S_N2 displacement reaction on a "bridgehead" boron atom. Analogous reactions in organic chemistry are virtually unknown. An S_N2 frontal reaction could take place via a 3-center mechanism involving the bridgehead boron and the two OH groups involved. The OH group on the organic diol acts as the nucleophile displacing the OH group from the vertex boron in the form of H_2O. The inductive effects of the R-group also favor the S_N2 mechanism, since substitution of methyl for hydrogen in the glycol series results in a pronounced increase in yield*.

---

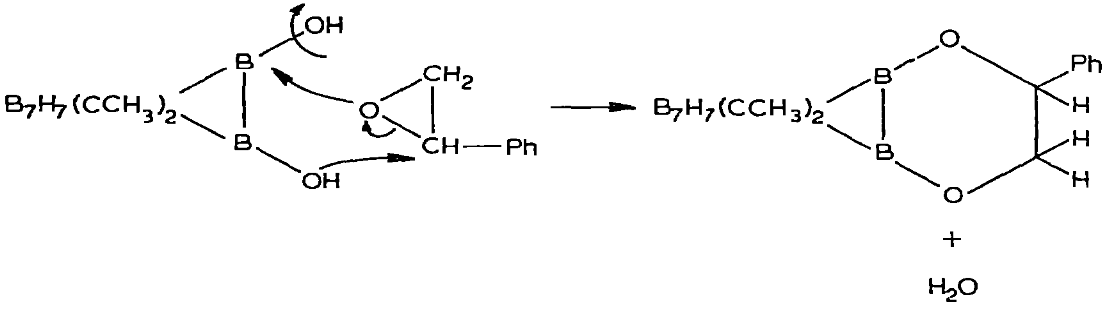
* The nature of the intermediate complex in the condensation reaction is difficult to identify. A referee has suggested a *nido* intermediate, which could lose water to produce the condensation product or react with additional nucleophiles to excise the boron atoms yielding the $B_7C_2H_{13}$ derivatives.

Exopolyhedral ring system

Both six and seven membered exopolyhedral rings form with equal ease. This is reminiscent of the *o*-carborane series, where the exopolyhedral rings are formed at the carbon site. In contrast to the *o*-carborane series the formation of exocyclic five membered ring systems is extremely difficult. A five membered ring system has been invoked to explain the dynamic behavior of the variable temperature ^{1}H NMR of I [1], but the only successful condensation reaction involves the use of paraldehyde, $(CH_2O)_3$, and I. The yields were less than 1%. The lack of formation of any five membered exopolyhedral rings is probably due to the reagents used rather than any steric restraints. In all reactions considered, e.i., $C_6H_5B(OH)_2$, $C_6H_5PCl_2$, $(CH_3OBO)_3$ and $(CH_3)_2SiCl_2$ cyclization would depend on I acting as a nucleophile. Prior investigations have already demonstrated that the bis(hydroxy)carborane (I) is an extremely poor necleophile [1,2] and would not favor an S_N2 reaction.

The incorporation of functional groups in the organic diol, also, seriously hinders the condensation reaction. The condensation reaction appears to be most successful with organic diols that are liquids up to temperatures of 200°. Catechol has a melting point of 105° and reacts in 75% yield with I. In contrast, 3,4-dihydroxy cinnamic acid or 3,4-dihydroxy benzoic acid yields no condensation products. As already indicated by the successful reaction of 3,4-dihydroxytetrahydrofuran some heteroatoms do not interfere with the condensation reaction.

Due to limitations imposed on the condensation reaction alternate methods of synthesizing the condensation products are being examined. The reaction of styrene oxide appears to give the desired condensation product as indicated below. Further work is being conducted in this area.



Experimental

Materials. The bis(hydroxy)carborane (I) was prepared according to published procedures [1, 2]. The ^{18}O enriched ethylene glycol [8], and *trans-* and *cis-*1,2-cyclopentanediols [9] were prepared according to published procedures. The (—)-2,3-butanediol was purchased from Strem Chemical Company. The remaining organic diols were purchased commercially and used without further purification. The gas chromatographic separations were done on a column containing 30% Apiezon L on Chromosorb P (60/80 mesh).

Spectra. Mass spectra were measured on an MS-902 or a Perkin—Elmer 270 Gas Chromatograph-Mass Spectrometer. The 70 MHz ^{11}B NMR were recorded

TABLE 3

REACTION CONDITIONS, AND ANALYTICAL DATA OF THE CONDENSATION PRODUCTS

Condensation product	M.p. (°C)	Reaction time (h) and temperature (°C)	Yield (%)	Found (calcd.) (%)	
				H	C
4,7-(OC_2H_4O)-2,3-$(CH_3C)_2B_9H_7$, VII	59	0.25/150	50.3	7.90 (7.90)	33.29 (33.24)
4,7-(OC_3H_6O)-2,3-$(CH_3C)_2B_9H_7$, IX	82	0.75/140	13.9	8.03 (8.29)	36.41 (36.42)
4,7-$(OCH(CH_3)CH(CH_3)O)$-2,3-$(CH_3C)_2B_9H_7$, III	52	1/155	36.1	8.86 (8.65)	39.13 (39.24)
4,7-$(OCH(CH_3)CH_2CH(CH_3)O)$-2,3-$(CH_3C)_2B_9H_7$, XI	72-80	1/140	39.7	8.87 (8.95)	41.37 (41.73)
4,7-(OC_6H_4O)-2,3-$(CH_3C)_2B_9H_7$, V	105	0.5/180	75	6.44 (6.39)	45.48 (45.11)

on a Varian Associates Model HA-220 spectrometer interfaced with a Nicolet pulsed Fourier transform computer. Proton NMR spectra were recorded on a Varian A60-A. Chemical shifts are reported relative to $BF_3 \cdot OEt_2$ and $Si(CH_3)_4$, respectively.

Reactions. The condensation reactions were all conducted under near identical conditions. A sample of I is placed in a pyrolysis tube and a 10 fold excess of the organic diol added. The pyrolysis tube is evacuated and sealed and heated at 160°. After cooling the sample the tube is opened, the residue washed with water to remove the organic diol and the crude condensation product is purified by sublimation or extracted into pentane and analyzed by gas chromatography. Table 3 contains experimental data for a list of reactions.

Acknowledgements

The authors gratefully acknowledge the support of NSF Grant GP-17053 and also wish to thank Professor Lee J. Todd, University of Indiana for the 70 MHz ^{11}B NMR data.

References

1 G.D. Mercer and F.R. Scholer, Inorg. Chem., 12 (1973) 2102.
2 G.D. Mercer and F.R. Scholer, Inorg. Chem., 13 (1974) in press.
3 L.I. Zakharkin, V.N. Kalinin and V.V. Gedymin, J. Organometal. Chem., 16 (1969) 371.
4 R.N. Grimes, Carboranes, Academic Press, New York, 1970, p. 198.
5 R.M. Adams, Pure Appl. Chem., 30 (1972) 683.
6 E.L. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York, 1962.
7 R. Criegee, E. Büchner and W. Walter, Ber., 73 (1940) 571.
8 C.R. Noller, Chemistry of Organic Compounds, W.B. Saunders, Philadelphia, 3rd Ed., 1965, p. 818.
9 K.B. Wiberg and K.A. Saegebarth, J. Amer. Chem. Soc., 79 (1957) 2822; Roebuck and Adkins, Org. Syn., 28 (1948) 35.