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STUDIES OF METHYL DERIVATIVES OF 1,2-DICARBACLOVOPENTA-BORANE(5)

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INTRODUCTION

The recent synthesis[1,2] of the unexpectedly stable carborane C,3-dimethyl-1,2-dicarbaclovopentaborane (5), in which the cage carbon atoms are adjacent, is of interest in regard to the relative stabilities of carborane isomers and of their alkyl derivatives. Molecular orbital calculations for several polyhedral carborane cage systems have been reported[3,4], including trigonal bipyramidal $C_2B_3H_5$, octahedral $C_2B_4H_6$, pentagonal bipyramidal $C_2B_5H_7$ and icosahedral $C_2B_{10}H_{12}$. In each case, structures having adjacent cage carbons were predicted to be less stable than isomers in which the carbon atoms are nonadjacent, and facile rearrangements from adjacent-carbon isomers to form nonadjacent-carbon structures were expected[5].

These conclusions have received substantial experimental support. For example, 1,2-dicarbaclovohexaborane(6) is converted at 250° to the more stable 1,6-dicarbaclovohexaborane(6)[6], while 1,2-dicarbaclovododecaborane(12) undergoes thermal rearrangement[7] to the corresponding 1,7-isomer. Moreover, in the $C_2B_3H_5$ and $C_2B_5H_7$ systems the only known unsubstituted isomers are 1,5-$C_2B_3H_5$ and 2,4-$C_2B_5H_7$ despite the fact that three isomeric possibilities exist in the former case and four in the latter. Similarly, the recently reported $C_2B_6H_8$[8,9], $C_2B_7H_9$[9], and $C_2B_8H_{10}$[9] carboranes are all believed to have nonadjacent-carbon structures.

In view of this and other evidence, the existence and surprising stability of C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ (I) has led us to investigate this compound with particular interest in its possible thermal or base-catalyzed rearrangement to the "normal" 1,5-isomer.

RESULTS AND DISCUSSION

The pyrolysis of (I) was studied both in the pure liquid phase and as a vapor diluted in helium. Although the results in the two cases were significantly different, no cage rearrangement of (I) was detected under any conditions studied. Pure liquid (I) remained unchanged during several hours at 60°, but at 130° extensive decomposition occurred with formation of trimethyl and tetramethyl derivatives of 1,2-$C_2B_3H_5$ plus trimethylborane and nonvolatile solids (Table 1).

In an effort to determine whether a low-energy intramolecular cage rearrangement of (I) is possible, dilute solutions ($\sim$4 mole %) of (I) in helium were heated in sealed tubes, with the results indicated in Table 1. The major product of the 220°

pyrolysis, characterized as C,5-dimethyl-1,2-dicarbaclovopentaborane(5) (II), is identical with a previously isolated trace product* from the acetylene/diborane discharge reaction in which (I) was prepared[2].

TABLE 1

PYROLYSIS OF C,3-DIMETHYL-1,2-DICARBACLOVOPENTABORANE(5) (I)

Mmoles of (I) at start	*Temp. (°C)*	*Time (h)*	*(I) recov. (%)*	*Volatile products[a] (Mmoles × 10^3)*
0.034 (vapor) +0.90 He	115	4.5	100	none
0.034 (vapor) +0.90 He	220	17.0	83	C,5-$(CH_3)_2$-1,2-$C_2B_3H_3$ (3.2) C, 3,5-$(CH_3)_3$-1,2-$C_2B_3H_2$ (0.6) $(CH_3)_3B$ (2.0)
0.20 (liquid)	130	2.5	4.2	3,4,5-$(CH_3)_3$-1,2-$C_2B_3H_2$ (7.7) C,3,4,5-$(CH_3)_4$-1,2-C_2B_3H (1.2) C′,3,4,5-$(CH_3)_4$-1,2-C_2B_3H (3.5) $(CH_3)_3B$ (9.7); unidentified (1.0)

[a] Exclusive of H_2.

The products of the pyrolysis reactions were isolated by vapor phase chromatography and structurally characterized from their infrared and mass spectra. Although the quantities obtained were insufficient for meaningful NMR work, structural assignments were made with reasonable confidence from infrared spectra of the pure compounds (Table 2) by comparison with the spectra** of known carboranes and derivatives. The characterization of individual compounds is discussed in detail in the next section.

The possibility that (I) might rearrange in the presence of a mild Lewis base, as is reported for several boranes and alkylboranes [*e.g.* pentaborane(9)[14], 1-methyl- and 1-ethylpentaborane(9)[15], and decaborane(16)[16]] was examined by warming a frozen mixture of (I) and 2,4,6-collidine to room temperature. A deeply colored red solution quickly formed which persisted on standing, but only traces of volatile products were formed and no unreacted (I) was recovered. An infrared spectrum of the red solution disclosed the gross structural features of (I), so that a collidine/(I) complex may have formed. The nature of this material, apparently the first of its kind to be encountered in small carborane chemistry, is under investigation. It is reminiscent, however, of the colored π-complexes formed between decaborane(14) and pyridine[17-21] or lutidine[16].

It is clear that the adjacent-carbon cage structure in (I) is stable with respect

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* This compound, labelled X in ref. 2, was correctly judged in the earlier work to be a $(CH_3)_2C_2B_3H_3$ isomer, but lacking additional data it was assumed at the time to be a derivative of 1,5-$C_2B_3H_5$.

** Infrared spectra of a number of available carboranes and methylcarboranes of known structure[2,10] have permitted some useful correlations. Particularly relevant is a strong, characteristic band at 1250–1280 cm^{-1} which is present in small polyhedral carboranes having one or more equatorial B-methyl groups. Other assignments of interest here are already well established, *e.g.* C–CH_3 symmetric and asymmetric methyl deformations[11] between 1370 and 1470 cm^{-1}, the B–CH_3 symmetric methyl deformation[12] at 1330–1280 cm^{-1}, and the normal B–H stretching mode[12] at 2630–2350 cm^{-1}.

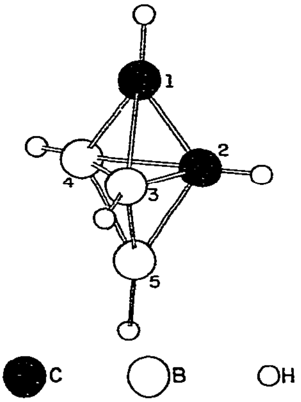

Fig. 1. Structure of the unsubstituted 1,2-dicarbaclovopentaborane(5) molecule, showing the numbering system used in the text. The cage borane nomenclature system now generally used is described by R. ADAMS, *Inorg. Chem.* 2 (1963) 1087.

to thermally-induced rearrangement. Indeed the stability of (I) appears comparable to that of the "normal" parent carborane 1,5-$C_2B_3H_5$[6]. Furthermore, the liquid pyrolysis experiments indicate that although (I) decomposes at 130°, further methylation of some of the (I) molecules takes place at the same time to produce, among others, trimethylated and tetramethylated species which are more stable than (I) itself. Thus a net effect of the liquid pyrolysis is a partial conversion of (I) to derivatives in which all of the boron atoms are methylated and the 1,2-cage structure remains intact.

The considerable thermal stability of (I) molecules isolated in a helium gas matrix contrasts with the liquid pyrolysis and implies that the decomposition of (I) in the latter case is not unimolecular. The fact that the primary effect of the vapor pyrolysis is to shift the B-methyl group from an equatorial boron to the apical boron [in (II)] may be an indication that the latter structure is the more stable, although (II) is formed in much smaller yield than (I) in the C_2H_2/B_2H_6 discharge reaction[2]. The only other product detected in the vapor pyrolysis, a trace of C,3,5-trimethyl-1,2-dicarbaclovopentaborane(5), is assumed to result from further B-methylation of (II) during partial breakdown of the starting material.

It was suggested earlier[2] that the stability of (I) might be more reasonably attributed to the influence of the methyl substituents upon the electronic distribution in the cage than to steric or other kinetic effects. The increased thermal stability, compared to (I), of the higher methylated derivatives obtained in this study may be ascribed at least partially to the lack of B–H groups, but the existence of at least two stable B,C-dimethyl derivatives of 1,2-$C_2B_3H_5$ supports the view that the cage structure in these molecules has been thermodynamically stabilized with respect to rearrangement. There is, in addition, some evidence that alkylated small carboranes in general tend to be more stable than the parent compounds. This may well be true for 2-carbahexaborane(9)[22], which is known only in the form of alkyl derivatives, and the same effect has been observed during studies of other open-cage carboranes in this laboratory[23].

If this phenomenon is general, it is possible that derivatives will be prepared of carborane species which are incapable of existence in the unsubstituted form. 1,2-$C_2B_3H_5$ itself may well belong in this category, and there is little doubt that it

TABLE 2

INFRARED ABSORPTION SPECTRA OF DICARBACLOVOPENTABORANE(5) DERIVATIVES[a]

(I)	*(II)*	*(III)*	*(IV)*	*(V)*	*(VI)*	*(VII)*[b,c]	*(VIII)*[b,d]	*Assignments*
2960 sh		2980 sh		2960 sh	2960 sh		2960 m	CH_3 stretch
		2930 s		2925 sh	2930 s			CH_3 stretch
2910 vs	2910 s		2880 s	2890 s	2900 sh		2890 m	CH_3 stretch
2870 sh	2850 m		2850 sh	2850 sh	2850 sh			CH_3 stretch
2830 sh				2800 sh	2800 sh			CH_3 stretch
2590 vs	2580 vs	2585 s				2600 vs	2600 vs	B–H stretch
1450 m	1450 m	1450 m	1460 w	1450 m	1450 m		1450 w	C–CH_3 deformation
1320 vs	1325 s	1320 vs	1320 vs	1320 vs	1320 vs		1330 vs	B–CH_3 deformation
1260 s		1255 s	1260 s	1250 s	1265 s		1278 s	Equatorial B–CH_3
							1270 s	
1190 vs	1175 s	1190 s	1192 s	1170 m	1190 s	1232 m		
						1224 m	1235 w	
						1214 m	1195 s	
1100 s	1095 s	1100 m				1100 vs, b	1100 vs	B–H
980 w	983 w	980 w		1040 m, b	1030 m, b	918 m, b	1015 w, b	Cage vibrational
935 m	885 w	920 w, b	940 m	900 m	950 w, b	902 vs	970 s	modes + others
900 w, b	845 w		890 m		910 w	890 m	902 vs	
					870 w	800 w, b	893 s	
						785 w	842 w	
						760 w, b		

[a] Key: (I) = C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$; (II) = C,5-$(CH_3)_2$-1,2-$C_2B_3H_3$; (III) = C,3,5-$(CH_3)_3$-1,2-$C_2B_3H_2$; (IV) = 3,4,5-$(CH_3)_3$-1,2-$C_2B_3H_2$; (V) = C,3,4,5-$(CH_3)_4$-1,2-C_2B_3H; (VI) = C′,3,4,5-$(CH_3)_4$-1,2-C_2B_3H; (VII) = 1,5-$C_2B_3H_5$; (VIII) = 2-CH_3-1,2-$C_2B_3H_4$. [b] Principal bands. [c] Reported previously[13]. [d] Reported previously[2].

will prove to be unstable if it should be isolated at all. Obviously a clear understanding of the role of alkyl substituents in stabilizing carborane structures must await an intensive experimental effort in this area.

EXPERIMENTAL SECTION

Gas chromatography

A 9.8 ft. × 0.25 in column packed with 30% Kel-F on Chromosorb-W was used for all separations. Retention volumes [$(CH_3)_3B = 1.00$] are: C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$, 2.8 (40°), 2.4 (60°); 3,4,5-$(CH_3)_3$-1,2-$C_2B_3H_2$, 4.6 (40°); C,3,4,5-$(CH_3)_4$-1,2-C_2B_3H, 6.6 (40°); C′,3,4,5-$(CH_3)_4$-1,2-C_2B_3H, 9.3 (40°); C,5-$(CH_3)_2$-1,2-$C_2B_3H_3$, 3.6 (60°); C,3,5-$(CH_3)_3$-1,2-$C_2B_3H_3$, 6.6 (60°).

Spectroscopic data

Mass spectra were obtained on a CEC 21-103C spectrometer, infrared spectra were run in a 3.5-ml gas cell with 9 cm path length on a Beckman IR-8 linear wavenumber instrument, and ^1H NMR spectra were recorded with a 60 mc Varian A-60 spectrometer.

Pyrolysis of C,3-dimethyl-1,2-dicarbaclovopentaborane(5)

(*a*) *Liquid sample.* A 0.20 mmole quantity of C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$, prepared as described earlier[1,2], was sealed in a 5-mm diameter Pyrex NMR tube and heated 4.5 h at 60°, which produced no change in the ^1H NMR spectrum[1]. After 2.5 h at 130° the ^1H NMR spectrum had changed considerably* and brown solids had formed. Chromatographic separation of the volatile components afforded the products and yields indicated in Table 1, together with 8.5×10^{-3} mmole unreacted starting material and traces of unidentified materials, probably including pentamethyl-1,2-dicarbaclovopentaborane(5).

(*b*) *Vapor sample.* C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ (0.034 mmole) and He (0.90 mmole, $P = 342$ mm) were sealed in a 50-ml Pyrex tube equipped with a breakoff, and heated 4.5 h at 115°. The original carborane was recovered quantitatively and a chromatogram disclosed no other components.

The same carborane sample was replaced in the reaction tube with an identical quantity of helium. After pyrolysis at 220° for 17 h the contents were chromatographed, yielding 0.028 mmole of starting material plus the products and yields given in Table 1. No solid deposits were observed.

Identification of products

Trimethylboron was easily identified from its published infrared spectrum. Structures assigned to the carborane products were based on their infrared and mass spectra (parent peaks and fragmentation patterns consistent with the formulas given were obtained in all cases). In addition to the band assignments indicated in Table 2, use was made of the close resemblance between the infrared absorptions of these compounds and those of C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ in the 700–1100 cm^{-1} region characteristic of cage vibrational modes. There is a marked similarity in this part of

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* The cage C–H resonance nearly disappeared while the methyl peak broadened and moved 0.50 ppm to lower field. This is attributed to a relatively high concentration of B-methylated species, including $B(CH_3)_3$, compared to the starting material.

the spectrum between C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ and the products obtained in this study. On the other hand, the spectra of 1,5-dicarbaclovopentaborane(5) and its 2-methyl derivative are quite different in this region, both featuring a strong band group near 900 cm^{-1} which is not present in the product spectra. The identity of these products as derivatives of 1,2-$C_2B_3H_5$ rather than the 1,5-isomer is therefore strongly indicated, but further evidence lies in the fact that two tetramethyl $C_2B_3H_5$ derivatives having no B–H groups were isolated. Since only one such derivative is possible for 1,5-$C_2B_3H_5$, the existence of two compounds of this type with similar infrared spectra and nearly identical mass spectra virtually assures that they are derivatives of 1,2-$C_2B_3H_5$. In addition, the mass spectroscopic fragmentation patterns of all of the products were very similar to that of (I) and differed significantly from those of 1,5-$C_2B_3H_5$ and its dimethyl derivative.

Reaction of C,3-dimethyl-1,2-dicarbaclovopentaborane(5) *with* 2,4,6-*collidine*

C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ (0.035 mmole) was distilled into a tube at −196° containing 0.5 ml of 2,4,6-collidine (Baker) and the mixture was warmed under vacuum. As room temperature was neared, the solution became yellow and quickly turned to orange. After five minutes at room temperature the homogeneous liquid was cherry red. After 45 min the volatile materials were distilled off, giving on chromatography only collidine and a trace of an unidentified carborane-like product. The material remaining in the reaction tube was a dark red glassy solid which yielded no additional volatile material even on prolonged vacuum distillation at 60°. A portion of the solid was redissolved in collidine, giving a red solution whose infrared spectrum (*vs.* pure collidine) resembled the spectrum of C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ but without the B–H stretching band near 2500 cm^{-1}. The significant absorptions were at 2870 (m), 2810 (s), 1335 (s), 1285 (s), 1230 (s), 1080 (m), 1050 (m, b) and 920 (w, b) cm^{-1}. Another portion of the red solid was dissolved in dry acetonitrile to give an orange solution. The infrared spectrum (*vs.* pure CH_3CN) was very similar to that of the collidine solution, with bands at 2910 (m), 1335 (s), 1285 (s), 1230 (s), and 1070 (m, b).

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SUMMARY

The thermal stability of C,3-dimethyl-1,2-dicarbaclovopentaborane(5) was examined in the liquid and vapor states. Pyrolysis of the liquid at 130° yielded a trimethyl and two tetramethyl derivatives of 1,2-$C_2B_3H_5$ plus trimethylborane and nonvolatile solids. The vapor diluted in helium was unreactive at 115° but at 220° partially reacted to give C,5-$(CH_3)_2$-1,2-$C_2B_3H_3$ and C,3,5-$(CH_3)_3$-1,2-$C_2B_3H_2$. No rearrangement of the 1,2-carborane cage structure was observed, and the higher methylated derivatives were more stable than C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$. C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ reacted with 2,4,6-collidine to produce a red complex. The significance of the stability of the methylated 1,2-$C_2B_3H_5$ structure is discussed in relation to other experimental and theoretical studies of the carboranes.

REFERENCES

1 R. N. Grimes, *J. Am. Chem. Soc.*, 88 (1966) 1070.
2 R. N. Grimes, *J. Am. Chem. Soc.*, 88 (1966) 1895.
3 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36 (1962) 3489.
4 W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York, 1963.
5 R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, 2 (1963) 231.
6 T. Onak, R. P. Drake and G. B. Dunks, *Inorg. Chem.*, 3 (1964) 1686.
7 D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2 (1963) 1128.
8 R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, 87 (1965) 3513.
9 F. N. Tebbe, P. M. Garrett, D. C. Young and M. F. Hawthorne, *J. Am. Chem. Soc.*, 88 (1966) 609.
10 R. N. Grimes, unpublished results.
11 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 2nd ed., 1958.
12 L. J. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.*, (1958) 2412.
13 I. Shapiro, C. D. Good and R. E. Williams, *J. Am. Chem. Soc.*, 84 (1962) 3837.
14 T. P. Onak, R. E. Williams and H. G. Weiss, *J. Am. Chem. Soc.*, 84 (1962) 2830, footnote 2.
15 T. P. Onak, *J. Am. Chem. Soc.*, 83 (1961) 2584.
16 R. N. Grimes and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, 48 (1962) 496.
17 L. A. Burkardt and N. R. Fetter, *Chem. Ind. (London)*, (1959) 1191.
18 L. A. Burkardt and N. R. Fetter, *Abstr. Papers 135th Meeting Am. Chem. Soc.*, Boston, Mass., p. 45-M.
19 B. M. Graybill and M. F. Hawthorne, *J. Am. Chem. Soc.*, 83 (1961) 2673.
20 H. C. Beachell, D. E. Hoffman and B. F. Dietrich, *Angew. Chem.*, 72 (1960) 40.
21 W. A. Mosher, H. C. Beachell, *et al.*, *Univ. of Delaware*, Newark, Del., *Adducts of Boron Compounds*, Quarterly Report Nos. 1–5, Contract No. DA-36-034-ORD-2526-RD (unclassified).
22 T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart and R. E. Williams, *J. Am. Chem. Soc.*, 88 (1966) 2061.
23 C. L. Bramlett and R. N. Grimes, *J. Am. Chem. Soc.*, 88 (1966) 4269.