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Synthesis of Carboranes from Dihydrocarboranes¹

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Carborane-2,5 is the major volatile carborane formed from the pyrolysis of dihydrocarboranes-2,4. The presence of trimethylamine during the pyrolysis significantly increases the yield of *sym*-carborane-2,4.

The carboranes *sym*-C₂B₃H₆, *unsym*-C₂B₄H₆, *sym*-C₂B₄H₆, and C₂B₅H₇ have been prepared in a silent electric discharge in very low yields.^{3,4} Since a high yield synthesis of the C-alkyl derivatives⁵ of C₂B₄H₆⁵ has been discovered, it was decided that catalytic removal of H₂ or removal of BH₃ by a Lewis base might lead to the preparation of C-alkyl derivatives of C₂B₄H₆ and C₂-B₃H₃,⁷ respectively.

Since loss of H₂ and/or BH₃ occurs in the related boron hydrides merely by heating, a preliminary experiment was undertaken to determine which reaction was preferred. No alkyl derivatives of C₂B₃H₃ were detected

(Mathieson) and 30 mmoles of 2-butyne (Columbia). After stirring the mixture for 5 hr. at room temperature the volatile components were vacuum fractionated through traps at -80° and -190°. To the contents in the -80° trap was added 25 ml. of freshly distilled boron trifluoride ethyl etherate (Eastman). After stirring the resulting heterogeneous mixture for 15 min. at room temperature the volatiles were fractionated through -20°, -80°, and -190° traps. The crude Ia in the -80° trap was stored over 1 g. of lithium aluminum hydride for 1 hr. and then fractionated through traps at -70° and -190°. The -70° trap contained 6.9 mmoles (40%) of Ia.

(b) **C-Propyldihydrocarborane-2,4 (Ib).**—The reaction was carried out in a manner essentially identical with that described above using 30 mmoles of 1-pentyne (Columbia) instead of 2-butyne. The yield of purified Ib was 6.5 mmoles (38%).

TABLE I

DATA FOR THE CONVERSION OF DIHYDROCARBORANES TO CARBORANES

Dihydrocarborane	Other material present	Minimum pyrolytic		Volatile products		
		Temp., °C.	Hr.	Carborane-2,5	<i>sym</i> -Carborane-2,4	Other
Ia	None	290	20	Ia, 25%	IIa, 5%	Ca. 10% alkanes, m.s. indicating 95% ethane, traces of boron hydrides, and possibly traces of propane and butane
Ib	None	300	20	Ib, 30	IIb, 2	Ca. 10% alkanes, m.s. indicating 80% propane, 15% <i>n</i> -butane, traces of boron hydrides, and possibly traces of ethane
Ia	Trimethylamine	260	20	Ia, 15	IIa, 25	Trimethylamine quant. recovd.
Ib	Trimethylamine	280	6	Ib, 15	IIb, 20	Trimethylamine quant. recovd.; however, contaminated with traces of a boron hydride (infrared)
Ia	Isobutane	280	35	Ia, 30	IIa, 5	Isobutane quant. recovd.

from the dihydrocarboranes (perhaps the alkyl groups interfered with the ejection of a BH₃ group). Alkyl derivatives of *sym*-C₂B₄H₆ were isolated; however, no alkyl derivatives of *unsym*-C₂B₄H₆⁹ were observed. Surprisingly, C-alkyl derivatives of C₂B₅H₇ were produced in unanticipated abundance.

Experimental

Preparation of Dihydrocarboranes. (a) C,C'-Dimethyldihydrocarborane-2,4 (Ia).—To 10 ml. of 2,6-lutidine (Matheson Coleman and Bell)¹⁰ were added 17 moles of pentaborane (Olin

Pyrolysis of Dihydrocarboranes to Carboranes. (a).—One mmole of the appropriate dihydrocarborane-2,4 was sealed into a 25-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The lowest temperature at which the disappearance of dihydrocarborane occurred at a reasonable rate is given in Table I. This was determined by following the H¹ n.m.r. while increasing the temperature. After the minimum conditions were applied to decompose 95–100% of the dihydrocarborane, the contents of the flask were gas chromatographed (Table II). In addition to the volatile carboranes an appreciable quantity of unidentified tan solids formed during the pyrolysis.

Anal. Calcd. for C₃B₅H₁₃ (IIb): C, 47.2; B, 42.5; H, 10.3. Found: C, 46.6; B, 42.8; H, 10.5.

TABLE II

PHYSICAL DATA FOR THE CARBORANES AND DIHYDROCARBORANES

Compound	Gas chromatography, R _f	Mass spectrum: obsd. parent peak	M.p., °C.
Ia	2.2	104	-64 to -63
Ib ^a	6.2	Not taken	Glass
IIa	1.9	114	-30 to -28
IIb ^a	5.4	128	-99 to -97
IIIa	1.1	102	-2 to -1
IIb	2.4	116	-88 to -87

^a Racemates.

(1) This investigation was supported in part by the Office of Naval Research.

(2) Participant in National Science Foundation Undergraduate Research Program (G-21893), Summer, 1962.

(3) R. E. Williams, C. D. Good, and I. Shapiro, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 14N; *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(4) C. D. Good and R. E. Williams, U. S. Patent 3,030,289 (1962).

(5) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).

(6) The discovery of the parent dihydrocarborane, C₂B₄H₆, by H. G. Weiss and its isolation by C. D. Good³ has been reported: I. Shapiro, Pacific Coast Conf. Anal. Chem. and Appl. Spectroscopy, Pasadena, Calif., Dec., 1962.

(7) We subscribe to the suggestion⁸ that C₂B₃H₃ is better than B₃C₂H₃ in that it reflects the carbon boron order in the name; it would appear that carborane 2,3 would be better than carborane-3 or triboradimethyne since carboranes with 4 or 6, etc., carbons and hydrocarboranes with more or less than two carbons will probably be discovered.

(8) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

(9) The suggestion that *unsym*-C₂B₄H₆ may rearrange to *sym*-C₂B₄H₆⁸ was made when the carboranes were first isolated by Good.^{3,4} This possibility, at elevated temperatures, is now under investigation.

(10) Purified according to the procedure described by H. C. Brown, S. Johnson, and H. Podall, *J. Am. Chem. Soc.*, **76**, 5556 (1954).

(b) **Addition of Trimethylamine.**—The reaction was carried out in a manner essentially identical with that described above; however, 1 mmole of trimethylamine (Matheson) was added to the contents of the flask. Tables I and II summarize the reaction conditions, yield of carboranes, and gas chromatographic results. Prior to the gas chromatography of the products the

TABLE III

 B^{11} N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS^a

	e ($\delta,^b J$, c.p.s.)	f or g	g or f
IIa	-5.6, 177	-4.5 (estd.), 165 (estd.)	+19.5, 176
IIb	-5.2, 176	-4.0 (estd.), 170 (estd.)	+21.0, 176
$C_2B_5H_7^3$	-5.0, 187	-2.0 (estd.), 170 (estd.)	+23.5, 178
	h		
IIIa		+16.3, 185	
IIIb		+18.6, 186	
<i>sym</i> - $C_2H_4H_6^3$		+19.4, 189	

^a B^{11} chemical shifts and coupling constants of the dihydrocarboranes have been reported previously.¹ ^b δ , p.p.m. relative to boron trifluoride ethyl etherate.

TABLE IV

 H^1 N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS

	a and b ($\delta,^a J$, c.p.s.)	c	d	i	j	k	l	m
Ia	-3.20, 156	+0.92, 178	+2.4 (estd.)	-2.07				
Ib	-3.37, 157	+0.85, 180	+2.4 (estd.)		-0.96	-1.65	-2.40	-6.10
	e		f or g		g or f			
IIa	-4.46, 176	-3.67, 165	-0.18, 175	-2.02				
IIb	-5.2, 180	-4.1 (estd.) ^b	-.2, 179		-0.87	-1.57	-2.43	-5.35
$C_2B_5H_7$	-5.0, ^c 183	-4.3, ^c 170	-.2, ^c 178					-5.7 ^c
	h							
IIIa	-1.83, 184			-1.33				
IIIb	-1.93, 187				-0.94	-1.42	-1.77	-2.87
<i>sym</i> - $C_2B_4H_6^3$	-1.29, ^c 190							-2.37 ^c

^a δ , p.p.m. relative to tetramethylsilane, negative values are to low field. ^b Only the lower member of the quartet was clearly distinguishable. ^c δ was calculated assuming $J = ca.$ 170 c.p.s. from B^{11} n.m.r. data (Table III). ^d Not corrected for bulk susceptibility.

trimethylamine was removed by fractionating through traps at -90° and -190° . Examination of the -190° bath indicated a nearly quantitative recovery of the trimethylamine originally present.

(c) Addition of Isobutane.—Using isobutane (Matheson) instead of trimethylamine the pyrolysis was carried out in a manner essentially identical with that described above. After the pyrolysis the reaction mixture was introduced immediately onto the gas chromatographic column for separation.

Gas chromatography was used for final purification of the dihydrocarboranes and carboranes. A 30% Kel-F column on firebrick¹¹ operated at 90° was used. The retention volumes (relative to pentaborane) are given in Table II.

Mass spectra were taken on a CEC 21-620 instrument. Table II lists the observed parent peaks.

Nuclear Magnetic Resonance Data.— B^{11} n.m.r. spectra were measured with a Varian V-4300 high resolution spectrometer operating at 12.83 Mc. (Table III). H^1 n.m.r. spectra were measured with a Varian A-60 spectrometer (Table IV).

Discussion

C,C' -Dimethylcarborane-2,5 (IIa) is the principal volatile carborane formed from the pyrolysis of C,C' -dimethyldihydrocarborane-2,4 (Ia). In addition, a small quantity of C,C' -dimethyl-*sym*-carborane-2,4 (IIIa) is formed. Similarly, C,n -propyldihydrocarborane-2,4 (Ib) upon pyrolysis yields C,n -propylcarborane-2,5 (IIb) and C,n -propyl-*sym*-carborane-2,4 (IIIb). Neither of the dihydrocarboranes subjected to pyrolytic conditions gives identifiable amounts of the alkyl substituted carboranes-2,3 or *unsym*-carboranes-2,4.

A reaction between trimethylamine (TMA) and dihydrocarborane-2,4 was expected to yield the carborane-2,3 by abstraction of a borane unit; however, no reaction is observed below 250° , and above this temperature the *sym*-carborane-2,4 and carborane-2,5 are major volatile carborane products. Within experimental error the TMA is quantitatively recovered. Although the total amount of volatile carboranes re-

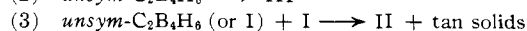
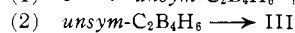
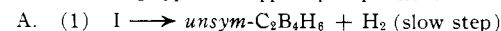
mains approximately unchanged when the pyrolysis is carried out in the presence of TMA, the relative quantity of the *sym*-carborane-2,4 is greatly enhanced. The TMA could be acting as a diluent during the pyrolysis; however, it is not likely that this is the major cause of the change in product distribution; for when the pyrolysis is carried out in the presence of isobutane, the same product distribution is obtained as when no diluent is used. Apparently, the unshared electrons of TMA play an important part in determining the course of the pyrolysis.¹²

Before this investigation was undertaken there were several uncertainties with respect to the structure or structures of the $C_2B_5H_7$ compound(s). For the previous B^{11} n.m.r. spectra did not unambiguously demonstrate

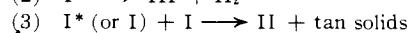
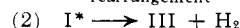
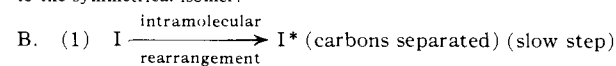
that only one isomer was present.³ Since the B^{11} n.m.r. spectra (Table III) of $C_2B_5H_7$, C,n -propyl- $C_2B_5H_6$, and C,C' -dimethyl- $C_2B_5H_5$ are all quite similar (two different synthetic routes are also involved), it seems probable that a single isomer is produced.

The evidence that $C_2B_5H_5$ and *sym*- $C_2B_4H_6$'s structurally resemble a trigonal bipyramid and an octahedron, respectively, appears convincing.³ The most likely candidate for the $R_2C_2B_5H_5$ is a pentagonal bipyramid and the B^{11} n.m.r. immediately eliminates a symmetrical structure with carbon at the apexes of a five-boron mutual base. Three other structures (about a pentagonal bipyramid) are possible wherein three different boron environments are created in the ratio 2:2:1; in two of these structures the carbons are adjacent. Previously, the most likely candidate was one with adjacent carbons for there was no evidence that the carbons from the original acetylene had become separated. During the present investigation it became evident that the $R_2C_2B_4H_4$'s produced had nonadjacent carbons (III, Fig. 1) which made the structure of $R_2C_2B_5H_5$ (II, Fig. 1) in which the carbons are nonadjacent more attractive. Two other considerations also recom-

(12) Although a detailed discussion of possible mechanisms is preliminary, several working hypotheses appear quite plausible.



If it is assumed that *unsym*- $C_2B_4H_6$, once formed, does not rearrange at 300° to the symmetrical isomer:



The presence of trimethylamine might catalyze reactions 1 and 2 (in both A and B schemes) and yet not appreciably affect reaction 3 because catalysis, in this case, would involve a three-body collision.

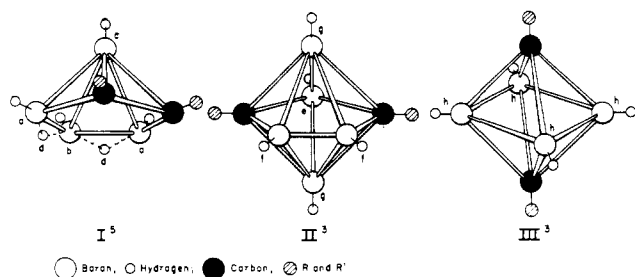
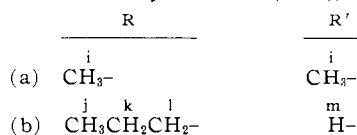


Fig. 1.—Ball and stick models of dihydrocarborane-2,4, carborane-2,5, and *sym*-carborane-2,4. No attempt is made to depict these structures in terms of two- and three-center bonds since we wish to avoid the problems associated with the valence bond structural ellipsis⁸ implied even by a sophisticated representation.⁸ For further discussion on this subject see Lipscomb and co-workers, *J. Chem. Phys.*, **35** 1329 (1961), and ref. 13.



mend this structure: First, the B¹¹ n.m.r. resonance assigned to the unique boron (e, Fig. 1) is quite narrow compared to the resonances assigned to the other boron nuclei; the partial isolation of the lone boron (carbons on sides) might account for this. Secondly, it seems reasonable that separation of the carbons should lead to a more thermodynamically stable molecular species¹³; certainly *sym*-C₂B₄H₆ is prepared in greater abundance

(13) This has been independently presumed by W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961); R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

from the pyrolysis than *unsym*-C₂B₄H₆ where the carbons are adjacent. The chemical shifts and spin-spin coupling constants (Tables III and IV) are related to the possible structure II (Fig. 1) for convenience.

The alkane side products produced during the pyrolysis are consistent with the assumption that the skeletal carbon-carbon bond is rather easily broken. Thus, *n*-butane is formed from the pyrolysis of Ib; however, no pentane is found. It is interesting to note that a considerable amount of propane is formed in addition to *n*-butane, and yet none of the parent (nonalkylated) carboranes are formed in the process. This may imply that dihydrocarborane and/or carborane radicals lead to the observed solids.

The observed melting points (Table II) are in good relative agreement with the symmetry of the proposed structures for the dihydrocarboranes-2,4,⁵ *sym*-carborane-2,4, and carborane-2,5. The series Ia, IIa, and IIIa and the series Ib, IIb, and IIIb represent a progression to greater symmetry, and, therefore, one would expect the observed increase in melting point. The "a" compounds, containing methyl substituents on each of the two skeletal carbons melt, expectedly, higher than the "b" compounds with a propyl group on only one of the skeletal carbons.

Although the carborane distribution from the pyrolysis of dihydrocarboranes is not the same as that found from the silent electric discharge reaction between pentaborane and acetylene,^{3,4} it is tempting to conclude that the silent discharge production of carboranes proceeds through a dihydrocarborane intermediate. A consequence of this conclusion is the prediction that a silent electric discharge through pure dihydrocarboranes may be a potential synthetic route to C₂B₃H₅ and *unsym*-C₂B₄H₆ derivatives.