

groups. However, it is clear that one does not have to assume an equilibrium between the *ob* and *lel* forms in order to explain the presence of sometimes one and sometimes two peaks for the mixed en-pn complexes. It must be largely the result of the fact that the configurational effect contributes most strongly to the E_a peak and the vicinal effect contributes most strongly to the A_2 peak, as observed for amino acids.⁶ The observed curve is the sum of the two effects which contribute differently in magnitude and in sign so that A_2 can be quite strong (Figures 1 and 4) or completely covered by E_a (Figures 1 and 4).

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CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICHIGAN

Facile Polyhedral Rearrangement of Icosahedral Silylcarboranes

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The thermal rearrangement of carborane ($C_2H_2-B_{10}H_{10}$) to neocarborane has been reported^{1,2} to take place at 465–500°, a change which moves the carbon atoms in the icosahedral cage from an *ortho* (1,2) to a *meta* (1,7) position. 1-Methylcarborane is isomerized to 1-methylnocarborane at 400° and is the only carborane derivative previously reported¹ to undergo this rearrangement.

A mechanism for this rearrangement (involving a cubeoctahedral intermediate) has been suggested,³ and the prediction has been made that $B_{12}H_{10}X_2^{2-}$ would undergo polyhedral rearrangement by the same mechanism. A comprehensive study⁴ of polyhedral rearrangements in $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ derivatives showed isomerizations in the $B_{12}H_{12}^{2-}$ series to be higher energy processes than those in the $B_{10}H_{10}^{2-}$ series. One of the most facile polyhedral rearrangements in the $B_{10}H_{10}^{2-}$ series involves 2,3- $B_{10}H_8[N(CH_3)_3]_2$, in which both steric interactions and electronic repulsions would be reduced by the isomerization. This reaction was reported to have an activation energy of only 37 kcal., with rearrangement exclusively to the 1,6 isomer being complete after 30 min. at 230° in solution. Attempts to observe such rearrangements in

1,2- $B_{12}H_{10}[N(CH_3)_3]_2$ (a member of the $B_{12}H_{12}^{2-}$ series which is analogous in structure and electronic configuration to the carboranes) failed because of decomposition of the compound at its melting point. Similar negative results were reported for 1,2- $B_{12}H_{10}[N(CH_3)_3]_2$ in Dowtherm A solution at 325°.

We now wish to report the *facile* rearrangement of suitably substituted icosahedral carboranes at relatively low temperatures. When the C-hydrogen atoms of carborane are replaced by the bulky methylphenylsilyl groups to give 1,2-bis(methyldiphenylsilyl)carborane (1), rearrangement to the neo isomer (2) is observed at 260°. Evidence for the rearranged species consists of a lower melting point, a shift in the methyl proton magnetic resonance signal from τ 9.45 to 9.23, and a change in the 9.3 μ region of the infrared spectrum. An authentic sample of 2 was synthesized from neocarborane and methyldiphenylchlorosilane *via* dilitioneocarborane and was found to be identical (infrared, n.m.r., mixture melting point, elemental analyses) with the above rearrangement product. Several related compounds were also examined; the results are summarized in Table I.

TABLE I
THERMAL REARRANGEMENT OF CARBORANES^{a,b}
TO NEOCARBORANES

R	Reaction conditions		Compound designation and m.p., °C.	
	Temp., °C.	Time, days	1,2-	1,7-
$CH_3(C_6H_5)_2Si$	260	2	1, 241–243	2, 138–140
$Cl(C_6H_5)_2Si$	260	2	3, 249–251 ^c	4, 121–122 ^a
$C_6H_5(CH_3)_2Si$	300 ^e	4	5, 138–139	6, 82–85
$(CH_3)_3Si$	300 ^e	10	7, 141–142	...
H	425	2

^a Rearrangements of 1, 3, 5, and 7 were followed qualitatively by infrared; of 1, 5, and 7 by n.m.r.; and of carborane by g.l.p.c. ^b Analytical results: 1. Calcd. for $C_{28}H_{36}Si_2B_{10}$: C, 62.7; H, 6.76; Si, 10.45. Found: C, 62.8; H, 6.70; Si, 10.23. 2. Calcd. for $C_{28}H_{36}Si_2B_{10}$: C, 62.7; H, 6.76; Si, 10.45. Found: C, 62.8; H, 7.17; Si, 10.84. 5. Calcd. for $C_{18}H_{32}Si_2B_{10}$: C, 52.4; H, 7.82; Si, 13.6. Found: C, 53.3; H, 8.15; Si, 13.6. 6. Calcd. for $C_{18}H_{32}Si_2B_{10}$: C, 52.4; H, 7.82; CH_3/C_6H_5 , 6/5. Found: C, 53.2; H, 8.03; CH_3/C_6H_5 , 6.1/5.0 (n.m.r.). 7. Calcd. for $C_8H_{28}Si_2B_{10}$: C, 33.3; H, 9.79; Si, 19.5; B, 37.5. Found: C, 33.8; H, 9.70; Si, 19.3; B, 37.3. ^c Lit. 244–245° [S. Papetti and T. L. Heying, *Inorg. Chem.*, **2**, 1105 (1963)]. ^d Lit. 131–133° [ref. c]. ^e At 260° no evidence for rearrangement is observed for 5 days. ^f Infrared spectra of these compounds are identical with those published.¹

The greater ease with which 1 rearranges is reasonably ascribed to the resulting relief of strain arising from juxtaposition of such large groups in the *ortho* isomer. 1,2-Bis(phenyldimethylsilyl)carborane (5), with presumably less internal strain, required a somewhat higher temperature for rearrangement. Even at this higher temperature, 1,2-bis(trimethylsilyl)carborane (7) rearranged considerably more slowly than did 5. The fact that 1,2-bis(chlorodiphenylsilyl)carborane (3) undergoes rearrangement at nearly the same rate as 1 argues against the importance of electronic effects; while chlorine is approximately isosteric with methyl

(1) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

(2) (a) S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *ibid.*, **3**, 1444 (1964); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(3) R. Hoffmann and W. N. Lipscomb, *ibid.*, **2**, 231 (1963).

(4) W. R. Hertler, W. H. Knoth, and E. L. Muettterties, *J. Am. Chem. Soc.*, **86**, 5434 (1964).

its greater electronegativity should cause an increased rate of isomerization if electronic effects were indeed responsible for the more facile rearrangement of the more highly phenylated silyl derivatives.

In order to examine more closely the effect of this postulated steric acceleration, kinetic data were obtained (Table II) for the polyhedral rearrangement of carborane itself and for a derivative bearing bulky substituents (1). The enthalpy of activation for the isomerization of 1 (45 kcal.) is considerably lower than that for the isomerization of unsubstituted carborane (62 kcal.). This result accords well with the above rationale involving relief of internal strain; *i.e.*, bond stretching, necessary for polyhedral rearrangement, is already present in the ground state of 1 and therefore results in a decreased ΔH^* .

TABLE II
RATE DATA^a FOR THERMAL REARRANGEMENTS
1,2-Bis(methyldiphenylsilyl)carborane (1)

Temp., °C.	263	280	300
$k \times 10^4$, sec. ⁻¹	0.03	0.22	1.28
$\Delta H^* = 45$ kcal., $\Delta S^* = -1$ e.u. at 280°			
Carborane			
Temp., °C.	425	455	475
$k \times 10^4$, sec. ⁻¹	0.22	1.54	4.7
$\Delta H^* = 62$ kcal., $\Delta S^* = 7$ e.u. at 455°			

^a The rate of isomerization of 1 was measured by determining the relative integrals of the methyl proton n.m.r. signal for 1 and 2. The isomerization of carborane was followed by g.l.p.c. First-order rate constants were determined from plots of log C vs. time. Activation parameters were calculated from an Arrhenius plot (A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 98-101). Because of difficulties in thermostating reactions at these temperatures, the activation parameters (particularly ΔS^*) can only be considered approximate.

The observed enhancement of the rearrangement rate by bulky C substituents suggests that carboranes bearing large groups other than the silyl groups studied in this investigation would also undergo polyhedral rearrangement at relatively low temperatures.

CONTRIBUTION FROM ETHYL CORPORATION,
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Reaction of Grignard Compounds with Diborane: Characterization of Chloromagnesium Borohydride

BY WARREN E. BECKER AND EUGENE C. ASHBY

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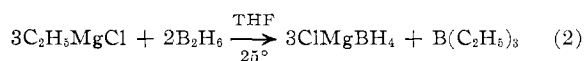
A study of the reaction of Grignard reagents with diborane was first reported by Wiberg and Strebel.^{1,2}

These workers reported this reaction to be useful for the synthesis of compounds having the composition HMgX. Using this system, they reported the preparation of HMgCl, HMgBr, and HMgI as the bis-diethyl etherates and HMgCl as the ditetrahydrofuranate, according to the equation



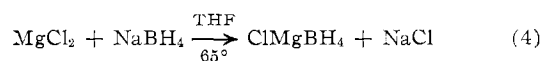
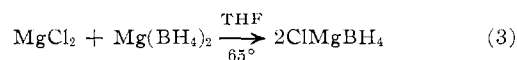
More recently Russian workers have also prepared these same compounds as the diethyl etherates by hydrogenolysis of the appropriate Grignard reagent.³

Before appearance of this latter publication, we attempted to prepare HMgX compounds according to the procedure of Wiberg and Strebel, using $\text{C}_2\text{H}_5\text{MgCl}$. A range of stoichiometries was investigated; in no case were we able to isolate HMgX, as reported by Wiberg and Strebel. Instead, we were able to isolate chloromagnesium borohydride, according to the equation



Chloromagnesium borohydride was proposed by Strebel² as being the product from further reaction of HMgCl and diborane. However, the material was not isolated or characterized.

We have now prepared and isolated chloromagnesium borohydride in quantitative yield and in good purity as the ditetrahydrofuranate by the reaction shown in eq. 2. It has also been prepared according to the equations.



Reaction 3 produces quantitative yields of ClMgBH_4 ; reaction 4 does not give good yields and is not recommended as a preparative method. None of the above reactions proceeds simply and in good yield in diethyl ether; however, a small amount of $\text{ClMgBH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ was obtained from reaction 2 in diethyl ether solvent. Physical and chemical properties are reported for the ditetrahydrofuranate.

Chloromagnesium borohydride, as the ditetrahydrofuranate, is a white crystalline material which is isolated simply by removal of the tetrahydrofuran solvent under vacuum at room temperature. One mole of tetrahydrofuran per mole of magnesium can be removed under vacuum at 100°. The monotetrahydrofuranate is somewhat gummy in appearance. Its properties were not investigated.

The material $\text{ClMgBH}_4 \cdot 2\text{THF}$ is soluble in benzene but is insoluble in ether and in diglyme. It evolves hydrogen upon addition to water. The cryoscopic molecular weight in benzene is 440 (437 calculated for a dimer), but in boiling tetrahydrofuran it is monomeric.

(1) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(2) P. Strebel, Dissertation, University of Munich, Oct. 1958.

(3) T. N. Dymova and N. G. Eleseeva, *Russ. J. Inorg. Chem.*, **8**, 820 (1963).