hydroperoxide, including a strong peak at 2.8 μ characteristic of the OH group.

Anal. Calcd for $C_{18}H_{16}GeO_2$: C, 64.17; H, 4.79; Ge, 21.5; active O, 4.75. Found: C, 64.39; H, 4.84; Ge, 21.8; active O, 4.76. The molecular weight (vapor pressure osmometer) determined in benzene was 382, 383 (calcd for $C_{36}H_{16}GeO_2$: 336.9), indicating association of the hydroperoxide molecules in this solvent.

The hydroperoxide was also obtained from the reaction of 98% hydrogen peroxide with triphenylgermanium oxide (65% yield) and with triphenylgermanol (60% yield).

The hydroperoxide is quite stable and can be stored at −20° without any decomposition. When left at room temperature (*ca.* 25°) for 30 days, the active oxygen decreased only 2% (to 98%) and the melting point was unchanged.

Thermal decomposition of the hydroperoxide in *o*-dichlorobenzene at 160–170° gave the following products.

$$\underset{\text{1 mole}}{(C_6H_5)_3GeOOH} \longrightarrow \underset{0.65}{(C_6H_5)_3GeOH} + \underset{ca.\ 0.20}{O_2} + \underset{ca.\ 0.05}{[(C_6H_5)_2GeO]_x} + \underset{ca.\ 20}{C_6H_5OH}$$

These products resemble those obtained from the thermal decompositions of triphenylsilyl hydroperoxide[5] and trimethyltin hydroperoxide.[6]

$$Ph_3SiOOH \longrightarrow \underset{0.45}{Ph_3SiOH} + \underset{0.23}{PhOH} + \underset{0.29}{Ph_2Si(OH)_2} + \text{polymer}$$

$$(CH_3)_3SnOOH \longrightarrow \underset{0.47}{(CH_3)_2SnO} + \underset{0.40}{CH_3OH} + \underset{0.49}{(CH_3)_2SnO} + \underset{0.24}{O_2}$$

The decomposition of the triphenylgermyl hydroperoxide has a first-order kinetic dependence on hydroperoxide concentration ($k = 2.38 \times 10^{-6}$ at 130°; $k = 4.34 \times 10^{-6}$ at 144°; $k = 13.3 \times 10^{-6}$ at 152°; $k = 22.0 \times 10^{-6}$ sec^{-1} at 163°). The energy of activation is 24.0 ± 1.0 kcal/mole. This is intermediate between the energies of activation for the first-order decompositions in nonpolar solvents of several silyl hydroperoxides (27 kcal/mole[5]) and that of trimethyltin hydroperoxide (21 kcal/mole[6]). Apparently an increased electropositive nature of the metal in these compounds leads to higher electron densities on the peroxide oxygens and thus promotes thermal dissociation.

Acknowledgment. This research was supported by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G720. Appreciation is expressed to Dr. Walter A. Aue for his aid in isolating the first sample of the pure germanium hydroperoxide.

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Received November 27, 1965

Order of Electrophilic Substitution in 1,2-Dicarbaclovododecaborane(12) and Nuclear Magnetic Resonance Assignment

Sir:

Certain restrictions[1] relating the ground-state charge distributions to transition states may allow predictions of sequential order of electrophilic or nucleophilic substitution in carboranes[2] from molecular orbital theories.[2–4] Here we show that o-$B_{10}C_2H_{12}$ brominates[5] under Friedel–Crafts conditions, first at B-9 and B-12, and then at B-8 (B-10). Photochemical chlorination occurs last at B-3 and B-6. These results permit a unique ^{11}B nmr assignment and a test of molecular orbital predictions.

The positions of bromination are here firmly established from three-dimensional crystallographic studies of 9,12-dibromo-*o*-carborane (Pbn2_1; $a = 7.42$, $b = 13.03$, $c = 11.75$ A; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.07$ for 909 reflections), of 8,9,12-tribromo-*o*-carborane (C2/c, $a = 12.28$, $b = 8.54$, $c = 23.42$ A; $\beta = 90.3°$; $R = 0.12$ for 1132 reflections), and of C,C′-dimethyl-8,9,10,12-tetrabromo-*o*-carborane (P2_1/n; $a = 13.18$, $b = 14.49$, $c = 8.20$ A; $\beta = 96.3°$; $R = 0.11$ for 1370 reflections). The distinction of C from B in the ordered 9,12-$Br_2B_{10}H_8C_2H_2$ structure was achieved from results on bond distances, electron densities, atom multipliers, and thermal parameters.

Molecular orbital calculations, made by a new nonempirical method,[4,6] are based upon parameters obtained from self-consistent field molecular orbital calculations on B_2H_6 and C_2H_6 in which Slater exponents were used for B and C, and an exponent of 1.2 was employed for H. Framework charges on BH or CH units in o-$B_{10}C_2H_{12}$ are 0.29 for C-1, 0.26 for B-3, −0.02 for B-4, −0.28 for B-8, and −0.24 for B-9. If, however, those occupied molecular orbitals which lie highest in energy are more easily distorted by electrophilic reagents, we may note that the highest five MO's, which are within 0.02 atomic unit of one another and separated by 0.05 au from the next lowest orbital, place 0.79 electron on B-9 but only 0.60 electron on B-8. Perhaps this charge difference, which is reversed when a number of lower lying orbitals are added, may contribute to the preference of electrophilic reagents for B-9 over B-8.

Zakharkin and Kalinin[7] have noted that the number of isomers prepared from *o*-carborane, C-methyl-*o*-carborane, and C,C′-dimethyl-*o*-carborane suggests that halogen substitution occurs first at 9,12 and then at 8,10. They must assume that 3,6 substitution is excluded on the basis of the charge distribution as given by molecular orbital theory. Their second assumption, that substitution of CH_3 for H on C does not change the sequential ordering of substitution, is now partly, supported by our X-ray results on C,C′-dimethyl-8,9,10,12-tetrabromo-*o*-carborane, at least for tetrabromination.

The published[8–10] ^{11}B spectra of *o*- and *m*-carborane

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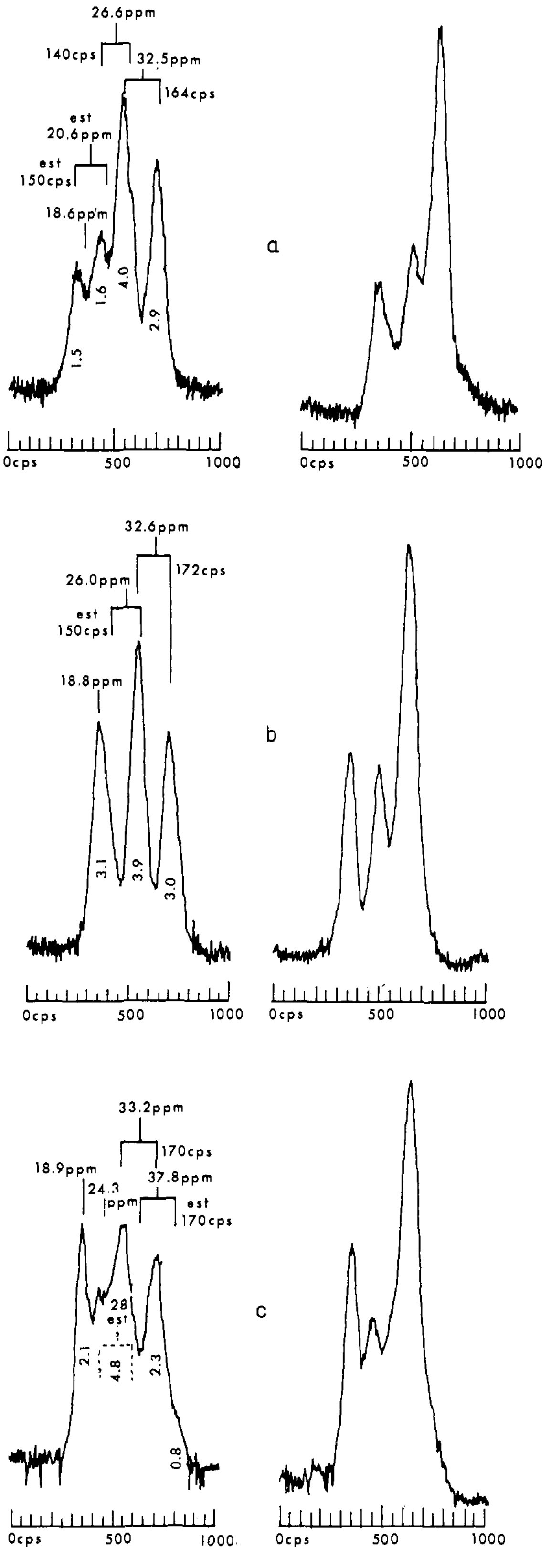

Figure 1. ^{11}B nmr spectra at 19.3 Mc/sec (Varian HR-60 modified with an NMR specialties HD-60 heteronuclear decoupler operating at 60 Mc/sec): (a) monobromo-*o*-carborane (30% concentrated in $CHCl_3$), (b) dibromo-*o*-carborane (30% in acetonitrile), (c) tribromo-*o*-carborane (30% in acetonitrile). Decoupled spectra are on the right. Solvent effects were shown to be negligible. All spectra were swept from low to high field, and chemical shifts were measured by interpolation between the resonance of external trimethyl borate and its audio side band. Spectra completely decoupled from ^{1}H were taken by a new procedure (G. D. Vickers and M. J. Nadel, to be published) and interpreted by methods reported elsewhere.[11]

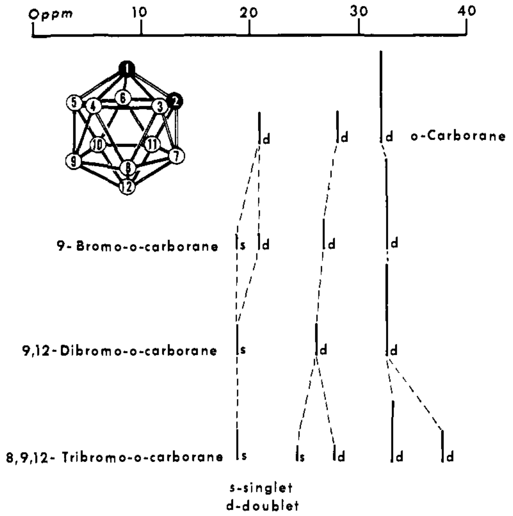

Figure 2. Tabulation of spectra idealized by collapse of ^{1}H fine structure.

have suggested molecular symmetry,[9] but not complete nmr assignments. A suggestion[11] that B atoms closest to C show resonances at higher field than those further removed seems incongruous with simple arguments, such as electron densities inferred from MO theory or halogenation reactions. Here we complete the ^{11}B nmr assignment for *o*-carborane by comparison of normal (Figure 1) and decoupled (Figure 2) spectra of the dibromo- and tribromo-*o*-carboranes, assigned as 9,12 and 8,9,12 in these X-ray studies. Chemical shifts refer to the 19.3-Mc/sec spectra.[11] The 20.8-ppm resonance is affected in monobromo- and dibromo-*o*-carborane and is thus assigned to B-9 and B-12. Next to be affected by bromination (in the tribromo derivative) is the 28.0-ppm resonance which is assigned to B-8 (B-10). The 32.0-ppm doublet in *o*-carborane is resolved in the 60.0[10] or 60.2 Mc/sec[11] spectrum into two unequal doublets, intensities of which correlate the 32.5-ppm doublet to B-4, B-5, B-7, and B-11 and the 33.3-ppm doublet to B-3 and B-6. This assignment is confirmed by the high-field doublet in the ^{11}B spectrum of the established[1,8] *o*-$B_{10}H_2Cl_8C_2H_2$ structure, in which B-3 and B-6 are BH units.

Thus C atoms in the *o*-carborane framework produce ^{11}B resonances at higher field to the closer B atoms,[11] the effect diminishing with distance. Hence we suggest that the *m*-carborane [1,7-dicarbaclovododecaborane(12)] spectrum be assigned as B-2, B-3 (35.4 ppm); B-4, B-6, B-8, B-11 (31.7 ppm); B-5, B-12 (29.1 ppm); and B-9, B-10 (25.1 ppm).

Acknowledgment. The authors are indebted to Mr. E. A. Pier and Dr. H. Agahigian for suggesting these spectral assignments, and to the Office of Naval Research for support of this work.

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Received December 20, 1965