A New Boron Hydride, $B_{20}H_{16}$

Sir:

We wish to report the synthesis and characterization of a new boron hydride, $B_{20}H_{16}$, which is the first example of a volatile borane that has fewer hydrogen than boron atoms.[1] Preparation was effected by catalytic pyrolysis of decaborane-14 at 350° (<1 mm.). With methylaminodimethylborane as the catalyst, yields of $B_{20}H_{16}$ averaged about 10%. The product was purified by repeated vacuum sublimation. The new hydride is a white, hygroscopic crystalline solid that melts at 196–199°, sublimes at 100–120° (<1 mm.), and is soluble in most common organic solvents.

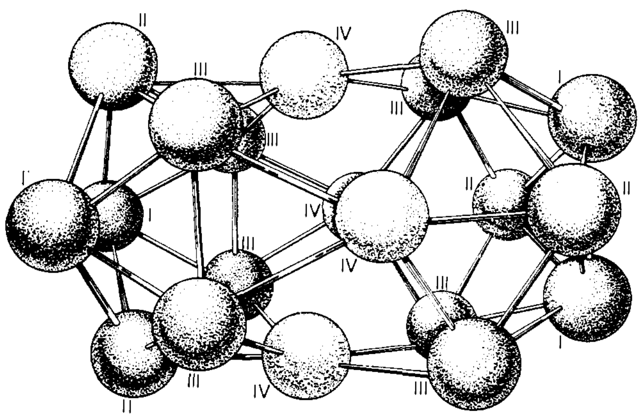

Fig. 1.—Proposed boron atom arrangement in $B_{20}H_{16}$. The unique boron atoms not directly bonded to hydrogen atoms are the central four atoms labeled IV.

Characterization is based on a thrice-sublimed sample of $B_{20}H_{16}$ which showed only one peak of any significance on gas chromatographic analysis using a 1 m. apiezon-on-firebrick column.

Anal. Calcd. for $B_{20}H_{16}$: B, 93.1; H, 6.9; C, 0.0; mol. wt., 232.5. Found: B, 92.9; H, 7.1; C, 0.3.

These data establish a hydrogen deficiency; the B–H ratio is about 20:16.3. Isopiestic molecular weight determinations in *n*-pentane gave values of 235 and 239 using as standards $B_{10}C_2H_{12}$ and azobenzene, respectively. The mass spectrum showed positive ions of every mass up to 236, and those clustered around the 100% peak at 232 were by far the most abundant. The highest mass of any significance is 236 which corresponds to $^{11}B_{20}H_{16}$. Additional molecular weight data were obtained from a preliminary single crystal X-ray study (*vide infra*). With a measured density of 1.13 g./cc., the X-ray molecular weight is 231.

With the number of boron atoms determined by molecular weight and elemental analysis data, the hydrogen atom number was confirmed as 16 by aqueous acid hydrolysis. Values of 163.9 ± 0.8 and 164.4 ± 0.8 check with that of 163.4 mmoles of H_2/g. required for $B_{20}H_{16}$. Since $B_{20}H_{16}$ is diamagnetic, odd hydrogen atom numbers are excluded. Formulations as $B_{20}H_{14}$ and $B_{20}H_{18}$ fall well outside the precision and accuracy of the acid hydrolysis experiment; respective hydrolysis values would be 160.5 and 166.2 mmoles of H_2/g. Thus the $B_{20}H_{16}$ composition is fully established.

The infrared spectrum of $B_{20}H_{16}$ shows no evidence of a bridge hydrogen stretching absorption. In the spectrum of the solid (Nujol mull), the B–H stretch at 2600 cm.$^{-1}$ has just discernible fine structure. This splitting must be a crystalline lattice effect, since it is absent in solution spectra. No ultraviolet absorption maxima were detected in cyclohexane solution.

The B^{11} n.m.r. spectrum at 19.2 Mc. in CCl_4 solution consists of three peaks of unequal intensity at +7.8, +18.5, and +27.4 p.p.m.[2] On irradiation of the hydrogen nuclei at 60 Mc., the peak at +7.8 p.p.m. was not significantly altered, indicating these boron atoms are not directly bonded to hydrogen. On sweeping with the saturating proton field, two other boron resonances are detected at +15.6 and +22.4 p.p.m. Relative intensities in the decoupled B^{11} spectra are ~4, 4, and 12 for the 7.8, 15.6, and 22.4 resonances, respectively.

X-Ray studies have shown the crystals to be tetragonal with the cell dimensions of a = 9.60 ± 0.05 Å. and c = 29.4 ± 0.1 Å. and space group $I4_1/acd$. There are eight molecules per unit cell and the required molecular symmetry is $\bar{4}$ or 222.

The X-ray and n.m.r. data indicate a model of D_{2d} symmetry formed by joining two decaborane cages so that the 6 and 9 boron atoms of each decaborane cage contact the 5,10 and 7,8 boron atoms of the other cage (Fig. 1). Four boron atoms in the center plane are not bonded to hydrogen in agreement with analysis of the B^{11} n.m.r. spectrum.[3]

The chemistry of this novel boron hydride is under study. We have established that $B_{20}H_{16}$ dissolves with reaction in water. No hydrogen is evolved and a strongly acidic solution is generated. The titration curve of the aqueous solution is typical of that of a strong acid. Equivalent weight determined by titration was 116 ± 2 indicating that the species in solution is a diprotic acid.

Acknowledgments.—We wish to thank Dr. John Whitney for the X-ray data, and Mr. W. B. Askew and Mr. R. J. Berndt for the mass spectral information.

(1) L. F. Friedman, R. D. Dobrott, and W. N. Lipscomb, have independently found and characterized $B_{20}H_{16}$, *J. Am. Chem. Soc.*, **85**, 3505 (1963). This information was kindly given to us before publication by W. N. Lipscomb.

(2) Trimethyl borate external reference.

(3) In the model in Fig. 1, there is a total of 4 boron atom environments. This requires accidental coincidence of two boron chemical shifts. B^{11} n.m.r. assignments are I (or II), 15.6 p.p.m.; II (or I) and III, 22.4 p.p.m.; and IV, 7.8 p.p.m.

CONTRIBUTION NO. 922 N. E. MILLER
CENTRAL RESEARCH DEPARTMENT E. L. MUETTERTIES
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON 98, DELAWARE

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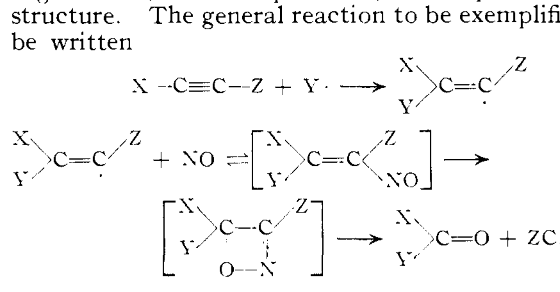
Reactions of Unsaturated Free Radicals with Nitric Oxide. Radical-Induced Scission of Carbon–Carbon Triple Bonds

Sir:

We have recently examined the gas phase reactions, at room temperature, of nitric oxide with vinyl and substituted vinyl radicals, where the radicals were formed *in situ* by the addition of an inducer radical (Y·) to an alkyne (X—C≡C—Z). The results suggest a new family of free-radical reactions involving degradation, at the triple bond, of the parent alkynyl structure. The general reaction to be exemplified may be written



(1)

(2)