follow literature procedures for hydrogenations. For example, the hydrogenation of cholesterol is a capricious reaction. However, Hershberg, *et al.*, reported that the erratic tendencies of this reaction could be overcome by performing the hydrogenation with platinic oxide in ethyl acetate in the presence of a small quantity of perchloric acid.[2] The reaction was carried out (on a scale 1/150 that described) utilizing the automatic hydrogen generator. The reaction required approximately one hour for completion. By doubling the amount of platinic oxide, the hydrogenation was complete in 20 min.

These new procedures should greatly facilitate laboratory-scale hydrogenations. The technique is also proving valuable for chemical analysis and for following the rates of hydrogenation.

We wish to acknowledge the generous assistance of Engelhard Industries, Inc., in supplying the chloroplatinic acid utilized in this study.

(2) E. B. Hershberg, E. Oliveto, M. Rubin, H. Staeudle and L. Kuhlen, *J. Am. Chem. Soc.*, **73**, 1144 (1951).

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THE SYNTHESIS OF $B_4C_nH_{2n+4}$ COMPOUNDS FROM PENTABORANE-9 AND ALKYNES CATALYZED BY 2,6-DIMETHYLPYRIDINE

Sir:

Compounds having the general formula $B_4C_nH_{2n+4}$ (I) have been prepared from reactions between pentaborane-9 and several alkynes (propyne, 2-butyne, and 1-pentyne) in the presence of 2,6-dimethylpyridine. The stoichiometry of the reaction is believed to be

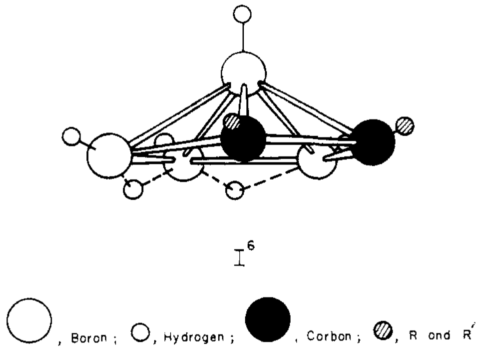
$$B_5H_9 + R—C{\equiv}C—R' + \text{2,6-dimethylpyridine} \longrightarrow B_4H_6C_2RR' + \text{2,6-dimethylpyridine}{\cdot}BH_3$$

A competing reaction involving the decomposition of pentaborane to give two moles of 2,6-dimethylpyridine-borane and $(BH)_x$ polymer[1] prevents the quantitative formation of I. In the absence of 2,6-dimethylpyridine alkynes do not react noticeably with pentaborane at ambient temperature. 2,6-Dimethylpyridine also has been shown to catalyze a rearrangement in pentaborane[2] and in pentaborane derivatives.[3,4]

The procedure adopted to prepare I was to shake vigorously a 1:1:5 mole ratio mixture of pentaborane, alkyne, and 2,6-dimethylpyridine for two to ten hours at ambient temperature. I was isolated after the addition of excess boron trifluoride ethyl etherate to the reaction mixture and the subsequent separation of the volatiles by vapor phase chromatography. The general formula $B_4C_nH_{2n+4}$ for I was determined on the basis of elemental and mass spectroscopic analysis as well as B^{11} and H^1 n.m.r. evidence.

Anal. Calcd. for $B_4C_5H_{14}$, Ic: C, 51.16; H, 12.02. Found: C, 51.01; H, 12.40.

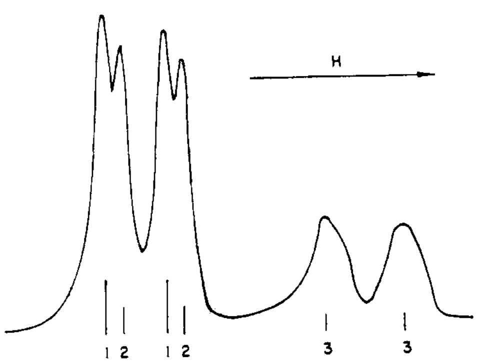
The B^{11} and H^1 n.m.r. spectra indicate that the structure is similar to B_6H_{10}[5] and that two of the base borons are identical. The structure depicted in Fig. 1 for I is compatible with the data.[6] The



I[6]

	R	R′
(a)	—H	-CH_3 (from propyne)
(b)	—CH_3	–CH_3 (from 2-butyne)
(c)	—H	—$CH_2CH_2CH_3$ (from 1-pentyne)

Fig. 1.—The basic structure of $B_4C_nH_{2n+4}$ compounds.[6]



	1		2		3	
Compound	δ^a	J, c./s.	δ	J	δ	J
Ia	2.1	152	5.1	151	49.9	175
Ib	3.7	151	7.2	156	47.7	186
Ic	1.7	156	4.8	156	49.7	175

[a] Relative to $BF_3{\cdot}Et_2O$; T. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

Fig. 2.—The B^{11} n.m.r. spectra and δ and J values of the $B_4C_nH_{2n+4}$ compounds.

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(1) A similar decomposition of pentaborane with trimethylamine has been observed by A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957).

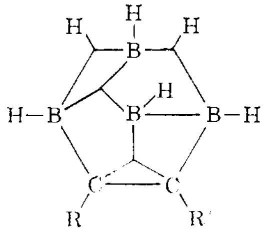
(2) B^{11} nuclear magnetic resonance studies show the deuterium in 1 deuteriopentaborane equilibrates between the apical and basal (and perhaps bridge) positions within one hour in the presence of 2,6-dimethylpyridine.

(3) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2581 (1961).

(4) R. N. Grimes and W. N. Lipscomb, *Proc. Nat. Acad. Sci.*, **48**, 496 (1962).

(5) R. E. Williams, S. G. Gibbons and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6164 (1959); *J. Chem. Phys.*, **30**, 333 (1959).

(6) I′ is a projection formula of I in which bonding electrons are accounted in terms of two and three center bonds. The two and three center bonds between the apical and basal atoms are depicted in only one of many canonical forms.



I′

B^{11} spectra of Ia,b,c, (Fig. 2) contain three sets of doublets having estimated area ratios of 2:1:1 (low field to high field). The high field doublet has a chemical shift value characteristic of an "apical environment,"[5] whereas the low field doublets have chemical shift values quite similar to the base boron atoms in B_6H_{10}. The H^1 n.m.r. spectra are compatible with the B^{11} n.m.r. spectra and with structure I. A low field quartet and high field quartet are present in the ratio of 3:1 which represent the terminal hydrogens attached to the basal and apical boron atoms, respectively. The bridge hydrogen unresolved multiplet, as well as the sharper absorptions due to the hydrogens attached to carbon, are present where expected. In compounds Ia and Ib a singlet represents the methyl protons. The propyl group in Ic gives rise to three distinct C–H absorptions with barely resolved multiplet structure reflecting the interactions of the adjacent CH_2 and CH_3 groups. In compounds Ia and Ic (where –R equals –H) a single low field peak may be assigned to those hydrogens attached to carbon in the basic molecular skeleton.

The compounds $B_4C_nH_{2n+4}$ (or more generally, $B_mC_nH_{m+n+2}$) may be considered to fit between the boron hydrides which have bridge hydrogens but no carbon in the molecular skeleton and the recently reported carboranes[7] ($B_mC_nH_{m+n}$) which contain carbon and boron but no bridge hydrogens. Perhaps the compounds might be named dihydrocarboranes.

It is interesting to compare the "stable" partial three-center bond character of the carbon atoms in the dihydrocarboranes, as well as in the carboranes, with the relatively unstable bridge (or three center) intermediates normally postulated in carbonium ion chemistry, *e.g.*, protonated double bonds.

We wish to thank the Office of Naval Research for financial support.

(7) R. E. Williams, C. D. Good and I. Shapiro, 140th ACS Meeting, Chicago, Sept., 1961.

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ELECTRON SPIN RESONANCE AND ISOTOPIC EXCHANGE STUDIES IN THE TRITIUM-POLYSTYRENE FLUFF SYSTEM[1]

Sir:

In a recent publication by Ingalls and Wall,[2] a technique was disclosed for stabilizing free radicals at room temperature through the use of finely divided polymer fluff as the reaction medium. Such a rigid and finely spaced system not only has the advantage of minimizing radical recombination, but also permits essentially complete mixing with gases. We wish to report here an application of the above technique to the study of reactions induced by the β-radiation of tritium gas. The use of polymer fluff permits the utilization of tritium gas as an internal radiation source in electron spin resonance (e.s.r.) studies of various model organic systems, and direct observation of radical intermediates is possible as an aid to a mechanistic study of the Wilzbach[3] method of labeling organic compounds by exposure to tritium gas. Advantages arising from such a technique are at least comparable to those for tritiated water as radiation source in condensed media.[4]

Polymer fluffs were cast in thin-walled quartz tubes by freeze-drying dilute benzene solutions of polystyrene.[5] Our experimental apparatus consisted simply of a quartz tube connected through a stopcock to a gas reservoir bulb. Reaction gases were pre-mixed in the reservoir bulb and admitted to the quartz tube containing a fluff capsule. The resulting e.s.r. spectrum in the tritium-polystyrene fluff system is essentially identical with that observed in gamma-irradiated polystyrene.[6] The e.s.r. signal growth for a series of experiments is presented graphically in Fig. 1.[7] As expected, the rate of signal growth is a function of tritium pressure. The presence of xenon or helium enhanced the initial rate of increase in radical concentration. Nitric oxide not only inhibited radical build-up but also caused a change in the e.s.r. spectrum to an asymmetric structure.

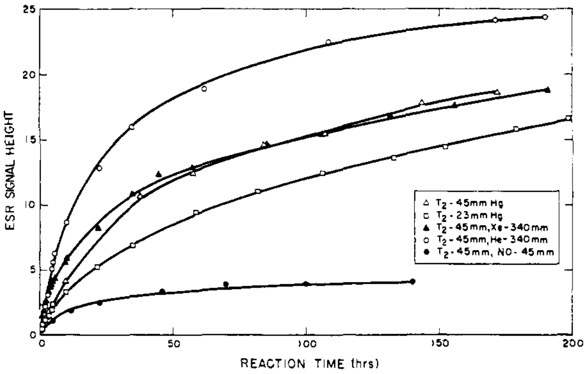

Fig. 1.—E.s.r. signal growth in the T_2–polystyrene system.

Following evacuation of the gas, the observed radicals were found stable at room temperature over periods of weeks. The addition of deuterium or ethylene caused a gradual but small decrease of the e.s.r. signal intensity. On the other hand, nitric oxide appeared to react with the intermediate radicals at a rate faster than our e.s.r. response, and the residue e.s.r. signal was similar in structure and in magnitude to that observed in the tritium–nitric oxide–polystyrene fluff system.

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(1) Work performed for the U. S. Atomic Energy Commission under Contract AT(11-1)-GEN-8, and presented in part at the 141st ACS National Meeting.

(2) R. B. Ingalls and L. A. Wall, *J. Chem. Phys.*, **35**, 370 (1961).

(3) K. E. Wilzbach, *J. Am. Chem. Soc.*, **79**, 1013 (1957).

(4) (a) J. Kroh, J. W. T. Spinks and B. C. Green, *Nature*, **189**, 655 (1961); (b) J. Kroh and J. W. T. Spinks, *J. Chem. Phys.*, **35**, 760 (1961); (c) J. Kroh, B. C. Green and J. W. T. Spinks, *Can. J. Chem.*, **40**, 413 (1962).

(5) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem. Anal. Ed.*, **17**, 134 (1945).

(6) R. E. Florin, L. A. Wall and W. D. Brown, *Trans. Faraday Soc.*, **56**, 1304 (1960).

(7) Each unit of e.s.r. signal height represents radical concentration in the order of 10^{15} spins (for a 3-mg. sample) and the radiation dose rates are approximately 3.4 × 10^{16} ev./hr. for T_2 pressure at 45 mm. and 1.7 × 10^{16} ev./hr. for T_2 pressure at 23 mm.