

gen exchange occurred at random between any of the deuterium atoms of chlorophyll and water, it must have been confined to less than 5% of the hydrogen atoms at any location. Hydrogen exchange confined to only a few special chlorophyll molecules (constituting less than 5% of the chlorophyll) in a large photosynthetic unit<sup>9</sup> probably would not be revealed by our procedure.

In these organisms and under the conditions employed in our experiments, then, the bulk of the chlorophyll exists in a form that precludes hydrogen exchange especially at the  $\delta$ , 7, and 8 positions, either by photosynthesis or by subsequent hydrogen transport.

(9) R. K. Clayton in "Photophysiology," A. C. Giese, Ed., Academic Press New York, N. Y., 1964, p. 159 *et seq.*

CHEMISTRY DIVISION  
ARGONNE NATIONAL LABORATORY  
ARGONNE, ILLINOIS

JOSEPH J. KATZ  
RALPH C. DOUGHERTY  
WALTER A. SVEC  
HAROLD H. STRAIN

RECEIVED JULY 9, 1964

### Novel Six-Membered Aluminum-Nitrogen Heterocycles via Metalative Cyclization

Sir:

Current interest in novel heterocycles isoelectronic with aromatic hydrocarbons has inspired the synthesis of many unsaturated organoboron ring systems. The physical and chemical properties of borazines<sup>1</sup> and borepins<sup>2</sup> have been studied with particular attention since  $\pi$ -bonding involving boron might be expected to confer aromatic character upon such heterocyclic nuclei. Dewar's comprehensive studies of boron-nitrogen analogs of aromatic nuclei, such as 10,9-borazarophenanthrene,<sup>3</sup> have adduced convincing evidence for such cyclic conjugation. Our recent discovery of a novel metalative cyclization pathway to the hitherto unknown aluminole ring system<sup>4</sup> awakened the hope that aluminum-nitrogen heterocycles, such as the 10,9-aluminazarophenanthrene system,<sup>3</sup> might result from suitably conceived intramolecular metalations. Since the problem of  $\pi$ -bonding between aluminum and adjacent electron-rich centers is still uncertain,<sup>5</sup> the study of such heterocycles might prove significant in evaluating possible  $\pi$ -electronic interactions.

In light of the foregoing, we are pleased to describe the synthesis and properties of the novel, six-membered, aluminum-nitrogen heterocycle formally isoelectronic (*cf. infra*) with the phenanthrene nucleus. Thus, the heating of an equimolar melt of 2-(methylamino)-biphenyl (I)<sup>6</sup> and triphenylaluminum at 160° led to the evolution of 1 equiv. of benzene; further heating at 240° produced *ca.* 1 more equiv. of benzene (total benzene (2 equiv.): 93-100%). The resulting pale amber-colored 9-methyl-10-phenyl-10,9-aluminazarophenanthrene (III) did not melt under 500°; however, decomposition commenced at temperatures over 350°.

(1) *Cf., inter alia*, M. J. S. Dewar, *et al.*, *J. Chem. Soc.*, 3073, 3076 (1958); *ibid.*, 2728 (1959); *J. Am. Chem. Soc.*, **84**, 2648 (1962).

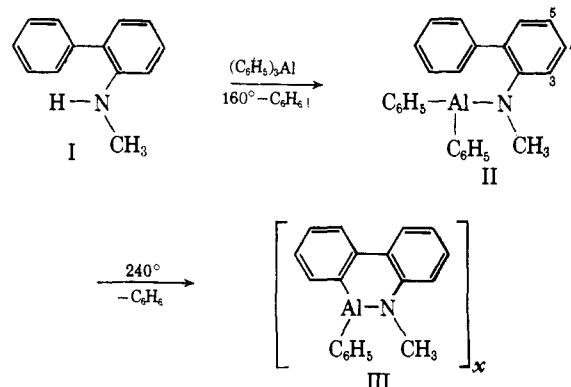
(2) E. E. van Tamelen, G. Brieger, and K. G. Untch, *Tetrahedron Letters*, **No. 8**, 14 (1960).

(3) *Chemical Abstracts* favors the naming of six-membered boron-nitrogen heterocycles as azaborines and this pseudophenanthrene member as 5,6-dihydrodibenz[*c,e*][1,2]azaborine. However, the nomenclature employed in Dewar's papers [*cf.* M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959)] conveys a more immediate relationship to pertinent aromatic systems.

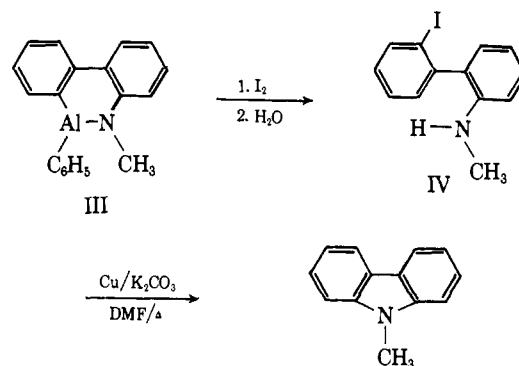
(4) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **84**, 1501 (1962).

(5) A. W. Laubengayer, Special Publication No. 15, The Chemical Society, London, 1961, p. 150.

The product III was insoluble in most aliphatic and aromatic hydrocarbons and only very slightly soluble in anhydrous tetrahydrofuran or N-methylpyrrolidine. Traces of moisture rapidly cleaved III to regenerate I. Ultraviolet spectra of III in the latter two solvents displayed only end absorption in the region  $>325$  m $\mu$ .



Although the foregoing reaction product III is clearly a highly associated substance ( $x > 1$ ), it was desirable to demonstrate that benzene evolution had arisen from metalative cyclization leading to the 9-methyl-10-phenyl-10,9-aluminazarophenanthrene monomer (III), and not from metalation *ortho* or *para* to the methylamino group (C-3 or C-5 in II). Therefore, III was treated successively with a benzene solution of iodine and with water to yield, as oils, iodobenzene and *ca.* 80% of an iodo-2-(methylamino)biphenyl (IV)<sup>6</sup> (picrate, m.p. 178-180°; *p*-toluenesulfonamide, m.p. 153-154°). Proof that IV is 2'-iodo-2-(methylamino)-biphenyl was obtained by heating IV with copper bronze in dimethylformamide to produce N-methylcarbazole (m.p. 87-88°; mixture melting point undepressed). Consequently, the structure proof of the molecular unit in III can be summarized in the following manner.



The properties of 9-methyl-10-phenyl-10,9-aluminazarophenanthrene (III) form a sharp contrast to those of the corresponding boron system.<sup>7</sup> 9-Methyl-10-phenyl-10,9-borazarophenanthrene (V) is reported to be monomeric (m.p. 123°), soluble without decomposition in 95% ethanol, and quite stable to hydrolytic cleavage. Moreover, it exhibits a prominent ultraviolet maximum at 332 m $\mu$ , ascribable to boron-nitrogen conjugation. The latter contention is supported by the absence of such absorption in the spec-

(6) All new compounds encountered in this study have been characterized by satisfactory elemental analyses and spectral data consonant with the assigned structures.

(7) M. J. S. Dewar and P. M. Maitlis, *J. Am. Chem. Soc.*, **83**, 187 (1961).

trum of 9,9-dimethyl-10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (VI) in the region  $>320 \mu$ . Since the ultraviolet spectrum of III appears to bear a closer resemblance to that of VI than to that of V, this implies that the aluminum and nitrogen centers in III are tetracoordinated also. Whether the degree of association ( $x$ ) of aluminazarophenanthrene units in III is variable<sup>8</sup> or whether the attractive possibility of a compact dimer unit ( $x = 2$ ) is realized<sup>9</sup> remains to be resolved.

The foregoing study enhances the feasibility of synthesizing other pseudophenanthrene systems by treating suitable 2-substituted biphenyls (HO-, HS-, HP(R)-, etc.) with group III organometallics. These extrapolations are receiving our earnest attention.

**Acknowledgment.**—The authors wish to express their appreciation to the donors of the Petroleum Research Fund for the support of this investigation by PRF Grant 723-A.

(8) A. W. Laubengayer, K. Wade, and G. Lengnick, *Inorg. Chem.*, **1**, 632 (1962).

(9) Cf. J. I. Jones and W. S. McDonald, *Proc. Chem. Soc.*, 366 (1962).

DEPARTMENT OF CHEMISTRY JOHN J. EISCH  
THE CATHOLIC UNIVERSITY OF AMERICA  
WASHINGTON, D. C. 20017 SR. MARY ESTHER HEALY,  
P.V.B.M.

RECEIVED AUGUST 24, 1964

### A New Carborane, $B_9C_2H_{11}$ , and Its Derivatives

Sir:

In recent months a great deal of interest has developed with regard to the carboranes *o*-,<sup>1</sup> *m*-,<sup>2</sup> and *p*-<sup>3</sup>  $B_{10}C_2H_{12}$ ,  $B_5C_2H_7$ ,<sup>4</sup>  $B_4C_2H_5$ ,<sup>5</sup>  $B_4C_2H_6$ ,<sup>4b,c</sup> and  $B_3C_2H_5$ .<sup>4c</sup> We have recently prepared a new carborane,  $B_9C_2H_{11}$ , and representative C-alkyl, C-aryl, and C,C'-dialkyl derivatives. These carboranes were obtained in moderate to high yields by pyrolysis of the corresponding  $B_9C_2H_{13}$  derivatives<sup>6</sup> at 110–150° in a suitable organic solvent. The  $B_9C_2H_{13}$  intermediates were generated *in situ* by treating the cesium or potassium salts of the proper  $B_9C_2H_{12}^-$  ion<sup>6</sup> with polyphosphoric acid in the presence of solvent. At temperatures above 100°, hydrogen is briskly evolved and the resulting carborane is separated by distillation *in vacuo*. Table I presents representative yield and characterization data. The  $B_9C_2H_{11}$  carboranes survive brief exposure to moist air.

(1) (a) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); (b) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963); (c) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); (d) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963); (e) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963); (f) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963); (g) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963); (h) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963); (i) D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. P. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963); (j) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963); (k) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1874 (1964).

(2) (a) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(3) S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

(4) (a) R. A. Beaudet and R. L. Poynter, *ibid.*, **86**, 1258 (1964); (b) T. P. Onak, F. J. Gerhart, and R. E. Williams, *ibid.*, **85**, 3378 (1963); (c) I. Shapiro, C. D. Good, and R. E. Williams, *ibid.*, **84**, 3837 (1962).

(5) T. P. Onak, R. E. Williams, and H. G. Weiss, *ibid.*, **84**, 2830 (1962); see also footnote 6 in that paper.

(6) R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964).

TABLE I

YIELD AND CHARACTERIZATION DATA FOR  $B_9C_2H_9RR'$  SPECIES

R	R'	M.p., °C.	Yield, %	Analysis, %					
				Calcd.			Found		
				C	H	B	C	H	B
H	H	212–213	22	18.13	8.37	73.50	18.40	8.64	73.44
CH <sub>3</sub>	H	84–84.5	60	24.59	8.94	66.46	24.66	8.90	66.63
CH <sub>3</sub>	CH <sub>3</sub>	57–58	75	29.92	9.42	60.66	30.17	9.61	60.38
C <sub>6</sub> H <sub>5</sub>	H	37–37.8	57	46.07	7.25	46.69	46.87	7.57	46.14

Aside from the elemental analyses obtained, each carborane described in the table exhibited the parent peaks in its mass spectrum which coincided with the assigned empirical formulas containing a random distribution of <sup>10</sup>B and <sup>11</sup>B isotopes in their natural abundance.

The infrared spectrum of the parent  $B_9C_2H_{11}$  contained a B–H stretching band at  $3.88 \mu$  and a C–H stretching band at  $3.27 \mu$ . Although the <sup>11</sup>B n.m.r. spectra of  $B_9C_2H_{11}$  and its alkyl and aryl derivatives have not been unequivocally interpreted, the spectra obtained at 60 Mc./sec.<sup>7</sup> are consistent with an eleven-particle icosahedral fragment related to  $B_9C_2H_{12}^-$ ,<sup>6</sup>  $B_{11}H_{14}^-$ ,<sup>8</sup> and  $B_{11}H_{13}^{2-}$ .<sup>8</sup> Degradation of the C-phenyl and C,C'-dimethyl derivatives with a palladium catalyst and propionic acid at the reflux temperature was quite vigorous and afforded toluene (7% yield) and ethane (67% yield), respectively. The similar degradation of the C-phenyl derivative of *o*- $B_{10}C_2H_{12}$  produced only ethylbenzene (21% yield). Thus, the chemical evidence available suggests that the carbon atoms in  $B_9C_2H_{11}$  are not near neighbors and that carborane formation is accompanied by rearrangement of the carbon atoms.<sup>9</sup>

Additional evidence suggests that the gross structural features present in  $B_9C_2H_{12}^-$  are retained in  $B_9C_2H_{11}$ . Treatment of the  $B_9C_2H_{11}$  carboranes described above with a variety of ligands produced monoadducts of the general formula  $B_9C_2H_{11}(\text{ligand})$  which are iso-electronic with  $B_9C_2H_{12}^-$ . Representative ligands include triphenylphosphine (m.p. for the C-phenyl derivative, 255° dec. *Anal.* Calcd. for  $B_9C_{26}H_{30}P$ : C, 66.32; H, 6.42; B, 20.68. Found: C, 65.78; H, 6.79; B, 22.62) and triethylamine (m.p. for the C-phenyl derivative, 157–159° dec. *Anal.* Calcd. for  $B_9C_{14}H_{30}N$ : C, 54.28; H, 9.77; B, 31.44. Found: C, 52.57; H, 9.89; B, 32.24). Titration of  $B_9C_2H_{10}-(C_6H_5)$  with methoxide ion in methanol was typical for a strong acid and 1 equiv. of base was consumed (equiv. wt., 206.8; theory, 208.6).

Further studies are in progress and will be reported at a later date.

**Acknowledgments.**—This work was performed under Grant CA-06773 MCHB from the National Cancer Institute, U. S. Public Health Service, and was supported, in part, by the Advanced Research Projects Agency through the Army Research Office (Durham). This support is gratefully acknowledged. The authors wish to thank Mr. Eugene A. Pier of Varian Associates for the 60 Mc./sec. <sup>11</sup>B n.m.r. spectra, Mr. Donald C. Young of the Union Oil Company for the mass spectra,

(7) N.m.r. spectra of the <sup>11</sup>B nucleus at 60 Mc./sec. were obtained by Mr. E. A. Pier at Varian Associates, Palo Alto, Calif.

(8) V. D. Aftandilian, H. C. Miller, G. W. Parrshall, and E. L. Muettterties, *Inorg. Chem.*, **1**, 734 (1962).

(9) This argument assumes that the formation of  $B_9C_2H_{12}^-$  from *o*- $B_{10}C_2H_{12}$  (ref. 6) retains the near neighbor relationship of the carbon atoms present in the starting material.