

Figure 1. Dependence of the apparent second-order rate constant on sodium or potassium ion concentration.

concentration. The ATP formed was assayed by means of the fluorometric method described by Esterbrook.² A Farrand A2 fluorometer was used with Siliclad glass sample cells.

At constant concentration of Na⁺ or K⁺, it was found that the initial rate of phosphoryl group transfer according to the equation $2\text{ADP} \rightleftharpoons \text{ATP} + \text{AMP}$ is proportional to the square of the ADP concentration. However, the apparent second-order rate constant, k' , varies with the nature and concentration of the alkali ion in a way which can be quantitatively accounted for by assuming that the rate-determining step involves the reaction between two ADP-Na⁺ or ADP-K⁺ complex ions. For example, if we define the apparent stability constant, K' , of the ADP-Na⁺ complex as

$$K' = \frac{[\text{ADP-Na}^+]}{[\text{ADP}][\text{Na}^+]} \quad (1)$$

then the initial rate of dismutation may be written as

$$\frac{1}{2} \frac{d[\text{ATP}]}{dt} = k'[\text{total ADP}]^2 = k[\text{ADP-Na}^+]^2$$

Hence we have

$$\left(\frac{1}{k'}\right)^{1/2} = \left(\frac{1}{k}\right)^{1/2} \left(1 + \frac{1}{K'[\text{Na}^+]}\right) \quad (2)$$

where k is the true second-order rate constant.

In Figure 1 the values of $(1/k')^{1/2}$, where k' is the measured apparent second-order rate constant, are plotted vs. the reciprocal of alkali ion concentration. For these measurements solutions of the bis(tetra-*n*-butylammonium) salt of ADP in DMSO solution at 60° were used. The initial concentration of total ADP was in the range 5.9 to $6.6 \times 10^{-4} M$. The Na⁺ or K⁺

(2) R. W. Esterbrook, *Anal. Biochem.*, **4**, 231 (1962).

was added in the form of its perchlorate. Enough tetra-*n*-butylammonium bromide was added in each of these solutions to keep the ionic strength constant at $0.04 M$. The plots are, within experimental uncertainties, linear as required by eq. 2. The apparent stability constants, K' , and the true second-order rate constants, k , are calculated from the slopes and intercepts of these linear plots according to eq. 2 to be $K' = 37 M^{-1}$, $k = 0.21 M^{-1} \text{sec}^{-1}$ for K⁺; $K' = 2.1 \times 10^2 M^{-1}$, $k = 0.031 M^{-1} \text{sec}^{-1}$ for Na⁺.

The conclusion that Na⁺ and K⁺ catalyzed the phosphoryl group transfer through complex formation is further supported by the observation that cations such as Li⁺ and Mg²⁺ are not only themselves inactive but can also suppress the catalysis by Na⁺ or K⁺ through competition for the same ligands. The reverse reaction $\text{ATP} + \text{AMP} \rightarrow 2\text{ADP}$ was also found to be catalyzed by Na⁺ or K⁺, although the kinetics are more complex since the ATP molecule may transfer its phosphoryl group either to an AMP molecule or to another ATP molecule.

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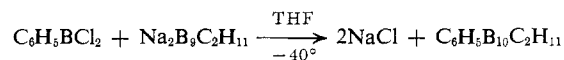
B-Phenyl-1,2-dicarbaclododecaborane(12) from B₉C₂H₁₁⁻² through an Insertion Reaction

Sir:

We wish to report the first derivative of 1,2-dicarbaclododecaborane(12) which bears an aryl substituent on boron and the novel insertion reaction which led to the formation of this derivative.

Previous work¹⁻⁴ established the existence of B₉C₂H₁₁⁻² [(1)-2,3-dicarbollide ion³] and its reactions with transition metal derivatives. The latter reactions reconstituted the icosahedron by inserting the metal atom in the open face of the B₉C₂H₁₁⁻² ion. We now report the re-establishment of the 1,2-dicarbaclododecaborane(12) structure by the similar insertion of a boron atom.

Phenylboron dichloride and B₉C₂H₁₁⁻² reacted at -40° in tetrahydrofuran to produce a B-phenyl-1,2-dicarbaclododecaborane(12) (I) which probably bears the phenyl group in the 3-position. I was purified by



sublimation under high vacuum and obtained as a

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).

(3) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965), propose the modified nomenclature system used herein. The nomenclature system as devised for carboranes (R. M. Adams, *Inorg. Chem.*, **2**, 1087 (1963)) does not take into account species such as B₉C₂H₁₂⁻. We suggest that the position of the hole in these species be identified by the number in parentheses preceding the name using the numbering system of Adams.

(4) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

white crystalline solid, m.p. 108–109°. The yields of purified I were 80–85% and the recovery of sodium chloride based on the above equation was quantitative. The ^1H n.m.r. spectrum of I in CCl_4 solution contained resonances at δ 3.53 (broad, relative area 2) and 7.41 (multiplet, relative area 4.8) relative to tetramethylsilane. These resonances were assigned to the hydrogen atoms bonded to the two carborane carbon atoms and the phenyl group, respectively. The 19.3-Mc./sec. ^{11}B n.m.r. spectrum of I in CCl_4 solution exhibited three unresolved resonances and the spectrum envelope was very similar to that of 1-phenyl-1,2-dicarboclovododecaborane(12). The singlet due to the aryl-substituted boron atom was not resolved. The ^{11}B n.m.r. chemical shifts are δ 17.5, 26.8, and 35.8 relative to $\text{B}(\text{OCH}_3)_3$. *Anal.* Calcd. for $\text{B}_{10}\text{C}_8\text{H}_{16}$: B, 49.20; C, 43.65; H, 7.28; mol. wt., 220. Found: B, 49.13; C, 43.61; H, 7.46; mol. wt., 227.

Treatment of I with ethanolic potassium hydroxide⁵ produced an anion which could be isolated as the white tetramethylammonium salt (II) in 90% yields. II was recrystallized from ethanol-water, m.p., 132–133°. The ^1H n.m.r. spectrum of II in CH_3NO_2 solution gave resonances (p.p.m.) at δ 7.55 (broad, relative area 2.1), 7.29 (multiplet, relative area 3.1), 3.18 (relative area 11.7), and 2.08 (broad, relative area 2.0) relative to tetramethylsilane. The first two resonances were assigned to the protons of the phenyl group. The two remaining resonances represent the tetramethylammonium protons and the two protons attached to carborane carbon atoms, respectively. The infrared spectrum of II also confirmed the presence of a phenyl group. The ^{11}B n.m.r. spectrum of II contained six unresolved peaks and was not interpreted. It is quite likely that II contains the (1)-7-phenyl-2,3-dicarbododecahydroundecaborate(–1) ion.^{3,5} *Anal.* Calcd. for $\text{B}_9\text{C}_{12}\text{H}_{12}\text{N}$: C, 50.90; B, 34.40; H, 9.91; N, 4.95. Found: C, 50.81; B, 34.68; H, 10.05; N, 4.91.

Previous studies with the $\text{B}_9\text{C}_2\text{H}_{11}^{-2}$ ion have shown a striking similarity of this ion to the cyclopentadienide anion. However, the interaction of the $\text{B}_9\text{C}_2\text{H}_{11}^{-2}$ ion with a nonmetal deviates from the established chemistry of the cyclopentadienide ion and suggests a broader scope. Further work on these reactions is now in progress and will be reported in full at a later time.

Acknowledgment. The authors wish to thank the Army Research Office (Durham) for their generous support of this research.

(5) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964), report the alkaline degradation of 1-phenyl-1,2-dicarboclovododecaborane(12).

(6) Alfred P. Sloan Research Fellow.

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3a,6a-Diazapentalene (Pyrazolo[1,2-a]pyrazole)

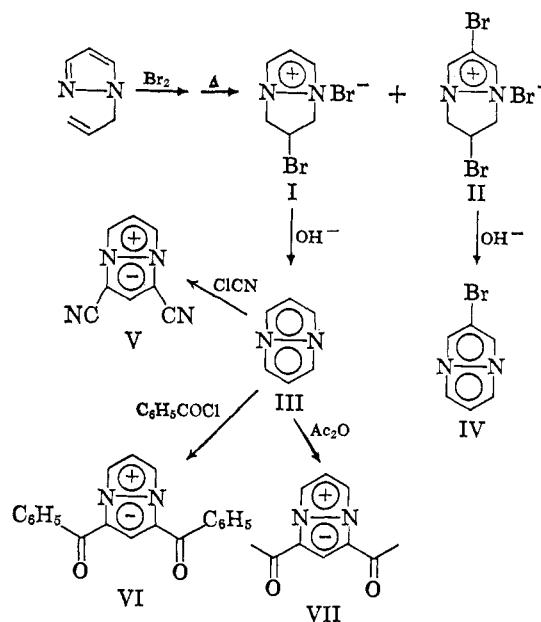
Sir:

Polyazapentalenes meeting the Hückelian aromaticity criterion and isoelectronic with pentalene dianion¹

(1) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).

have been the object of recent attention. While diversely substituted tetraazapentalenes^{2–4} and diazapentalenes⁵ have been reported, the parent compounds remained unknown. We report herewith synthesis of 3a,6a-diazapentalene (III), the simplest parent polyazapentalene capable of aromaticity,⁶ and some of its reactions.

1-Allylpyrazole⁷ was brominated and the resulting product was thermally quaternized to yield a mixture of I, m.p. 158–159°, and II, decomposing slowly around 230°, separated by fractional crystallization (*Anal.* Calcd. for $\text{C}_8\text{H}_8\text{Br}_2\text{N}_2$ (I): C, 26.9; H, 2.99; Br, 59.8. Found: C, 26.8; H, 2.81; Br, 60.1); n.m.r. (D_2O): doublet, τ 1.65 ($J = 2.9$), triplet, τ 3.02 ($J = 2.9$); multiplet, τ 4.52 ($J = 3.5$) and doublet τ 5.32 ($J = 3.5$)⁸ with relative intensities 2:1:1:4; ultraviolet λ_{max} 224 m μ (ϵ 4450); (*Anal.* Calcd. for $\text{C}_8\text{H}_7\text{Br}_3\text{N}_2$ (II): C, 20.8; H, 2.08; Br, 69.2; N, 8.07. Found: C, 21.1; H, 2.23; Br, 69.1; N, 7.89); n.m.r. (D_2O): singlet τ 1.16, multiplet, τ 4.30 ($J = 3.4$), doublet, τ 4.65 ($J = 3.4$),⁸ with relative areas 2:1:4; ultraviolet λ_{max} 244 m μ (ϵ 3130).



Treatment of I with aqueous sodium hydroxide afforded a solid which was purified by vacuum sublimation. The colorless crystals of III turned green-black immediately upon exposure to even traces of air, thus precluding elemental analysis. Nevertheless, structure III for the product follows from (a) its simple infrared spectrum with peaks at 3160 (s), 1430, 1140, 1139 (s), 1040, and 929 (s) cm^{-1} , indicating a highly symmetrical structure; (b) its n.m.r. spectrum, which consists of a doublet at τ 2.99 and a triplet at τ 3.35

(2) R. A. Carboni and J. E. Castle, *ibid.*, **84**, 2453 (1962).

(3) R. Pfeifer, E. Garthe, and K. Rauer, *Ber.*, **96**, 1827 (1963); M. Brufani, W. Fedeli, G. Giacomello, and A. Vaciago, *ibid.*, **96**, 1840 (1963).

(4) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, to be published.

(5) T. W. G. Solomons and F. W. Fowler, *Chem. Ind. (London)*, 1462 (1963); T. W. G. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, **87**, 528 (1965).

(6) Monoazapentalenes and diazapentalenes with unsubstituted nitrogen atoms at positions other than 3a,6a are not 10- π -electron systems.

(7) L. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

(8) At high resolution the low-field peak of this doublet is split in both I ($J = 1.7$) and II ($J = 1.3$).