

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 ^{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-dicarbadodecaborane(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-dicarbadodecahydroundecaborate(–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.

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

(6) Alfred P. Sloan Research Fellow.

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

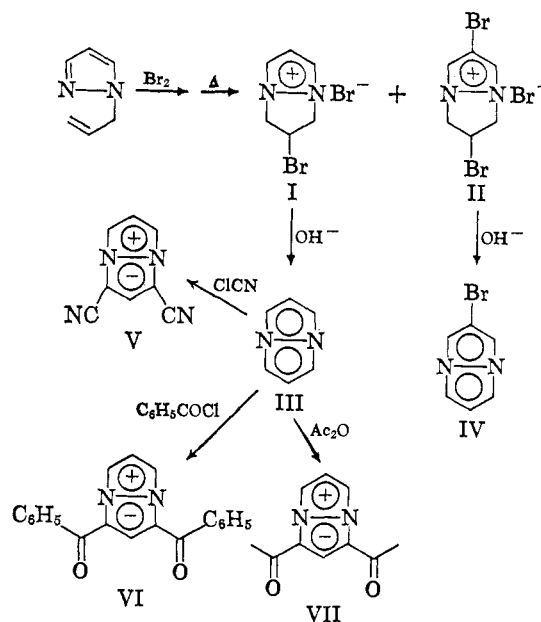
Sir:

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 $\text{C}_6\text{H}_8\text{Br}_2\text{N}_2$ (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 $\text{m}\mu$ (ϵ 4450); (*Anal.* Calcd. for $\text{C}_6\text{H}_7\text{Br}_3\text{N}_2$ (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 $\text{m}\mu$ (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. Pfeiffer, 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 ($J = 1.3$).

($J = 2.5$), with relative areas 2:1, and (c) its mass spectrum where the most abundant peak is that of the parent ion, m/e 106.

As further confirmation, derivatives V, m.p. 226 dec., VI, m.p. 188°, and VII, m.p. 155°, were prepared from III by treating it with excess cyanogen chloride, benzoyl chloride, and acetic anhydride, respectively. In contrast to III, they are relatively stable in air. *Anal.* Calcd. for $C_8H_4N_4$ (V): C, 61.5; H, 2.58; N, 35.9; mol. wt., 156. Found: C, 61.7; H, 2.73; N, 35.8; mol. wt. (osmometric in chloroform), 163. Calcd. for $C_{20}H_{14}N_2O_2$ (VI): C, 76.4; H, 4.49; N, 8.90; mol. wt., 314. Found: C, 76.4; H, 4.59; N, 8.66; mol. wt. (osmometric in chloroform), 323. Calcd. for $C_{10}H_{10}N_2O_2$ (VII): C, 63.1; H, 5.30; N, 14.7. Found: C, 62.9; H, 5.29; N, 14.7.

The 1,3-location of substituents in the above derivatives follows from n.m.r. Thus, in VII, the 4,6 hydrogens appear as a doublet at τ 1.66 ($J_{4,5} = 2.8$), the 2-hydrogen as a doublet at τ 2.60 ($J_{2,5} = 1.1$), the 5-hydrogen as a triplet at τ 3.26 ($J = 2.8$) further split into doublets ($J = 1.1$), and the methyls as a singlet at τ 7.57, with relative intensities 2:1:1:6. In the n.m.r. spectrum of VI the 4,6-hydrogens appear as a doublet ($J = 2.9$) at τ 1.36; the 2-hydrogen is overlapped by the phenyl hydrogens (a multiplet in the τ 2.15–2.58 range). Nevertheless, the presence of a triplet ($J = 2.9$) further split into doublets ($J = 1.1$) at τ 3.12 is diagnostic of 1,3-disubstitution. The observed direction of electrophilic substitution in 3a,6a-diazapentalene is consistent with its charge distribution and the concentration of negative charge in the ring bearing an electron-localizing substituent.

2-Bromo-3a,6a-diazapentalene (IV) was obtained from II and identified by techniques employed for 3a,6a-diazapentalene.

The synthetic scheme employed in the present work is a versatile one and has led to diversely substituted 3a,6a-diazapentalenes. They will be reported along with the details of this work in a forthcoming publication.

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Carbonium Ion Rearrangements. VII. Protonated Cyclopropanes in the Nitrous Acid Deamination of *n*-Propylamine

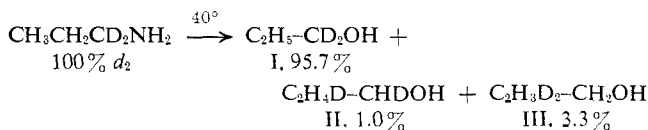
Sir:

From n.m.r. studies we concluded¹ that 11.8% of the 1-propanol obtained from the deamination of 1-aminopropane-1,1,2,2- d_4 had resulted "mainly, if not exclusively," from 1,2-hydride shifts rather than successive 1,2 shifts. Protonated cyclopropanes were excluded by evidence² that the deamination of 1-aminopropane-1-¹⁴C gave 1-propanol labeled exclusively at C-1 and C-3.

To clarify the discrepancy between the 11.8% isotopically rearranged 1-propanol and the 8% reported

from the deamination^{2,3} of 1-aminopropane-1-¹⁴C and to identify the source of the small proton resonance detected¹ at τ 8.5, we have studied the reaction further by using mass spectrometry for isotopic analysis. We wish to present evidence supporting protonated cyclopropanes.⁴

The 1-propanol obtained from the deamination⁵ of 1-aminopropane-1,1- d_2 (96.6%)⁶ and 1-aminopropane-1- d_1 (3.4%) was converted with hexamethyldisilazane to the trimethylsilyl ether.⁷ Isotopic composition of the silyl ether, estimated from the parent-less-methyl peaks, was 96.4% d_2 and 3.6% d_1 . Good agreement of these values with isotopic composition of the diacetamide supports the view that methyl loss occurs solely from the trimethylsilyl group and that no deuterium-proton exchange occurred between substrate and solvent during the reaction. The parent-less-ethyl ion had the composition 3.5% d_0 , 4.9% d_1 , and 91.6% d_2 . If this ion arose solely from primary loss of the ethyl group, then these values would correspond to the isotopic composition of the α -methylene group of 1-propanol. Mass spectral analysis of the trimethylsilyl ether of 1-propanol-1,1- d_2 that was prepared from reduction of propionic anhydride with lithium aluminum deuteride gave: parent-less-methyl, 98.8% d_2 and 1.2% d_1 ; parent-less-ethyl, 98.3% d_2 , 1.6% d_1 , and 0.1% d_0 . From a second reduction the results were: parent-less-methyl, 99.0% d_2 and 1.0% d_1 ; parent-less-ethyl, 98.3% d_2 , 1.6% d_1 , and 0.1% d_0 . The ether of a third sample of 1-propanol-1,1- d_2 that was prepared from reduction of propionyl chloride with a different batch of lithium aluminum deuteride gave: parent-less-methyl, 88.4% d_2 , 11.5% d_1 , and 0.1% d_0 ; parent-less-ethyl, 87.7% d_2 , 12.0% d_1 , and 0.3% d_0 . After correction (0.5% d_1 and 0.1% d_0) the isotopic composition of the α -methylene group of 1-propanol obtained from the deamination becomes 3.4% d_0 , 4.4% d_1 , and 92.2% d_2 . Since about 95% of the 1-propanol is isotopically unrearranged, the ether of the 1-propanol resulting from 1-aminopropane-1- d_1 (3.6%) contributes 0.2% d_0 and 3.4% d_1 . The composition therefore of the methylene group of 1-propanol resulting solely from 1-aminopropane-1,1- d_2 (96.4%) should be 3.2% d_0 , 1.0% d_1 , and 92.2% d_2 . The results are summarized.



The trimethylsilyl ether of the 1-propanol obtained from the deamination of a new sample of 1-aminopropane-1,1- d_2 gave: parent-less-methyl, 98.0% d_2 and 2.0% d_1 ; parent-less-ethyl, 93.6% d_2 , 3.2% d_1 , and 3.2% d_0 . Correcting as before gives 96.0% I, 0.8% II, and 3.2% III. When the reaction was run at 0° the results were 97.8% I, 0.6% II, and 1.6% III.

(3) J. D. Roberts and M. Halman, *J. Am. Chem. Soc.*, **75**, 5759 (1953).

(4) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964); A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).

(5) Reaction conditions were those described in ref. 3. The temperature in the reaction flask was about 40°.

(6) Isotopic composition was estimated from mass spectral analysis of the 1-propyldiacetamide. Uncertainties in these and other isotopic compositions reported here are about ± 0.1 .

(7) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(1) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

(2) O. A. Reutov and T. N. Shatkina, *Dokl. Akad. Nauk SSSR*, **133**, 606 (1960); *Tetrahedron*, **18**, 237 (1962).