Preparation of 8-Bora-7,9-diazaro-*peri*-naphthene[1] and Derivatives

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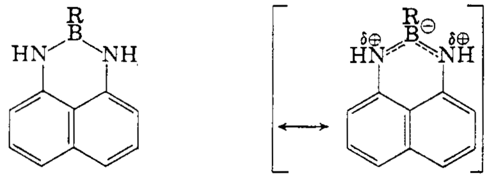
In view of the recent interest in pseudo-aromatic heterocyclic compounds containing boron and nitrogen,[1,4] we wish to report the preparation of 8-bora-7,9-diazaro-*peri*-naphthene (I).



I. R = H
II. R = OCH$_3$
III. R = C$_6$H$_5$

The unsubstituted compound (I) was prepared in 54% yield by reaction of 1,8-diaminonaphthalene with boron trichloride followed by reduction with lithium aluminum hydride without isolation of the B-chloro intermediate. The product was a colorless to slightly pink crystalline solid which discolored to purple during prolonged storage under nitrogen or exposure to air for several hours. Methanolysis of (I) produced 8-methoxy-8-bora-7,9-diazaro-*peri*-naphthene (II) and hydrogen. 8-Phenyl-8-bora-7,9-diazaro-*peri*-naphthene (III) was prepared in 64% crude yield by reaction of 1,8-diaminonaphthalene with phenyldichloroborane in benzene solution. Compounds I and III were very difficult to purify, apparently because they are easily oxidized when in solution, but can be handled in air as the pure solids for short periods without oxidizing significantly. The structures of these compounds were assigned on the basis of their method of preparation, carbon and hydrogen analyses, infrared, and ultraviolet spectra. A previously published attempt[5] to prepare (III) from 1,8-diaminonaphthalene and benzeneboronic acid gave an unidentified crude product melting about 18° lower than III.

It is of interest to note that the ring structure of compounds I–III is isoelectronic with the red *peri*-naphthenide anion[6,7] and the as yet unknown cyclo[3.3.3]azine[8] which both have calculated resonance energies of about 5.8 β.[8,9] If the assumption is made that the 8-boron atom is coplanar with the naphthalene ring system, the 8-bora-7,9-diazaro-*peri*-naphthene ring system might have as a first approximation a calculated resonance energy similar to those of the *peri*-naphthenide anion and cyclo[3.3.3]azine and therefore be predicted to possess considerable aromatic character above that attributable to the naphthalene ring system (calcd. resonance energy = 3.68 β). This prediction is not clearly supported by the ultraviolet spectra of compounds I–III (Figs. 1 and 2) which are little different from that of *peri*-naphthene[6] (included along with the spectrum of 1,8-diaminonaphthalene in Fig. 1 for reference). Furthermore, the prediction is not clarified by the fact that $2.7M$ sodium hydroxide and $1.9M$ hydrochloric acid in 50% aqueous ethanol caused respectively about 83 and 66% hydrolysis of III in sixteen hours at 80° to 1,8-diaminonaphthalene as the main product. However, III may be recrystallized unchanged from neutral aqueous ethanol solutions. The question of whether or not compounds having the ring system of I–III do indeed possess more aromatic character by virtue of the possibility for a highly delocalized 14-π electron system than that furnished by the naphthalene system alone awaits heat of combustion data and proof that the boron atom lies in the same plane as the other atoms of the molecule.

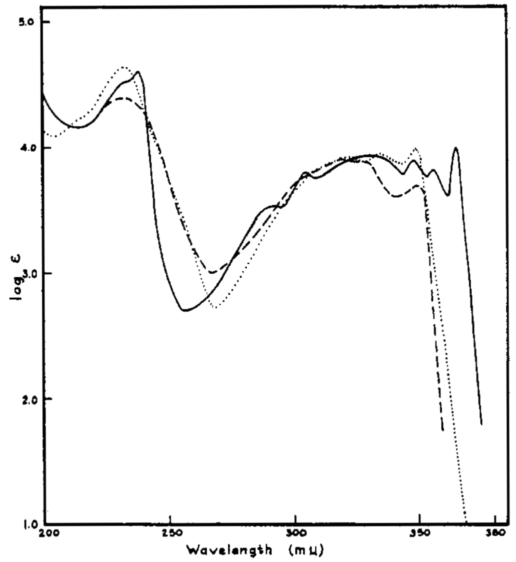


Fig. 1. Ultraviolet spectra: ———, 8-bora-7,9-diazaro-*peri*-naphthene (I) in cyclohexane; – – – –, *peri*-naphthene in 95% ethanol[6]; . . . . , 1,8-diaminonaphthalene in cyclohexane

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[1] For a discussion of nomenclature see M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

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[4] M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959) and preceding papers.

[5] R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5412 (1958).

[6] V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1245 (1950).

[7] D. H. Reid, *Tetrahedron*, **3**, 341 (1958).

[8] R. J. Windgassen, Jr., W. W. Saunder, Jr., and V. Boekelheide, *J. Am. Chem. Soc.*, **81**, 1459 (1959).

[9] R. Pettit, *Chem. & Ind.* (*London*), **1956**, 1306.

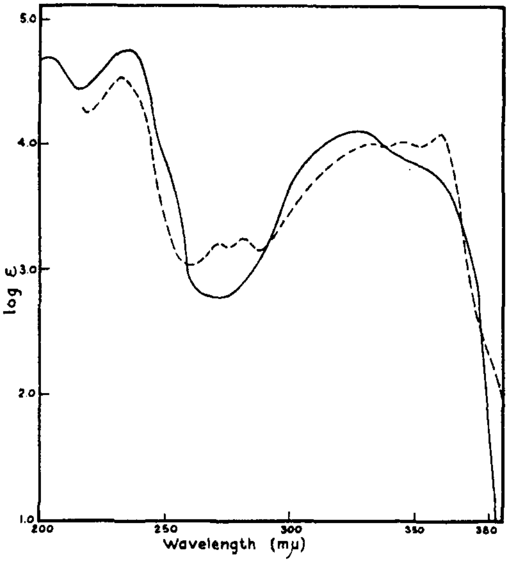

Fig. 2. Ultraviolet spectra: ———, 8-phenyl-8-bora-7,9-diazaro-*peri*-naphthene (III) in cyclohexane; - - - -, 8-methoxy-8-bora-7,9-diazaro-*peri*-naphthene (II) in methanol

EXPERIMENTAL

8-Bora-7,9-diazaro-peri-naphthene (I). A solution of 2.0 g. (17 mmoles) of boron trichloride in 25 ml. of benzene was added dropwise at room temperature to a stirred solution of 2.80 g. (17.7 mmoles) of 1,8-diaminonaphthalene in 65 ml. of benzene. The reaction was carried out under an atmosphere of dry nitrogen and the condenser exit gases were passed successively through a −78° trap and a sodium hydroxide scrubber. After about one fourth of the boron trichloride had been added, the initially purple solution turned yellow-brown, became thick and 50 ml. of benzene was added to render stirring effective. After boron trichloride addition was complete, the mixture was refluxed overnight and then swept with nitrogen. Boron and chlorine analyses of the scrubber contents indicated 64.2% of the expected hydrogen chloride had been trapped. About two thirds of the solvent was removed under water aspirator pressure and then 25 ml. of ether was added, followed by dropwise addition of 80 ml. of 0.39*M* (31 mmoles) lithium aluminum hydride in ether. The mixture was refluxed 1 hr. and then allowed to remain at room temperature overnight. The excess hydride was hydrolyzed by slow addition of 21 ml. of 6*N* hydrochloric acid. The ether solution was immediately decanted from the acid aqueous layer and combined with three 20-ml. ether washes. The yellow ether solution was dried over magnesium sulfate, treated with carbon, filtered, evaporated on a steam bath and then in a stream of nitrogen at room temperature, and finally dried in high vacuum. The crude yellow-brown product weighed 1.80 g. (60.7%) and became purple in air. The crude product was sublimed in high vacuum (90–100°/10^{-6} mm.) giving 1.25 g. (42.1%) of still impure product, part of which after another sublimation and three recrystallizations from *n*-hexane followed by two more sublimations yielded a very pale pink crystalline solid, m.p. 97–99° (corr., under nitrogen).

Anal. Calcd. for $C_{10}H_9N_2B$: C, 71.48; H, 5.40. Found: C, 71.34; H, 5.34. The infrared spectrum (potassium bromide disk) had bands at 3410 (NH), 2550 (BH), 1494, 1344, 1101, and 868 cm.$^{-1}$

Another preparation of I on a 36-mmole scale after purification yielded 54% of colorless crystalline product, m.p. 97.5–99° (corr., under nitrogen).

8-Methoxy-8-bora-7,9-diazaro-peri-naphthene (II). A sealed, evacuated heavy-wall bomb tube containing 0.150 g. (0.890 mmole) of crude I, m.p. 86–93° and 1.5 ml. of absolute methanol was allowed to remain at room temperature for 2 days, then was heated for 1 hr. at 100°. The tube was opened and the hydrogen removed. The solid contents of the tube were recrystallized from dry methanol as colorless needles which were sublimed at 60–100°/10^{-6} mm. yielding 0.06 g. (34.1%) of (II), m.p. 115.2–120.6° (corr., under nitrogen).

Anal. Calcd. for $C_{11}H_{11}ON_2B$: C, 66.70; H, 5.60. Found: C, 66.55; H, 5.68.

The infrared spectrum (potassium bromide disk) had a band at 3390 cm.$^{-1}$ (NH) but none in the BH region.

8-Phenyl-8-bora-7,9-diazaro-peri-naphthene (III). A solution of 4.34 g. (27.3 mmoles) of phenyldichloroborane in 40 ml. of dry benzene was added dropwise to a well stirred solution of 4.22 g. (26.7 mmoles) of 1,8-diaminonaphthalene in 150 ml. of benzene at room temperature forming a reddish-yellow solid. The apparatus was maintained under an atmosphere of argon during reaction. The mixture was refluxed 3 hr. and then the solvent was removed under aspirator pressure. The residue was sublimed twice in high vacuum (160–180°/10^{-6} mm.) to yield 4.17 g. (64%) of yellow product, part of which was further purified by sublimation at 125–130° in high vacuum, two recrystallizations from 50:50 cyclohexane-*n*-hexane and one recrystallization from 80:20 cyclohexane-*n*-hexane followed by a final sublimation. The product was a very pale yellow microcrystalline solid, m.p. 92.5–93.5° (corr., under nitrogen).

Anal. Calcd. for $C_{16}H_{13}N_2B$: C, 78.72; H, 5.37. Found: C, 78.78; H, 5.33.

The infrared spectrum (potassium bromide disk) had bands at 3400 (NH) and 697 cm.$^{-1}$ (C_6H_5) and none in the BH region. Treatment of 0.18 mmole of (III) with 2.7*M* sodium hydroxide in 50% aqueous ethanol in the absence of oxygen for 16 hr. caused about 83% hydrolysis to occur as determined qualitatively from infrared spectral analyses. The main product was 1,8-diaminonaphthalene. Similarly, 0.24 mmole of III was treated with 1.9*M* hydrochloric acid in 50% aqueous ethanol and about 66% hydrolysis occurred.

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Thermal Decomposition Higher of the Alkyl Orthoborates

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The thermal decomposition of alkyl orthoborates in the liquid phase has bearing on the mechanism of the dehydration of alkanols to alkenes catalyzed by boric acid. Brandenberg and Galat[1] suggested that the dehydration proceeds in two stages, viz., formation of the orthoborate with elimination of water, followed by its decomposition into the olefin and boric acid. O'Connor and Nace,[2] however, have evidence that the metaborate is the reactive intermediate.

We have studied the thermal decomposition of three orthoborates in the liquid phase. The results are summarized in Table I.

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(1) W. Brandenberg and A. Galat, *J. Am. Chem. Soc.*, **72,** 3275 (1950).

(2) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77,** 1578 (1955).