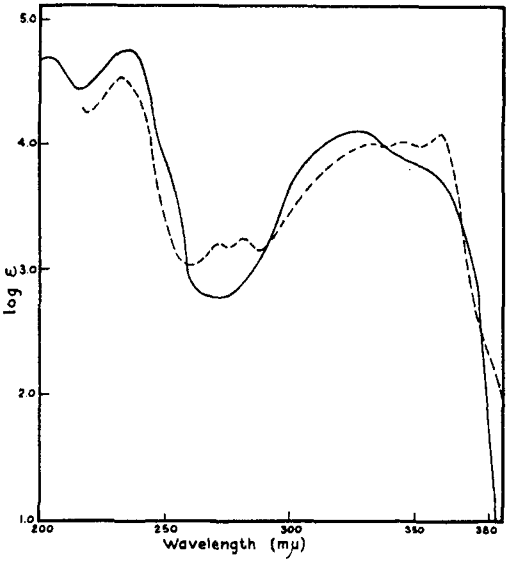

Fig. 2. Ultraviolet spectra: ———, 8-phenyl-8-bora-7,9-diazaro-*peri*-naphthene (III) in cyclohexane; – – – –, 8-methoxy-8-bora-7,9-diazaro-*peri*-naphthene (II) in methanol

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 0.39M (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 6N 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 2.7M 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 1.9M 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).

TABLE I

R in $B(OR)_3$	Decomp. Temp.	Total Alkene Yield, %	Composition of Alkene Product, Mole %		
			1-	*trans-*[a]	*cis-*[b]
C_6H_{13}	250–316	73	55	45	—
C_8H_{17}	300–350	84	49	38	13
C_8H_{17}[a]	294–350	78	49	38	13
$C_{10}H_{21}$	320	83	54	22	24

[a] Pyrolyzed in presence of equimolar quantity of boric oxide. [b] The positions of the double bonds were not established; these figures are approximate.

In a separate experiment, tri-*n*-octyl orthoborate was heated with an equimolar quantity of boric oxide. At the start of the decomposition reaction, the boric oxide had all dissolved in the ester, presumably forming the corresponding metaborate (Equation 1). Despite this, the reaction was not affected by adding boric oxide, which rules out the possibility that the boric acid-catalyzed dehydration of *n*-octyl alcohol proceeds through formation of the metaborate as an intermediate. Further evidence that this reaction involves tri-*n*-octyl orthoborate as an intermediate is furnished by the fact that tri-*n*-octyl orthoborate decomposed smoothly below 350°, the temperature at which Brandenberg and Galat[1] dehydrated 1-octanol in the presence of boric acid.

$$(C_8H_{17}O)_3B + B_2O_3 \longrightarrow (C_8H_{17}OBO)_3 \qquad (1)$$

The primary reaction in the decomposition of the present alkyl orthoborates is probably the formation of the alkene and orthoboric acid (Equation 2), the latter subsequently undergoing dehydration to metaboric acid (Equation 3) and finally to boric oxide (Equation 4). In all cases, the amount of water recovered was greater than that expected from Equation 3, showing that some further dehydration to boric oxide had occurred.

$$(R{-}CH_2CH_2O)_3B \longrightarrow 3\ R.CH{=}CH_2 + H_3BO_3 \qquad (2)$$

$$H_3BO_3 \longrightarrow HBO_2 + H_2O \qquad (3)$$

$$HBO_2 \longrightarrow {}^1/_2\ B_2O_3 + {}^1/_2\ H_2O \qquad (4)$$

EXPERIMENTAL

Tri-*n*-hexyl and tri-*n*-octyl borates were supplied by the U. S. Borax and Chemical Corp., Pacific Coast Borax Co. Division. Tri-*n*-decyl borate was prepared from *n*-decyl alcohol and boric acid, the eliminated water being taken off as an azeotrope with ethylbenzene. The crude borate was vacuum distilled, b.p. 250° (1.5 mm.) measured with a thermocouple housed in a vacuum-jacketed distilling head (reported[3] b.p. 275° (0.15 mm.)).

Anal. Calcd. for $C_{30}H_{63}O_3B$: B, 2.24. Found: B, 2.25.

The pyrolyses were carried out in a 250 ml. round-bottom flask fitted with a thermometer well and connected to a Todd fractionating column filled with Berl saddles. The experiments were conducted at atmospheric pressure, except with tri-*n*-decyl borate which was pyrolyzed at 53–54 mm.

Decomposition of tri-n-octyl orthoborate. Decomposition of 109.7 g. (0.275 mole) of this ester occurred on heating to 300°, as evidenced by boiling and distillation of a mixture (b.p. 113–119°) of two immiscible liquids. The pot temperature range for the pyrolysis was 300–350°. The crude distillate consisted of 5.6 g. (0.310 mole) of water and 85 g. of crude octenes. Distillation of the dried octene phase gave 77 g. (0.686 mole, 84% yield) of octenes (b.p. 121–124°) and 1.5 g. of a colorless oily liquid identified by infrared spectroscopy as *n*-octyl alcohol. The infrared analysis of the pure octene fraction is given in Table I.

A sample of the solid residue (total wt. 12.3 g.) was dissolved in water, in which it was only partially soluble, mannitol added and the mixture titrated against 0.1*N* sodium hydroxide to the phenolphthalein end point (found B = 22.6%). The nonboronaceous part of the residue was estimated by repeatedly evaporating a sample to dryness with methanol, to remove boric oxide and acids as methyl borate. A 4.37%-residue of the sample was involatile in methanol; this was not identified. The boronaceous part of the pyrolysis residue thus contains 23.6% boron (HBO_2 requires 24.7%). The boron content of the residue did not change on pumping.

The course of this decomposition was not significantly affected by adding an equimolar quantity of orthoboric acid. Moreover, decompositions of tri-*n*-hexyl and tri-*n*-decyl orthoborates proceeded in much the same manner.

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(3) G. A. Arbuzov and V. S. Vinogradova, *Compt. rend. acad. sci.* (*U.R.S.S.*), **55**, 411 (1947).