

the ester bond than the collapse of a metastable intermediate. More important is the observation that acetate and formate ions act as general-base catalysts and acetic acid and formic acid act as inhibitors of the neutral water rate. Thus in (3) acetic acid and formic acid can replace hydronium ion as general-acid catalysts and acetate and formate ions can replace water as general-base catalysts. Only a steady-state assumption allows the derivation of an equation consistent with the experimental data obtained in acetate and formate buffers. The value of $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ at $a_{\text{H}} = a_{\text{D}}$ for acetate was determined to be 2.1. From (2) and (4) $k_1 = 0.433 \text{ min.}^{-1}$ and k_2/k_3 , the partitioning coefficient, = 2.86. As would be predicted from (3), k_2/k_3 increased in deuterium oxide solution to 4.95.

The reaction of ethyl trifluorothiolacetate with other oxygen nucleophiles as well as with nitrogen nucleophiles has been investigated and will be reported in detail. Whereas in the hydroxylaminolysis and methoxylaminolysis of thiol esters and lactones the partitioning is symmetrical, in both general-base and general-acid catalysis, the reaction discussed herein must involve unsymmetrical partitioning. On the basis of this study it is clear that the requirement of microscopic reversibility should not be confused with any requirement for symmetry.

Acknowledgments.—This study was supported by grants from the National Institutes of Health and the National Science Foundation.

(4) Postdoctoral fellow of the Department of Biological Sciences, University of California, Santa Barbara.

(5) To whom inquiries should be addressed.

DEPARTMENTS OF BIOLOGICAL SCIENCES
AND CHEMISTRY

UNIVERSITY OF CALIFORNIA, SANTA BARBARA
SANTA BARBARA, CALIFORNIA

LEO R. FEDOR⁴

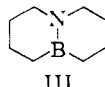
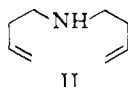
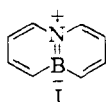
THOMAS C. BRUCE⁵

RECEIVED NOVEMBER 11, 1964

Synthesis and Nuclear Magnetic Resonance Spectrum of 10,9-Borazonaphthalene¹

Sir:

During the past six years a new series of heteroaromatic compounds has been reported in which boron atoms appear in six-membered aromatic rings.² We have now prepared one of the more interesting members of this series, 10,9-borazonaphthalene (I), a compound isoelectronic with naphthalene but containing no boron-free aromatic rings.



Treatment of 1-chloro-3-butene (200 g.) with liquid ammonia (350 g.) in an autoclave at 100° gave a mixture of the known 3-butenylamine (61 g.) together with

(1) This work was supported by grants from the Robert A. Welch Foundation and the National Institutes of Health, U. S. Public Health Service (Grant No. CA 07172-01).

(2) See M. J. S. Dewar in "Boron-Nitrogen Chemistry," R. F. Gould, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964.

di-3-butenylamine (II) (38 g.), b.p. 153–155°. Hydroboration of II (25 g.) with trimethylamine borane (15 g.) in boiling toluene gave octahydro-10,9-borazonaphthalene (III, 2.8 g.), b.p. 73–75° (20 mm.), as a colorless oil which oxidized rapidly in air. *Anal.* Found: C, 68.6; H, 12.1; N, 10.8. The structure of III was confirmed by its mass spectrum and by its n.m.r. spectrum which showed peaks at τ 7.1, 8.5, and 9.1 in the ratio 1:2:1; the peak at low field corresponds to a methylene adjacent to nitrogen and that at high field to one adjacent to boron. Dehydrogenation of III (3.6 g.) over palladized charcoal at 300–350° gave, after chromatography on alumina, I (0.1 g.), which after sublimation formed colorless plates, m.p. 41–43°. *Anal.* Found: C, 74.5; H, 6.3; N, 10.6. The high-resolution mass spectrum showed peaks at 128.0782 \pm 0.0004 and 129.0743 \pm 0.0006 μ . (Calcd. for $\text{C}_8\text{H}_8\text{NB}^{10}$: 128.0786. Calcd. for $\text{C}_8\text{H}_8\text{NB}^{11}$: 129.0750.)

10,9-Borazonaphthalene forms colorless plates, resembling naphthalene in both appearance and odor. Its chemical and physical properties are consistent with its formulation as a new aromatic system, isomeric with 2,1-borazonaphthalene,² and the proton n.m.r. spectrum is also consistent with this. It consists of a well-defined doublet centered at τ 2.28, a well-defined quartet at τ 3.36, and lines in the region τ 2.5–2.8 that can be interpreted as a doublet centered at 2.67 and a quartet at 2.53. Evidently a ring current must be present since at least one pair of β -protons shows a resonance in the "aromatic" region, and any inductive effects of nitrogen or boron would be small in the β -positions.

The low-field doublet must clearly be assigned to the 1- and 8-protons, adjacent to nitrogen; likewise the high-field quartet must be ascribed to the 2- and 7-protons rather than the 3- and 6-protons, since all theories agree in predicting a much higher π -electron density at the 2- and 7-positions of I than at the 3- and 6-positions and since no other effect could account for the large difference between the two pairs of β -protons. The doublet at τ 2.67 must then be assigned to the 4- and 5-protons and the quartet at τ 2.53 to the 3- and 6-protons. The spacings of the multiplets are consistent with this assignment, the coupling constants for pairs of vicinal protons being $J_{12} = 6.5$, $J_{23} = 6.0$, and $J_{34} = 10.0$ c.p.s. Fine structure in the quartet at τ 3.36 indicates that there are also small long-range couplings.

If these assignments are accepted, some unexpected conclusions follow concerning the π -electron distribution in I. Data for other compounds (*e.g.*, III) indicate that signals for protons α to boron are shifted upfield relative to those α to nitrogen by *ca.* τ 2, due to the inductive effects of nitrogen and boron; in I the difference (τ 0.39) between the 1- and 8-protons and the 4- and 5-protons is very much less than this. It seems clear that the π -electron density at the 1- and 8-positions of I must be much greater than at the 4- and 5-positions. The position of the quartet at τ 3.36 likewise indicates that the π -electron density must be much greater in the 2- and 7-positions than elsewhere, for inductive effects of nitrogen and boron must be small in the β -positions of I, while differential effects

(3) All new substances gave satisfactory analyses.