the above reaction to give the ethanolamine ester of triethylcarbinylboronic acid as small white plates, m.p. 131° to 133°.

Anal. Calcd. for $C_{11}H_{24}NBO_2$: C, 61.99; H, 11.35; N, 6.57; B, 5.08; mol. wt., 213. Found: C, 62.13, 62.18; H, 11.49, 11.60; N, 6.52, 6.45; B, 4.96; mol. wt., 217, 209.

Acknowledgment.—The author is deeply indebted to Dr. T. H. Regan for the n.m.r. analyses and interpretations. Grateful acknowledgment is also made to Dr. G. R. Coraor and Prof. A. Streitwieser, Jr., for encouraging and helpful discussions.

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2-Bora- and 2-Thia-1,3-diazaazulenes

BY H. E. HOLMQUIST AND R. E. BENSON

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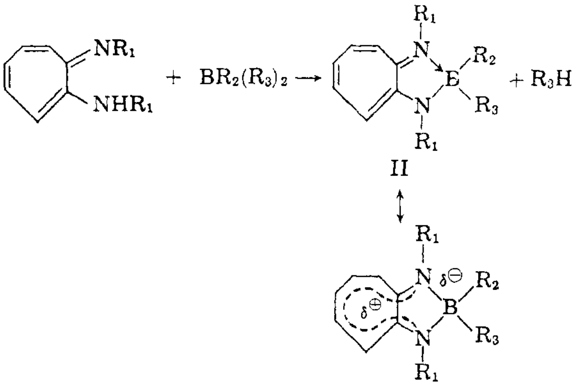
Reaction of 1-amino-7-imino-1,3,5-cycloheptatrienes with selected boron esters and halides has given chelated derivatives that are regarded as examples of the previously unknown 2-bora-1,3-diazaazulenes. This five-membered ring system is unusually stable to hydrolysis for a compound containing boron–nitrogen bonding. Aryl and alkoxyl substituents on boron are hydrolytically cleaved before the boron–nitrogen bond is ruptured. Condensation of the parent aminoimine with sulfur oxytetrafluoride has given 2-fluoro-2-oxo-2-thia-1,3-diazaazulene.

The 1-amino-7-imino-1,3,5-cycloheptatrienes (I) are non-classical aromatic compounds[1] readily accessible from the reaction of tetrafluorocycloheptadienes with primary amines. These compounds are bidentates and form chelate derivatives with metallic ions.[1,2] We have now found that the aminoimines I react readily with a variety of boron derivatives to give chelated boron compounds II in which the fourth valence of the boron atom is satisfied by a coördinate bond from the imino-nitrogen atom. These are appropriately regarded as derivatives of the previously unknown 2-bora-1,3-diazaazulene, the first completely conjugated system containing a boradiazole ring.

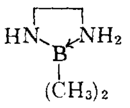


Ia, R_1 = H, CH_3, *p*-$CH_3OC_6H_4$
b, R_2 = F, OCH_3, C_6H_5, OH
c, R_3 = F, OH, OCH_3, OC_2H_5, C_4H_9

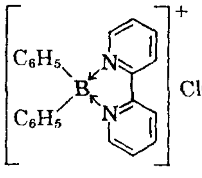
Hydrolytic Stability.—Evidence for appreciable electron delocalization in II was found in hydrolysis studies. Thus, the five-membered ring is stable to neutral, acidic and alkaline conditions, although the aryl and alkoxyl groups attached to the boron atom are replaced by hydroxyl groups.

The stabilization of boron esters toward hydrolysis through complex formation with amines has been observed previously. Thus, the hydrolytic stability of esters of ethanolamine with diaraneborinic acids,[3] diethanolamine with araneboronic acids,[4] and triisopropanolamine with boric acid[5] has been attributed to a transannular coördinate bond from the nitrogen atom to the boron atom. Compound II appears to be a special example of coördinate bonding of nitrogen to boron.

A number of 2,1,3-boradiazolines have been described in the literature. Goubeau and Zappel[6] found that A was obtained as one of the reaction products of ethylenediamine and trimethylborane. Later, several benzo-2,1,3-boradiazolines[7] were synthesized by condensation of *o*-phenylenediamines with various boron acids, esters and halides and are reported to be hydrolytically unstable. A further example of boron bonding to two nitrogen atoms in a five-membered ring is furnished by B.[8]



A



B

Although comparable results are not available, the greatest stability for a boron–nitrogen system appears to lie in the borazarenes of Dewar, in which the borazine ring contains tetracoördinate boron as a part of a conjugated bi- or tricyclic system, for example, C.[9]

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[1] W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

[2] The nickel chelates are paramagnetic and give large contact shifts in n.m.r. These studies have permitted the determination of electron spin densities in a variety of substituents located on the nitrogen atoms and on the seven-membered ring; see, for example, R. E. Benson, D. R. Eaton, A. D. Josey and W. D. Phillips, *ibid.*, **83**, 3714 (1961).

[3] R. L. Letsinger and N. Remes, *ibid.*, **77**, 2389 (1955); R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955).

[4] O. C. Musgrave and T. O. Park, *Chemistry & Industry*, 1552 (1955).

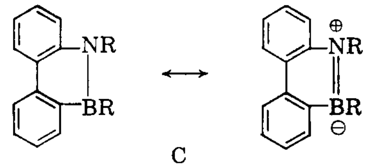
[5] H. Steinberg and D. L. Hunter, *J. Am. Chem. Soc.*, **82**, 853 (1960).

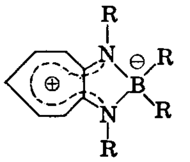
[6] J. Goubeau and A. Zappel, *Z. anorg. allgem. Chem.*, **279**, 38 (1955).

[7] (a) M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3076 (1958); (b) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958); (c) E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959); (d) L. F. Hohnstedt and A. M. Pellicciotto, Abstracts of 137th American Chemical Society Meeting, 1960, p. 7-O; P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[8] J. M. Davidson and C. M. French, *Chemistry & Industry*, 750 (1959).

[9] See M. J. S. Dewar and P. M. Maitlis, *Tetrahedron*, **15**, 35 (1961), and preceding papers.

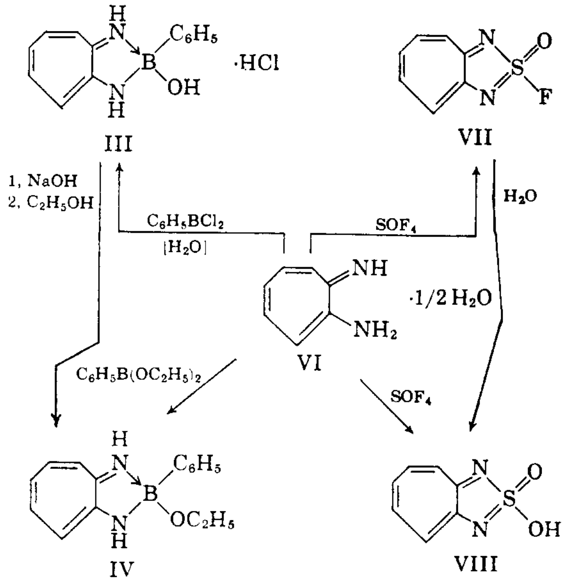

C


D

Like the borazarenes, in which high stability may be attributed to forms having tetracoördinate boron, the boradiazaazulenes of this study presumably derive their stability from contributions of the type D.

The hydrolytic stability of the boron–nitrogen bond in II indicates appreciable delocalization in this ring system. Verification was found in n.m.r. studies of II, $R_1 = CH_3$, $R_2 = R_3 = OCH_3$, in that the fine structure attributable to the ring protons is very similar to that of the ligand I, R = CH_3, and of the zinc chelate of I, R = CH_3. The ring proton resonances are shifted approximately 0.6 p.p.m. to lower field compared with those of I, R = CH_3. This result may be attributed to the more electropositive character of the seven-membered ring because of back-coördination of the nitrogen atoms with boron. The shifts of about 0.6 p.p.m. may be compared with those of about 1.2 p.p.m. that are observed for protonated I, R = CH_3.[1]

Preparation and Properties.—The condensation of the aminoimines I with boron compounds was carried out at 65–165°. The reaction was more facile with the more basic aminoimines. For instance, the parent aminoimine (I, R = H) and the N,N-dimethyl derivative (I, R = CH_3, pK_B 3.8) condensed with methyl borate at 65°, but the weakly basic diaryl analog (I, R = p-$CH_3OC_6H_4$, pK_B 9.0) did not react under these conditions. However, the latter underwent reaction with diethyl benzeneboronate at 111° and with boric acid at 100°. Other boron compounds successfully employed include boron trifluoride, phenyldichloroborane and tri-n-butylborane. The boradiazaazulenes II are yellow to orange solids that fluoresce in solution.



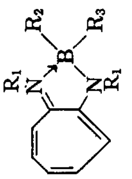


TABLE I

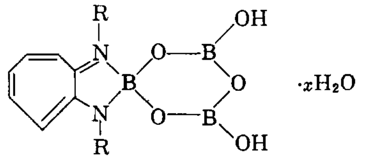
2-BORA-1,3-DIAZAAZULENES

R_1	R_2	R_3	Reaction[a] solvent	Yield, %	M.p., °C.	Recrystn. solvent	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Boron, % Calcd.	Boron, % Found	Other, % Calcd.	Other, % Found
H	OCH_3	OCH_3	$B(OCH_3)_3$	~100	>300 dec.	CH_3OH–toluene	$C_9H_{13}O_2N_2B$	56.30	56.69	6.82	6.84	14.59	14.69	5.63	5.56	...	...
H	C_6H_5	OC_2H_5	Benzene	20	253 dec.	$CHCl_3$–petr. ether	$C_{15}H_{17}ON_2B$	71.46	72.18	6.80	6.76	11.11	10.93	4.29	4.27	...	...
H	C_6H_5	OH	Toluene	~100[b]	>300	[c]	$C_{13}H_{13}ON_2B.HCl$	59.94	59.90	5.42	5.60			4.15	4.29	...	...
CH_3	C_6H_5	OH	Toluene	80[b]	163–164[d]	CH_2Cl_2–petr.	$C_{15}H_{17}ON_2B.HCl$	62.41	62.20	6.28	6.34	9.71	9.89	3.75	3.72	...	...
					96–98[e]	ether			62.00		6.48		9.69		4.15		
CH_3	F	F	Dioxane[f]	4[g]	117.5	CH_3OH	$C_9H_{11}N_2BF_2$	55.14	54.85	5.66	5.84	14.30	14.28	5.52	5.61	19.38[h]	19.81
			Diglyme[f,i]	19[g]	118–119												
CH_3	OCH_3	OCH_3	$B(OCH_3)_3$	33[j]	127–129	$B(OCH_3)_3$[k]	$C_{11}H_{17}O_2N_2B$					12.73	12.71	4.92	5.24	220[l]	235
CH_3	C_6H_5	OC_2H_5	Toluene	90	Indef.	Cyclohexane	$C_{17}H_{21}ON_2B$							3.86	4.02	...	...
p-$CH_3OC_6H_4$	C_6H_5	OC_2H_5	Toluene	93	181	CH_2Cl_2–petr. ether	$C_{29}H_{29}O_3N_2B$	75.01	74.85	6.29	6.51	6.03	6.27	2.33	1.61	464[l]	483

[a] Reactions were carried out at boiling point of solvent. [b] Product is the hydrochloride. [c] Not recrystallized, no satisfactory solvent found. [d] High-melting form obtained when recrystallized without use of charcoal. [e] Low-melting form obtained when recrystallized with use of charcoal; if m.p. is taken rapidly, compound reverts to high melting form. [f] BF_3 complex of the aminoimine, m.p. 218–219° from ethanol, prepared first. [g] Corrected for recovered BF_3 complex (44%). [h] Fluorine. [i] NaF catalyst. [j] An additional product was isolated from the reaction; see text. [k] Crystals which formed in cooled reaction mixture were washed with petroleum ether and analyzed. [l] Molecular weight.

The 2-chloro-2-phenyl derivatives of II, R_1 = H or CH_3, were not isolated in the condensations employing phenyldichloroborane, but apparently hydrolyzed during work-up to products regarded as the hydrochlorides (III) of the corresponding 2-hydroxy-2-phenyl derivatives. One of these hydrochlorides (III) was converted by dilute sodium hydroxide to the free base, which on recrystallization from chloroform (containing a little ethanol as stabilizer) gave the 2-ethoxy-2-phenyl derivative IV identical with that obtained by condensation of I, R = CH_3, with diethyl benzeneboronate.

Boric acid underwent reaction with the aminoimines I at 100°, but the expected 2,2-dihydroxy derivatives of II were not isolated. Instead the products formed apparently had structures of type V, although no consistent compositional analyses were obtained. Hydrolysis afforded the monomeric dihydroxy compounds, which reverted, however, to V on long standing or slow heating.



V

Tri-*n*-butylborane apparently reacted with VI to give a product of type II since one equivalent of butane was evolved, but the solid product could not be obtained in pure form.

2-Thia-1,3-diazaazulenes.—Sulfur oxytetrafluoride has been reported to react with amines to give iminosulfur oxydifluorides, $RN{=}S(O)F_2$.[10] In an extension of this reaction, 1-amino-7-imino-1,3,5-cycloheptatriene hemihydrate (VI) and sulfur oxytetrafluoride at room temperature gave 2-fluoro-2-oxo-2-thia-1,3-diazaazulene (VII) and 2-hydroxy-2-oxo-2-thia-1,3-diazaazulene (VIII) in 32% and 11% yields, respectively. Hydrolysis of VII with hot water converted it to the strongly acidic hydroxy compound VIII. These appear to be the first examples of thiadiazole or benzothiadiazole rings containing hexavalent sulfur.

Experimental

The preparation and properties of the 2-bora-1,3-diazaazulenes (II) are summarized in Table I. Approximately equimolar quantities of the reactants were heated together at the boiling point of the specified solvent for 5–24 hours. However, in the case of methyl borate, the ester was used in large excess, since it also served as the solvent for the reaction.

1,3-Di-*p*-methoxyphenyl-2,2-dihydroxy-2-bora-1,3-diazaazulene (II, R_1 = *p*-$CH_3OC_6H_4$, R_2 = R_3 = OH).—Compound II, R_1 = *p*-$CH_3OC_6H_4$, R_2 = C_6H_5, R_3 = OC_2H_5 (0.7 g.), was heated with 25 ml. of 5% hydrochloric acid and 10 ml. of ethanol until most of the solid dissolved, and the hot mixture was filtered. The orange dihydroxy compound crystallized from the filtrate upon cooling; m.p. 197–203° after recrystallization from chloroform–petroleum ether. The infrared spectrum showed absorption at 3.05 μ (OH), 3.25 μ (=CH), 3.4 μ (saturated CH), 6.2, 6.35 and 6.6 μ (conjugated unsaturation).

Anal. Calcd. for $C_{21}H_{21}O_4N_2B$: C, 67.05; H, 5.63; N, 7.45. Found: C, 67.83; H, 6.03; N, 7.74.

Condensations of Aminoimines I with Boric Acid.—From the mother liquor from the condensation of I, R = CH_3, with methyl borate (see Table I) there was obtained a yellow solid, m.p. 217–219°, which was also obtained from the 2,2-dimethoxy compound on long standing or by recrystallization in the presence of air, or by direct condensation of I, R = CH_3 with boric acid.

A mixture of I, R = CH_3 (10 g.), boric acid (5 g.), Drierite (10 g.) and dioxane (300 ml.) was stirred and refluxed for 22 hours. The resulting mixture was filtered while hot. From the filtrate crystallized 2.5 g. of a yellow solid; extraction of the initial solid with hot chloroform gave an additional 9.5 g. of the yellow substance, m.p. 217–219°, which did not depress the m.p. of the product obtained from the 2,2-dimethoxy compound (above). A typical sample, recrystallized from chloroform, was analyzed. *Anal.* Found: C, 44.27; H, 5.24; N, 10.60; B, 6.20; mol. wt., 547. The ratios of the four elements reported are in accord with structure V (x = 0), but the percentages and mol. wt. are not. A 0.7-g. sample was dissolved in 15 ml. of methanol and 5 ml. of water and the resulting solution heated on a steam-bath for several hours to evaporate most of the methanol. On cooling, the solution deposited 0.2 g. of yellow crystals of 1,3-dimethyl-2,2-dihydroxy-2-bora-1,3-diazaazulene (II, R_1 = CH_3, R_2 = R_3 = OH) which was recrystallized from water; m.p. 68° (rapid heating). If the melting point was taken slowly, the product reverted to the high-melting compound from which it had been obtained.

Anal. Calcd. for $C_9H_{13}O_2N_2B$: C, 56.30; H, 6.82; N, 14.59. Found: C, 55.89; H, 6.88; N, 14.47.

The hydrolysis could also be effected with 5% sodium hydroxide.

A mixture of I, R = *p*-$CH_3OC_6H_4$ (12 g.), boric acid (3 g.), Drierite (5 g.) and dioxane (500 ml.) was stirred and refluxed for 20 hours. The resulting mixture was filtered while hot. The filtrate was evaporated under reduced pressure and the residue recrystallized from methylene chloride–petroleum ether to give 3.4 g. of a yellow solid, m.p. 252–253°, that has the composition of a sesquihydrate of V, R = *p*-$CH_3OC_6H_4$.

Anal. Calcd. for $C_{21}H_{24}O_{8.5}N_2B_3$: C, 53.34; H, 5.12; N, 5.93; B, 6.86. Found: C, 53.33; H, 4.67; N, 5.88; B, 6.64.

2-Fluoro-2-oxo-2-thia-1,3-diazaazulene (VII).—To a stirred mixture of VI (13.9 g.), sodium fluoride (30 g.) and tetrahydrofuran (550 ml.), chilled in a solid carbon dioxide–acetone-bath and protected from atmospheric moisture, was added sulfur oxytetrafluoride (24 g., 19% excess allowing for water of hydration in VI). The cooling bath was removed, and the stirring continued for 4 hours under a condenser containing solid carbon dioxide. The mixture was filtered, and the solvent removed by distillation under reduced pressure.

The solid residue was leached repeatedly with hot cyclohexane; the cooled extracts gave yellow crystals of VII, 6.3 g. (32%). Recrystallization of VII from cyclohexane gave crystals, m.p. 110.5–111°. The ultraviolet spectrum in ethanol had λ_{max} 381 mμ (ϵ 3880) (shoulders at 373 and 363 mμ), λ_{max} 327 mμ (ϵ 8620), and λ_{max} 248 mμ (ϵ 388); infrared spectrum: 6.25 and 6.5 μ (conjugated unsaturation) and 7.1 and 7.75 μ (N=S=O linkage). The compound was stable for a short time in warm ethanol.

Anal. Calcd. for $C_7H_5ON_2SF$: C, 45.63; H, 2.74; N, 15.21; S, 17.41; F, 10.32. Found: C, 45.97; H, 2.58; N, 15.36; S, 17.55; F, 10.05.

Extraction of the residue insoluble in cyclohexane with hot water gave the hydroxy compound VIII (2.2 g., 11%), m.p. 265° dec. (see below).

2-Hydroxy-2-oxo-2-thia-1,3-diazaazulene (VIII).—Compound VII (0.87 g.) was warmed with 25 ml. of water on a steam-bath for 1 hour. Although dissolution was not complete, 0.73 g. (85%) of VIII was obtained, m.p. 268° dec. after recrystallization from water; VIII has a solubility in water of only 2 g./l.; the *p*H of the solution was 2.5.

Anal. Calcd. for $C_7H_6O_2N_2S$: C, 46.13; H, 3.32; N, 15.38; S, 17.60; F, 0.00. Found: C, 46.32; H, 3.21; N, 15.24; S, 17.79; F, < 0.25.

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[10] R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4010 (1961).