sample of the ketone was obtained after three recrystallizations from acetone–ligroin, mp 194–196°, $\nu_{C=O}$ 1775 cm^{-1}.

Treatment of the ketone with 2,4-dinitrophenylhydrazine dissolved in a mixture of phosphoric acid and ethanol afforded the corresponding hydrazone derivative, mp 262–263° dec, $\nu_{C=O}$ 1775 cm^{-1}. *Anal.* Calcd for $C_{14}H_{12}N_4O_6$: C, 50.60; H, 3.64; N, 16.86. Found: C, 50.37; H, 3.61; N, 16.81.

A thioketal derivative was prepared by the method of Fieser,[26] mp 134°. *Anal.* Calcd for $C_{10}H_{12}O_2S_2$: C, 52.60; H, 5.30. Found: C, 52.46; H, 5.18.

4-*exo*-Tosyloxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane (7). 4-*exo*-Hydroxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane,[22] 4.5 g, and *p*-toluenesulfonyl chloride, 9.0 g, were dissolved in 12 ml of dry pyridine. The reaction mixture was allowed to stand at room temperature overnight. At the end of this time, ice was added, and the precipitate which deposited was collected and washed thoroughly with water. After drying at room temperature, the crude crystalline product was recrystallized from ether–pentane, 7.6 g (76%), mp 86–87°. *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.50; H, 6.27.

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[26] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

New Heteroaromatic Compounds. XXV.[1] Studies of Salt Formation in Boron Oxyacids by ^{11}B Nuclear Magnetic Resonance

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Abstract: The ^{11}B nmr spectra of several compounds containing the group BOH have been measured in neutral and alkaline solution. Salt formation shifts the ^{11}B resonance far upfield (> 13 ppm) in the case of boric acid and simple arylboronic acids, the line width remaining unchanged or becoming narrower; this indicates that such compounds behave as Lewis acids toward base. The B–OH derivatives of several borazaro[3] compounds are quite different in this respect, salt formation leading to small downfield shifts (3–7 ppm) in the ^{11}B resonance, and also to extreme broadening of the lines. Here salt formation must involve proton transfer, in agreement with earlier conclusions[3] and implying that compounds of this type are indeed aromatic.

Trivalent boron compounds are well known to behave as Lewis acids, combining with base to form coordination compounds (*e.g.*, $H_3N \rightarrow BF_3$); an ambiguity therefore exists in the case of compounds which contain the grouping BOH and so could act either as protic acids, or as Lewis acids, toward base. Thus hydroxide ion could either deprotonate such a compound to give a planar ion, R_2BO^- (eq 1), or it could add to boron to form an ion in which boron is now quadricovalent and tetrahedral (eq 2).

$$R_2BOH + OH^- \longrightarrow R_2BO^- + H_2O \quad (1)$$

$$R_2BOH + OH^- \longrightarrow R_2B^-(OH)_2 \quad (2)$$

The Raman spectrum of boric acid in alkali indicates that it behaves as a Lewis acid,[4] forming the ion $B(OH)_4^-$, and the available evidence, while scanty, seems to suggest[5] that arylboronic acids act likewise. On the other hand, B–OH derivatives of borazaro compounds[3] seem to behave as protic acids, judging by comparisons of their ultraviolet spectra in neutral and alkaline solution; this difference has been attributed to the aromaticity of the boron-containing rings in compounds of this kind, the boron being consequently reluctant to adopt a tetrahedral geometry.

It seemed to us that ^{11}B nmr spectroscopy could provide a definite distinction between the two possible modes of salt formation. Conversion of trivalent planar boron to quadrivalent tetrahedral boron would be expected[6] to produce a large upfield shift in the ^{11}B resonance, due to the greater shielding of boron in compounds where four pairs of valence electrons surround the boron atom; the available evidence supports this conclusion. Thus the ^{11}B chemical shifts (relative to trimethyl borate) of quadrivalent boron compounds almost all lie above 7 ppm, while compounds with lower chemical shifts contain planar trivalent boron.[7] Salt formation according to eq 2 should therefore lead to a large upfield shift of the ^{11}B resonance, while salt formation according to eq 1 should produce a much smaller change.

Conversion of boric acid to borate ion is indeed accompanied[7] by a large upfield shift (17.5 ppm) in the ^{11}B resonance, as would be expected if the ion has the tetra-

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(1) Part XXIV: M. J. S. Dewar and J. L. Von Rosenberg, Jr., *J. Am. Chem. Soc.*, **88**, 358 (1966).

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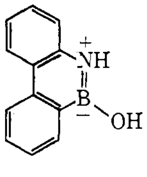
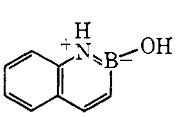
Table I. ^{11}B Chemical Shifts for Boron Compounds in Neutral and Basic Solutions

Compd	Ref	Solvent	δ_{TMB}[a]	δ_{EBT}[b]	$\Delta\delta$[c]	Line width at half-height, Hz
Boric acid (IV)	. . .	DMF	. . .	−19.9		370
		H_2O	. . .	−19.6		411
		1% NaOH–H_2O	. . .	−18.6		115
		5% NaOH–H_2O	. . .	−9.1		170
		10% NaOH–H_2O	. . .	−5.7	13.5	139
Phenylboronic acid (V)	*d*	EtOH	. . .	−28.4		272
		10% NaOH–H_2O	15.0	−3.15	25.3	74
o-Tolylboronic acid (VI)	*e*	EtOH	. . .	−32.2		191
		20% KOH–EtOH	. . .	−12.6	19.6	166
Boraphthalide (VII)	*f*	EtOH	. . .	−29.1		228
		20% KOH–EtOH	12.5	−5.6	23.5	291
10-Hydroxy-10,9-borazarophenanthrene (I)	*g*	EtOH	. . .	−36.8		623
		20% KOH–EtOH	. . .	−43.9	−7.1	>2500
2-Hydroxy-2,1-borazaronaphthalene (II)	*h*	EtOH	. . .	−29.7		223
		20% KOH–EtOH	. . .	−33.0	−3.3	>2500
4-Hydroxy-4,3-borazaroisoquinoline (III)	*e*	EtOH	. . .	−29.8		265
		20% KOH–EtOH	. . .	−33.2	−3.4	>1500
4-Hydroxy-4,3-boroxaroisoquinoline (VIII)	*i*	EtOH	. . .	−30.0		290
		20% KOH–EtOH	13.1	−5.0	25.0	210
4-Methyl-4,3-borazaroisoquinoline (IX)	*e*	Benzene	. . .	−36.5		140
		EtOH	. . .	−38.5		247
Trimethyl borate	. . .	(None)	. . .	−18.1		37
		10% NaOMe–MeOH	15.3	−2.8		54
		20% NaOMe–MeOH	15.6	−2.5	15.6	32
$C_2H_5O \cdot BF_3$	. . .	(None)	18.1	. . .		. . .

[a] Chemical shift (ppm) relative to trimethyl borate. [b] Chemical shift (ppm) relative to diethyl ether–boron trifluoride complex. [c] Change in chemical shift on passing from neutral to alkaline solution. [d] R. M. Washburn, E. Levers, C. F. Albright, and F. A. Billig, *Org. Syn.*, **39**, 3 (1959). [e] M. J. S. Dewar and R. C. Dougherty, *J. Am. Chem. Soc.*, **86**, 433 (1964). [f] K. Torsell, *Arkiv Kemi*, **10**, 507 (1957). [g] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958). [h] M. J. S. Dewar and R. Dietz, *ibid.*, 2728 (1959). [i] H. R. Snyder, A. J. Reedy, and W. J. Lennarz, *J. Am. Chem. Soc.*, **80**, 835 (1958).

hedral structure $B(OH)_4^-$. However this observation cannot in itself be taken as evidence for such a structure since one cannot estimate *a priori* what the chemical shift would be for a planar ion such as $(HO)_2BO^-$. In other words, one needs for comparison a reference compound R_3BOH in which salt formation involves loss of a proton (eq 1) rather than addition to boron (eq 2). Now independent evidence had suggested[3] that this is the case for B–OH derivatives of several borazaro compounds, in particular 10-hydroxy-10,9-borazarophenanthrene (I), 2-hydroxy-2,1-borazaronaphthalene (II), and 4-hydroxy-4,3-borazaroisoquinoline (III). It seemed to us that by comparing the ^{11}B nmr spectra of such compounds in neutral and alkaline solution with corresponding spectra for conventional boron oxyacids, we might kill two birds with one stone. Not only might the comparison provide a definite and general criterion between the two modes of salt formation, but it could also provide unambiguous evidence that compounds such as I–III do indeed act as protic acids. This is an important point, since the reluctance of boron to undergo addition provides one of the strongest lines of evidence that compounds of this type are indeed aromatic.[3]


I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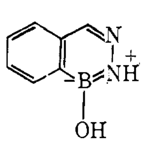
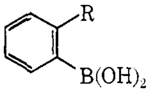
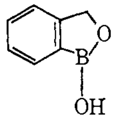
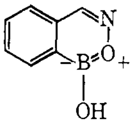
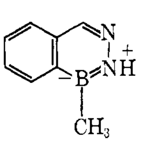

III

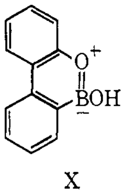
We have, therefore, measured the ^{11}B nmr spectra of I–III in neutral and alkaline solution, and also the corresponding spectra of boric acid (IV), phenylboronic acid (V), *o*-tolylboronic acid (VI), boraphthalide (VII), and 4-hydroxy-4,3-boroxaroisoquinoline (VIII). For comparison, we also measured the spectrum of 4-methyl-4,3-borazaroisoquinoline (IX) and that of trimethyl borate in methanol and in methanolic sodium methoxide; in the latter case salt formation can take place only by addition to boron, giving the tetrahedral ion $B(OMe)_4^-$.


V, R = H
VI, R = CH_3


VII


VIII


IX


X

Results

The nmr spectra were measured with a Varian DP-60 spectrometer, using trimethyl borate, or the diethyl ether–boron trifluoride complex, as external standards. The results are listed in Table I. The chemical shifts are believed to be accurate to ±0.5 ppm. The various compounds were prepared by the methods described in the references quoted and their physical properties agreed with those previously reported. The chemical shifts for trimethyl borate and the tetramethoxyboride ion, $B(OCH_3)_4^-$, are in good agreement with values reported by Phillips, *et al.*[8]

Discussion

It is immediately obvious that the compounds listed in Table I fall into two distinct categories. One group shows a large upfield shift (>13 ppm) on passing from neutral to alkaline solution, comparable with the difference between trimethyl borate and the ion $B(OCH_3)_4^-$, while the other group shows a small downfield shift (3–7 ppm). The arguments given above seem to suggest unequivocally that compounds of the first group are acting as Lewis acids, those of the second group as protic acids.

This conclusion is further supported by the changes in line width accompanying salt formation. Resonances due to ^{11}B are usually broad, due to quadrupole relaxation; two factors can influence the relative importance of this in a boron oxyacid and in its conjugate base. In the first place, there is a contribution due to unsymmetrical field gradients about boron inside the molecule or ion; these should be less important in an ion formed by addition to boron than in one formed by loss of a proton, since the electron distribution about a quadricovalent tetrahedral boron atom must, in general, be more symmetrical than that about a planar trivalent one. An effect of this kind is well known in the case of nitrogen, ^{14}N nmr lines being much sharper for ammonium ions than for the corresponding amines.[9] A second source of quadrupole relaxation is provided by fluctuating electric potentials due to surrounding molecules; these should be much more important in the case of an ion than a neutral molecule, since ions in solution tend to be surrounded by ionic atmospheres (Debye–Hückel effect). Now when a typical boron oxyacid forms a salt by addition of base, these two factors will act in opposition; the change in covalency of boron should tend to decrease quadrupole relaxation and so reduce the line width, whereas the acquisition of negative charge should tend to increase it. If, on the other hand, salt formation involves loss of a proton so that the boron atom remains planar and tricovalent, one might expect the line-broadening effect of the charge to operate unopposed. One might therefore expect the change in line width on passing from neutral to alkaline solution to serve as an additional criterion of acid type; boron protic acids should show a much greater increase. Examination of Table I shows that this prediction holds rather spectacularly. The line widths for Lewis acids are usually less in alkaline than in neutral solution and certainly show no significant increase with salt formation, whereas the line widths for the protic acids increase enormously on addition of alkali.

We can therefore conclude with some assurance that boric acid, the arylboronic acids V and VI, and boraphthalide (VII) behave as Lewis acids to hydroxide ion, while the hydroxyborazaro compounds I–III behave as protic acids. This difference can of course be attributed[3] to the aromatic nature of the latter compounds; addition of base to boron would destroy cyclic conjugation in the boron-containing ring.

The last of our hydroxy acids, 4-hydroxy-4,3-boroxaroisoquinoline (VIII), is particularly interesting in this respect. Boroxaro compounds should be less aromatic than their nitrogen counterparts and this is known to be the case for the oxygen analog of I,[10] 10-hydroxy-10,9-boroxarophenanthrene (X). Nevertheless ultraviolet spectral data seemed to suggest unambiguously that X behaves as a protic acid, the aromaticity of the central ring still being sufficient to inhibit addition to boron; it is therefore of interest to see if the same is true of VIII. The ultraviolet spectrum of VIII is almost the same in alkali as in neutral solution, suggesting that VIII also behaves as a protic acid;[11] however, the results in Table I show that this tentative conclusion was incorrect, VIII behaving as a Lewis acid toward hydroxide ion. This is indicated both by the large upfield shift (25 ppm), and by the decrease in line width (290 → 210 Hz), on passing from neutral to alkaline solution.

The chemical shifts listed in Table I are also of some general interest in connection with the problem of relating chemical shifts to structure. It will be noticed that the resonances for arylboronic acids appear downfield by *ca.* 10 ppm relative to boric acid, implying that replacement of hydroxyl by phenyl has a deshielding effect. Phillips, *et al.*,[8] have drawn attention to this surprising circumstance and have pointed out that it cannot be attributed to any effect of ring current or unsaturation, for the ^{11}B chemical shifts of phenylboronic acid and *n*-butylboronic acid differ by less than 1 ppm. The effect seems to be related in some way to the presence of boron–carbon bonds, for replacing the B–OH group in III by methyl (to form VIII) leads to a further downfield shift of 6.7 ppm. The most likely explanation seems to lie in a strong magnetic anisotropy of the C–B bond, resulting in a net deshielding effect on the boron atom.

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(9) See, *e.g.*, R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **26**, 1339 (1957).

(10) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960).

(11) Unpublished work by Dr. R. C. Doughtery; see M. J. S. Dewar and R. C. Doughtery, *J. Am. Chem. Soc.*, **86**, 433 (1964).