techniques. In some cases, final purification was obtained by gas chromatography using a column constructed of 0.25 in. copper tubing packed with 20% Kel F-3 polymer oil on Chromosorb P. Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrophotometer by using a 10-cm gas cell fitted with KBr windows. Varian HA-100 and EM-360 nuclear magnetic resonance spectrometers were used for ^{19}F and ^{1}H spectra with CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The mass spectra were determined on a Hitachi Perkin-Elmer RMU 6-E mass spectrometer. Vapor pressure studies were made by an isoteniscopic method. Elemental analysis were performed by Beller Laboratories in Göttingen, Germany.

General Procedure. Into a Pyrex reaction vessel containing an excess of potassium fluoride were condensed the proper ratio of trifluoromethyldisulfane and a carbonyl-containing compound. The reaction mixture was warmed slowly from −196 °C to the desired temperature and maintained at this temperature for 12 h. The resulting mixture was then separated via low temperature vacuum distillation techniques. The data characterizing the compounds are given below.

$CF_3SSC(O)F$: yield 55%; identified by NMR and ir.[18]

$CF_3SSC(O)SSCF_3$: yield 5%; ir 2290 (w), 1727 (vs), 1640 (w), 1305 (w), 1189 (vs), 1110 (vs), 832 (s), 761 (s), 491 (m), 454 (m); NMR ϕ^* 46.4, s. The compound decomposes slowly in glass at 25 °C.

$CF_3C(O)SSCF_3$: yield 60%; ir 1837 (w, br), 1768 (vs), 1282 (s), 1190 (vs), 1110 (vs), 928 (vs), 918 (m, sh), 760 (m), 738 (s); NMR ϕ^* 44.7 (s, CF_3S-), 73.1 (s, CF_3-C). The equation $\log P_{(mm)} = 7.29 - 1452.3/T$ describes the vapor pressure curve from which ΔH_v (6.64 kcal/mol), ΔS_v (20.2 eu), and the boiling point (56.2 °C) are obtained.

Anal. Calcd: C, 15.65; F, 49.6; S, 27.83. Found: C, 15.64; F, 49.7; S, 27.78.

$CF_3C(O)SSSCF_3$: yield 5%; identified by infrared spectrum.[6]

$CF_3SSC(O)C(O)F$: yield 30%; ir 1879 (m), 1836 (vs), 1753 (vs), 1232 (s), 1190 (vs), 1151 (s), 1115 (vs), 926 (vs), 760 (m), 725 (s); NMR ϕ^* 45.1 (s, CF_3S-), −16.3 (s, F–C). The equation $\log P_{(mm)} = 7.60 - 1820.2/T$ describes the vapor pressure curve from which ΔH_v (8.33 kcal/mol), ΔS_v (21.6 eu), and the boiling point (112.2 °C) are obtained.

Anal. Calcd: F, 36.5; S, 30.77. Found: F, 36.4; S, 30.71.

$[CF_3SSC(O)]_2$: yield 10%; ir 1739 (s), 1185 (vs), 1111 (vs), 895 (w), 760 (s); NMR ϕ^* 44.3, s. This compound decomposes in glass at 25 °C.

$CF_3SSC(O)(CF_2)_3C(O)F$: yield 10%; ir 1890 (vs), 1767 (m, sh), 1737 (vs), 1322 (m), 1180 (vs), 1110 (vs), 982 (s), 831 (m), 760 (m), 723 (m); NMR ($CF_3SSC(O)CF_2{}^ACF_2{}^BCF_2{}^CC(O)F^D$), ϕ^* 44.7 (s, CF_3-S), 114.7 (d, t, $CF_2{}^A$), 122.2 (d, $CF_2{}^B$), 117.3 (d, t, $CF_2{}^C$), −23.95 (t, t, t, $C(O)F^D$), $J_{AD} = 1.8$, $J_{AC} = 11.2$, $J_{BD} = 6.8$, $J_{CD} = 8.4$ Hz. Anal. Calcd: F, 53.1; S, 17.88. Found: F, 50.7; S, 17.60.

$[CF_3SSC(O)(CF_2)]_2CF_2$: yield 20%; ir 1740 (vs), 1328 (m), 1186 (vs), 1110 (vs), 988 (s), 837 (m), 759 (m), 571 (w), 493 (w); NMR ($CF_3SSC(O)CF_2{}^ACF_2{}^BCF_2{}^AC(O)SSCF_3$), ϕ^* 46.0 (s, CF_3S-), 119.2 (t, $CF_2{}^A$), 133.5 (p, $CF_2{}^B$), $J_{AB} = 10$ Hz. The equation $\log P_{(mm)} = 7.63 - 1758.0/T$ describes the vapor pressure curve from which ΔH_v (8.04 kcal/mol), ΔS_v (21.7 eu), and the boiling point (97.0 °C) are obtained.

Anal. Calcd: F, 48.3; S, 27.12. Found: F, 47.3; S, 29.68.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research. We thank Mr. Stan Morse for mass spectra.

References and Notes

(1) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3291 (1953).
(2) R. D. Dresdner and T. R. Hooper, *Fluorine Chem. Rev.*, **4** (1969).
(3) R. E. Banks and R. N. Haszeldine in "The Chemistry of Organic Sulfur Compounds", Vol. 2, N. Kharasch and C. Meyers, Ed., Pergamon Press, New York, N.Y., 1966, p 137.
(4) W. Gombler and F. Seel, *Z. Naturforsch. B*, **30**, 169 (1975).
(5) C. A. Burton and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **12**, 373 (1976)
(6) N. R. Zack and J. M. Shreeve, *J. Chem. Soc.*, *Perkin Trans 1*, 614 (1975).
(7) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Am. Chem. Soc.*, **93**, 3882 (1971).
(8) G. Schwarzenbach and A. Fischer, *Helv. Chim. Acta*, **43**, 1365 (1960).
(9) D. W. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 1450 (1964).
(10) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
(11) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
(12) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, **34**, 18 (1962).
(13) W. A. Pryor "Mechanisms of Sulfur Reactions", McGraw-Hill, New York, N.Y., 1962, p 59.
(14) J. L. Kice in "Mechanisms of Reactions of Sulfur Compounds", N. Kharasch, Ed., IntraScience Research Foundation, Santa Monica, Calif., 1968, p 91.
(15) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).
(16) W. Gombler, *Z. Anorg. Allg. Chem.*, **416**, 235 (1975).
(17) W. V. Rochat and G. L. Gard, *J. Org. Chem.*, **34**, 4173 (1969).
(18) A. Haas, J. Helmbrecht, W. Klug, B. Koch, H. Reinke, and J. Sommerhoff, *J. Fluorine Chem.*, **3**, 383 (1973–1974); *Angew. Chem., Int. Ed. Engl.*, **9**, 466 (1970).

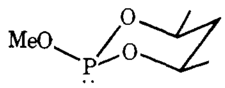
Axial and Equatorial Phosphorus–Oxygen Basicity in a Six-Membered Ring Phosphate Anion: Effect of the Countercation

A. P. Hong, J.-B. Lee, and J. G. Verkade*

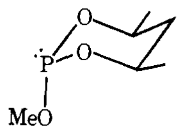
Contribution from the Department of Chemistry, Gilman Hall, Iowa State University, Ames, Iowa 50011. *Received November 17, 1975*

Abstract: Reaction of the rigid six-membered ring phosphate anion **4** in methanol with diazomethane in 1,2-dimethoxyethane under mild conditions yields an order of magnitude more of methyl ester **2b** than its isomer **2a** with the noncomplexing countercations Na^+, Cs^+, and Me_4N^+. With Li^+, however, the ratio of **2a**/**2b** is close to 1, while with NH_4^+ and $C_6H_{11}NH_3^+$ it is 1.6. It is concluded that preferential association of Li^+ with the axial P–O oxygen via complexation and of NH_4^+ and $C_6H_{11}NH_3^+$ via hydrogen bonding accounts for the increased tendency toward methylation of the equatorial P–O oxygen. A possible indication of the in vivo behavior of cyclic nucleotide anions is pointed out.

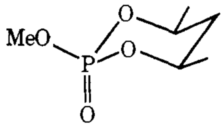
Evidence from a variety of chemical and spectral sources has established the greater basicity of axially compared to equatorially directed phosphorus lone pairs and phosphoryl oxygens in six-membered ring phosphite and phosphate esters, respectively, such as **1** and **2**.[1] The axial and equatorial P=O linkages in the biologically important cyclic 3′,5′-AMP and GMP nucleotide anions **3** are very likely differentiated in their bonding characteristics by electronic effects similar to those



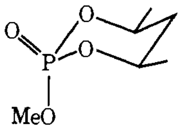
1a



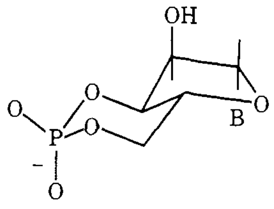
1b



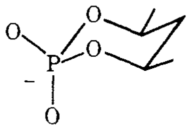
2a



2b



3



4

operating in **1** and **2**.[1-3] In order to test this idea, the model anion **4** was allowed to react with diazomethane in the presence of a variety of countercations to produce mixtures of the isomeric phosphate esters **2a,b**.

Experimental Section

Routine proton NMR spectra were obtained on either a Varian Associates A-60 or an Hitachi Perkin-Elmer R-20B spectrometer. Tier's salt ($Me_3SiCH_2CH_2CH_2SO_3Na$) was used as an internal standard for spectra run in D_2O. Ir spectra were run on a Beckman IR-12 spectrophotometer. Melting points are uncorrected.

Acid Form of 4. Using a procedure similar to the one described previously[4] for the preparation of 2-hydroxo-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane from the 2-chloro derivative, the title compound was prepared from the corresponding 2-chloro derivative. The preparation of the precursor 2-chloro-4,6-dimethyl-2-oxo-1,3,2-dioxaphosphorinane by this method[4] from *meso*-2,4-pentanediol[5] afforded a 78% yield; ^1H NMR ($CDCl_3$) multiplet at δ 1.17–2.17 and doublet of doublets ($J = 3$ Hz) centered at 1.41 (8 H), broad multiplet at 4.27–4.97 (2 H). From this derivative the title compound was made in 95% yield (mp 112 °C): ^1H NMR ($CDCl_3$) multiplet at δ 1.08–2.0 and doublet of doublets ($J = 2$ Hz) centered at 1.36 (8 H), broad multiplet at 4.27–5.0 (2 H), singlet at 10.82 (1 H). Anal. Calcd for $C_5H_{11}O_4P$: C, 36.15; H, 6.68; P, 18.65. Found: C, 36.02; H, 6.50; P, 18.41.

Cyclohexylammonium Salt of 4. To 2.0 g (12 mmol) of the acid of **4** dissolved in a minimum amount of acetonitrile was added 1.29 g (13.0 mmol) of cyclohexylamine. Complete precipitation of the white solid which formed was accomplished by adding ether. The filtered material was recrystallized from acetonitrile in 60% yield (mp 180–181 °C): ^1H NMR (D_2O) multiplet at δ 1.05–2.17 and doublet of doublets ($J = 2$ Hz) centered at 1.26 (8 H), multiplet at 2.73–3.33 (11 H), broad multiplet overlapping H_2O peak at 4.17–4.83. Anal. Calcd for $C_{11}H_{25}O_4NP$: C, 49.61; H, 9.46. Found: C, 49.89; H, 9.18.

Sodium Salt of 4. To 0.89 g (5.4 mmol) of the acid of **4** dissolved in 10 ml of H_2O was added dropwise a 20% aqueous NaOH solution to a pH of 7. The solid produced upon evaporation was washed with ether and recrystallized from methanol–ether in 49% yield (mp 323 °C): ^1H NMR (D_2O) multiplet at δ 1.08–2.08 and doublet of doublets ($J = 2$ Hz) centered at 1.26 (8 H), broad multiplet overlapping H_2O peak at 4.08–4.76. Anal. Calcd for $C_5H_{10}O_4PNa$: C, 31.93; H, 5.36; P, 16.47. Found: C, 31.78; H, 5.27; P, 16.73.

Lithium Salt of 4. To 0.5 g (3 mmol) of the acid of **4** dissolved in 10 ml of H_2O was added dropwise a 10% aqueous LiOH solution until pH paper indicated neutrality. Evaporation of the solvent and recrystallization from methanol–ether yielded 80% of the title compound (mp 345 °C): ^1H NMR (D_2O) multiplet at δ 1.09–1.89 and doublet of doublets ($J = 2$ Hz) centered at 1.27 (8 H), broad multiplet overlapping H_2O peak at 4.19–4.79. Anal. Calcd for $C_5H_{10}O_4PLi$: C, 34.91; H, 5.86; P, 18.00. Found: C, 34.64; H, 5.84; P, 17.74.

Tetramethylammonium Salt of 4. Tetramethylammonium bromide dissolved in methanol was passed through a column of Dowex 1-X2 (50–100 dry mesh) in the hydroxide form. The effluent methanol solution was added to a methanol solution of the acid form of **4** until a pH of 7 was reached as indicated by pH paper. Evaporation of the methanol and recrystallization of the residue from ethanol–ether gave a 97% yield of the title compound (mp 260 °C): ^1H NMR (D_2O) multiplet at δ 1.13–2.05 and a doublet of doublets ($J = 2$ Hz) centered at 1.27 (8 H), singlet at 3.17 (12 H), broad multiplet overlapping H_2O peak at 4.17–4.70. Anal. Calcd for $C_9H_{22}O_4PN$: C, 45.18; H, 9.27; P, 12.95. Found: C, 43.93; H, 9.30; P, 12.29.

Cesium Salt of 4. To 0.50 g (3.01 mmol) of the acid form of **4** dissolved in absolute ethanol was added a 20% aqueous solution of CsOH until neutrality was indicated by pH paper. Evaporation of the solvent produced the desired compound, which was recrystallized from ethanol–ether in 87% yield as the monohydrate. Overnight heating at 90 °C gave the anhydrous form (mp 210–212 °C): ^1H NMR (D_2O) multiplet at δ 1.11–2.00 and doublet of doublets ($J = 2$ Hz) centered at 1.25, broad multiplet overlapping H_2O peak at 4.11–4.82. Anal. Calcd for $C_5H_{10}O_4PCs{\cdot}H_2O$: C, 19.00; H, 3.83; P, 9.80. Found: C, 19.15; H, 3.86; P, 9.78.

Ammonium Salt of 4. To 0.80 g (4.8 mmol) of the acid of **4** in methanol was added a 58% aqueous solution of NH_4OH until basic. The solid remaining on evaporation in vacuo was washed with ether and recrystallized from methanol–ether, yielding 91% of the title compound (mp 197–200 °C): ^1H NMR (D_2O) multiplet at δ 1.03–2.02 and doublet of doublets ($J = 2$ Hz) centered at 1.26 (8 H), broad multiplet overlapping H_2O peak at 4.17–4.77. Anal. Calcd for $C_5H_{14}O_4PN$: C, 32.79; H, 7.71; P, 16.91. Found: C, 32.71; H, 7.75; P, 16.86.

Methylation of Salts of 4. To 5.0 ml of 0.1 M methanol solutions of the salts of **4** was added 3.0 ml of 1 M diazomethane in 1,2-dimethoxyethane. The solutions were stirred at room temperature or at 0 °C for 16 h. Following removal of the solvent and excess diazomethane under vacuum, 15 ml of $CHCl_3$ and 5 ml of H_2O were added to the residue. After the $CHCl_3$ layer was separated and dried with Na_2SO_4, the solvent was evaporated and the residue redissolved in a small amount of $CHCl_3$. Injection of this solution onto a 4.75 ft chromatographic column (15% 20M Carbowax on acid-washed Chromosorb G) at 199 °C resulted in peaks corresponding to **2a** and **2b** (determined by using authentic samples[8]), whose relative areas were determined by taking the ratio of the products of their heights and half-widths. Repetition of these reactions reproduced the product ester ratios within 10%. The retention times of the **2a** and **2b** using a helium flow rate of 35.4 ml/min were 12.5 and 18.5 min, respectively.

Diazomethane was prepared following a published procedure[6] from nitrosomethylurea[7] and its concentration in dimethoxyethane was estimated by titrating with 0.05 N aqueous NaOH the excess benzoic acid left after adding an ether solution of 0.2 N benzoic acid to an aliquot of the diazomethane solution diluted with ether. After the presence of excess acid was detected by disappearance of the yellow color, water was added to provide an aqueous medium for the titration.

The phosphate esters **2a,b** were shown to be stable once formed by subjecting authentic samples[8] of several different ratios to the methylation conditions, followed by the workup and analysis as described above. The ratios of **2a**/**2b** remained essentially unchanged.

Discussion

The ratios in Table I imply that axial methyl ester formation (**2b**) is greatly faovred over equatorial (**2a**) when the cation is Me_4N^+, Cs^+, or Na^+, whereas reaction at the equatorial site is somewhat favored with the Li^+, H^+, and $C_6H_{11}NH_3^+$ ions. This result can be rationalized by beginning with the postulate that the axial P–O oxygen is indeed more basic and that it is therefore more easily methylated despite its slightly more sterically encumbered position on the ring. While this is clearly observed in the case of Me_4N^+, Cs^+, and Na^+, the presence of Li^+, H^+, NH_4^+, or $C_6H_{11}NH_3^+$ countercations increases the formation of **2a** at the expense of **2b**. It appears that the Li^+ cation, which is small compared to the other alkali metal ions, preferentially polarizes the more negatively charged axial P–O oxygen and thereby hinders the attack of this ring site. Pref-

Table I. Ratios of **2a**/**2b** Formed from Salts of **4** with Diazomethane after 16 h

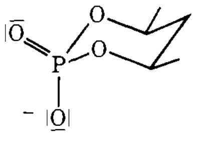
Cation	**2a**/**2b** (25 °C)	**2a**/**2b** (0 °C)
Na^+	0.12	0.18
Cs^+	0.07	0.07
Me_4N^+	0.15	0.11
Li^+	0.96	1.3
H^+	1.2	1.4
NH_4^+	1.6	1.5
$C_6H_{11}NH_3^+$	1.6	1.4

erential hydrogen bonding of the H^+, NH_4^+, and $C_6H_{11}NH_3^+$ ions to the more basic axial oxygen could account for a behavior similar to that of the Li^+ ion. The lack of substantial equatorial attack in the case of the fully alkylated NMe_4^+ cation supports this idea.

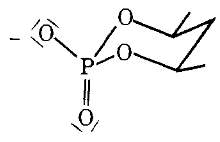
While alkylations of a variety of ambident anions have been studied,[9] the present investigation appears to be the first directed at elucidating the charge distribution on geminal atoms which are differentiated geometrically in the molecule. Pertinent to the work reported here, however, is the observation that O-alkylation of enolate salts is preferred to C-alkylation in the order $R_4N^+ > K^+ > Na^+ > Li^+$.[9] Since the cations are expected to be associated with the more electronegative oxygen, this trend suggests that as the cations increase their covalent bonding tendency toward oxygen by virtue of their rising charge/size ratio, C-alkylation will be increasingly favored.[9]

Because the alkylation site in enolates depends on the solvent as well as on the alkylating agent,[9] alkylations of **4** were also carried out under the same conditions using MeI in DMF. The ratios of **2a**/**2b** ranged from 0.44 to 0.52 without any apparent trend. This result tends to indicate that in this much more polar solvent (DMF, 3.8 D; MeOH, 1.7 D) the degree of ion separation is about the same in all cases. On the other hand, **2b** is still favored, although less so than with diazomethane in methanol. Using Me_3OBF_4 in the highly polar solvent MeCN (3.4 D) afforded even less selectivity in attack, although the ratios for the nonassociating cations Na^+, Cs^+, and Me_4N^+ (0.84, 0.82, and 0.75, respectively) were somewhat smaller than for NH_4^+, $C_6H_{11}NH_3^+$, and Li^+ (1.03, 1.06, and 1.94, respectively).

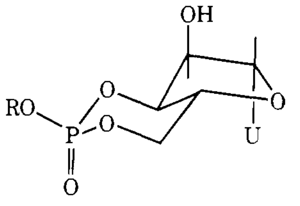
It seems reasonable to conclude from our results that the axial oxygen of **4** is preferentially alkylated under conditions where the cation does not hydrogen bond or covalently associate with this site. This can be interpreted to mean that the dominant resonance form of **4** is **4a** rather than **4b**. Very recently it was concluded from ^{31}P chemical shift and P=O stretching frequency measurements that the reaction of **3** in the acid form (B = uracil) in methanol with several diazoalkanes in ether gives the isomeric esters **4a,b** in the ratio **5a**/**5b** ≃ 0.4.[10] The combined evidence strongly suggests that in the absence of other dominating effects, the anionic forms of the cellular "second messengers" cyclic-3′,5′-AMP and GMP are expected to interact more strongly via their axial P–O oxygen with polarizing or hydrogen-bonding cationic sites, owing to the higher concentration of negative charge on this oxygen compared to the equatorial oxygen.



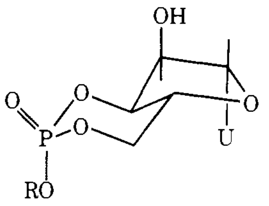
4a



4b



5a



5b

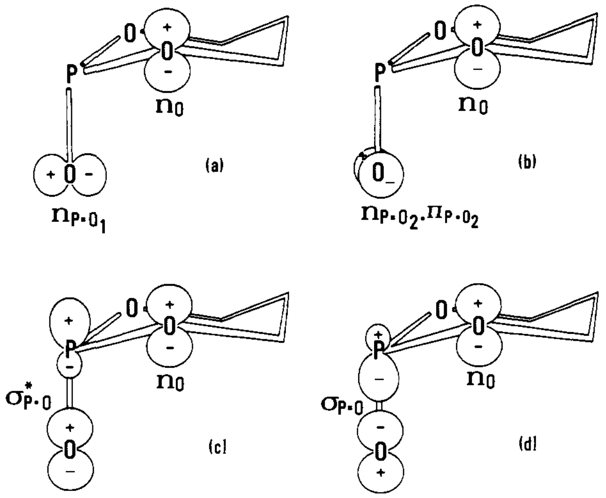


Figure 1. Major orbital interactions contributing to the stronger basicity of the axial oxygen in the six-membered ring phosphate diester anions.

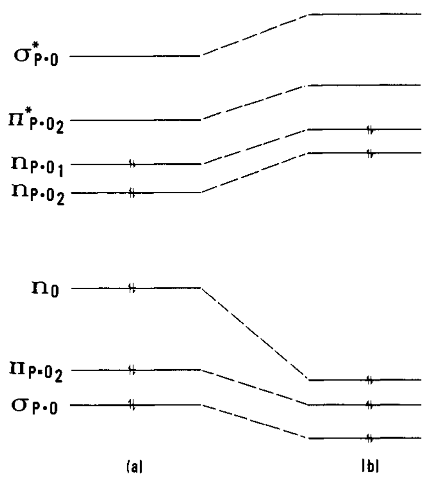
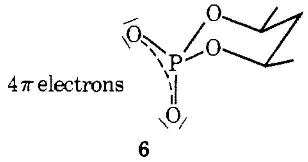


Figure 2. (a) Qualitative energy level diagram for the orbitals shown in Figure 1, in (a) the absence and (b) the presence of interaction.

The accumulation of negative charge on the axial P–O oxygen in these ring systems can be rationalized by extending an argument given earlier for the greater basicity of the phosphoryl oxygen of **2a** compared to **2b**.[3] Assuming for the moment that the ring oxygen lone pairs do not affect orbitals associated with the terminal oxygens, the electronic structure **6** can be invoked in which four π electrons are distributed in a three-center bonding and nonbonding MO. The negative charge would then be evenly distributed to the P–O bonds. In Figure 1 are shown the terminal orbitals on the axial oxygen, which can be expected to interact with the unhybridized p AO on each ring oxygen. It should be noted that in b of this figure is represented only the axial oxygen AO contribution to the three-center π bonding and nonbonding MO's. The delocali-



6

zation of these MO's permits only a fraction of the pair of electrons shown in these orbitals in Figure 2 to reside on the axial oxygen. Because of the negative charge on the terminal oxygens, the orbitals on these atoms may be expected to lie at higher energy than those on the ring oxygens. The energy level diagram in Figure 2b reflects the rise in energy of the axial oxygen lone-pair orbital as a result of the ring oxygen lone-pair interaction. The lower ionization potentials of the axial oxygen lone pairs could then account for the greater polarizability of this site by cations and alkylating nucleophiles.

Acknowledgment. J.G.V. thanks the National Cancer Institute of the National Institutes of Health for grant support of this research. The authors also thank one of the referees for bringing to their attention the relevance of enolate alkylations to the present work.

References and Notes

(1) J. G. Verkade, Plenary Lecture, 5th International Conference on Organic Phosphorus Chemistry, Gdansk, 1975; *Phosphorus*, in press, and references cited therein.

(2) J. G. Verkade, *Bioinorg. Chem.*, **3**, 165 (1974).

(3) R. F. Hudson and J. G. Verkade, *Tetrahedron Lett.*, 3231 (1975).

(4) R. S. Edmundson, *Tetrahedron*, **21**, 2379 (1965).

(5) D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 7125 (1970).

(6) D. M. G. Martin, C. B. Reese, and G. F. Stephenson, *Biochemistry*, **7**, 1406 (1968).

(7) "Organic Synthesis", Collect. Vol. 2, Wiley, New York, N.Y., 1943, p 462.

(8) J. A. Mosbo and J. G. Verkade, *J. Am. Chem. Soc.*, **95**, 4659 (1973).

(9) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Inc., Menlo Park, Calif., 1972, Chapter 9, and references cited therein.

(10) J. Engels and W. Pfleiderer, *Tetrahedron Lett.*, 1661 (1975).

High-Resolution Boron-11 Nuclear Magnetic Resonance Spectroscopy. 6.[1] Application of Relaxation Time Measurements to Boron Hydrides

Edward J. Stampf,[2] Albert R. Garber, Jerome D. Odom,* and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received February 10, 1976

Abstract: The spin-lattice and transverse relaxation times of small boron hydrides and several derivatives are reported. Measurement of T_1 and T_2 relaxation rates of magnetically dilute boron-10 in several compounds confirms that the quadrupolar mechanism dominates transverse as well as spin-lattice relaxation in small boron hydrides. Assured that $T_1 = T_2$, unresolved boron-boron coupling constants are estimated by line shape analyses employing measured T_1 relaxation rates. The magnitude of J_{BB} is related to the bonding between the coupled nuclei and a correlation of observed boron-boron coupling constants with current localized molecular orbital views of boron hydrides is demonstrated.

In earlier papers of this series, we have reported several factors that influence the magnitude of the boron-boron coupling constant, J_{BB}.[3] Of particular interest here is the dependence of the magnitude of J_{BB} on the bonding situation between the coupled atoms. For example, a rather large coupling constant of 19.4 Hz between the apex and basal borons in B_5H_9 has been reported.[4] In contrast, a reasonable upper limit for J_{BB} transmitted through a bridge hydrogen has been reported to be 1.1 Hz for B_2H_6 and 0.3 Hz for B_4H_{10}.[5] Prompted by this significant variance in the magnitude of J_{BB} for the two different bonding environments already investigated, we undertook this study to further investigate the value of J_{BB} for other common bonding situations, i.e., for boron atoms coupled through a pure three-center, two-electron bond or through a two-center, two-electron bond.

Several techniques have been established that were necessary for the determination of these coupling constants. Utilization of triple resonance techniques[5] and complete proton decoupling[4] met with limited success. For resonances in which J_{BB} approaches the natural line width, a poorly resolved multiplet or broad single line results. Line narrowing techniques[6] can overcome this problem to an extent and have made it possible to abstract additional coupling constants.[7] However, this method has a lower limit of resolution of approximately 10 Hz in this application.

In this paper we describe another technique which has allowed us to estimate coupling constants which were previously inaccessible by other methods. This technique involves measurement of spin-lattice relaxation times (T_1) and utilization of the T_1 data in an FT NMR line simulation program.[8]

For a Lorentzian line, the half-height line width ($\Delta\nu_{1/2}$) is defined as $1/\pi T_2^*$, where $1/T_2^* = 1/T_2 + (\gamma\Delta H_0/2)$. Thus the observed line width, in the absence of any coupling, contains contributions from the transverse relaxation time (T_2) and inhomogeneity in the magnetic field (ΔH_0).

For the ^{11}B nucleus, previous studies[9] have shown that the quadrupolar mechanism dominates spin-lattice relaxation and that all other mechanisms contribute negligibly. If the extreme narrowing condition[10] ($\omega_0^2\tau_c^2 \ll 1$) is valid, it has been generally assumed that $T_1 = T_2$. Implicit in this assumption is the requirement that no other mechanism (e.g., scalar coupling) contributes to transverse relaxation. This assumption is further investigated and shown to be valid.

We have measured the spin-lattice relaxation times of several boron hydrides and derivatives. Utilizing these data, we have abstracted J_{BB} by fitting the calculated spectrum to the experimental line shape. Since the observed resonance line shape contains a contribution from inhomogeneity in H_0, the coupling constants so derived represent an upper limit to J_{BB}. Qualitatively, we have found that there is a correlation between the magnitude of J_{BB} and the nature of the bond between the coupled nuclei.

Experimental Section

Standard high-vacuum techniques were used throughout this study.[11] The purity of all compounds was checked by vapor pressure