Table I. Positional Parameters and Their Estimated Standard Deviations for $V_2(tmp)_4 \cdot 2THF$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
V(1)	0.03279 (8)	0.49009 (4)	0.07724 (9)	C(18)	0.1695 (6)	0.3877 (3)	0.0708 (6)
O(1)	−0.0429 (3)	0.4602 (2)	−0.3132 (3)	C(19)	0.1222 (7)	0.2799 (3)	−0.3810 (6)
O(2)	0.1069 (3)	0.4209 (2)	0.0079 (3)	C(21)	−0.1047 (5)	0.4558 (2)	0.0348 (5)
O(3)	0.1500 (4)	0.2996 (2)	−0.2786 (4)	C(22)	−0.1104 (5)	0.4235 (3)	0.1236 (5)
O(4)	−0.1782 (3)	0.4857 (2)	−0.1173 (3)	C(23)	−0.1849 (5)	0.3897 (3)	0.1540 (5)
O(5)	−0.0269 (3)	0.4270 (2)	0.1833 (3)	C(24)	−0.2611 (5)	0.3903 (3)	0.0860 (6)
O(6)	−0.3408 (3)	0.3591 (2)	0.1035 (4)	C(25)	−0.2647 (5)	0.4212 (3)	−0.0067 (5)
O(S)	0.3566 (5)	0.2870 (2)	0.1350 (5)	C(26)	−0.1860 (5)	0.4525 (2)	−0.0262 (5)
C(11)	0.0308 (5)	0.4425 (2)	−0.1529 (5)	C(27)	−0.2431 (6)	0.4773 (3)	−0.2043 (5)
C(12)	0.0143 (4)	0.4255 (2)	−0.2573 (5)	C(28)	−0.0316 (6)	0.4167 (3)	0.2957 (5)
C(13)	0.0498 (5)	0.3791 (3)	−0.3038 (5)	C(29)	−0.3320 (6)	0.3125 (3)	0.1687 (6)
C(14)	0.1102 (5)	0.3476 (2)	−0.2427 (5)	C(S1)	0.3860 (9)	0.2802 (4)	0.0330 (8)
C(15)	0.1329 (5)	0.3598 (3)	−0.1394 (5)	C(S2)	0.3811 (7)	0.2390 (4)	0.1942 (8)
C(16)	0.0909 (5)	0.4071 (2)	−0.0987 (5)	C(S3)	0.3860 (8)	0.1937 (4)	0.1159 (7)
C(17)	−0.0757 (7)	0.4439 (4)	−0.4161 (6)	C(S4)	0.4187 (8)	0.2221 (4)	0.0189 (8)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table IIA. Important Interatomic Distances (Å) and Bond Angles (deg) for $V_2(tmp)_4 \cdot 2THF$[a]

Distances

V(1)-V(1)′	2.223 (2)	O(2)-C(16)	1.411 (5)
-O(2)	2.195 (3)	O(4)-C(26)	1.420 (5)
-O(4)	2.218 (3)	O(5)-C(22)	1.413 (5)
-O(5)	2.227 (3)	C(11)-C(16)	1.404 (6)
-C(11)	2.126 (5)	C(21)-C(22)	1.382 (6)
-C(21)	2.203 (5)	-C(26)	1.395 (6)
-C(21)′	2.204 (5)		

Angles

V(1)-V(1)′-O(2)	91.27 (9)	C(11)-V(1)-C(12)	90.7 (2)
-O(4)	122.3 (1)	-C(21)′	119.4 (1)
-O(5)	121.7 (1)	V(1)-O(2)-C(16)	119.6 (3)
-C(11)	92.5 (1)	-O(4)-C(26)	92.5 (3)
-C(21)	59.7 (1)	-O(5)-C(22)	92.4 (3)
-C(21)′	59.7 (1)	-C(11)-C(16)	121.9 (3)
O(2)-V(1)-O(4)	81.5 (1)	O(2)-C(16)-C(11)	114.6 (4)
-O(5)	83.1 (1)	V(1)-C(21)-V(1)′	60.6 (1)
-C(11)	175.7 (2)	-C(22)	94.4 (3)
-C(21)	91.8 (2)	-C(26)	153.8 (4)
-C(21)′	89.5 (2)	V(1)-C(21)′-C(22)′	154.5 (4)
O(4)-V(1)-O(5)	114.1 (1)	-C(26)′	93.8 (3)
-C(11)	94.8 (2)	C(22)-C(21)-C(26)	111.6 (5)
-C(21)	172.9 (2)	O(5)-C(22)-C(21)	110.5 (5)
-C(21)′	63.1 (2)	O(4)-C(26)-C(21)	110.6 (4)
O(5)-V(1)-C(11)	96.5 (2)		
-C(21)	62.5 (2)		
-C(21)′	172.5 (2)		

[a] Estimated standard deviations in the least significant digits are included in parentheses.

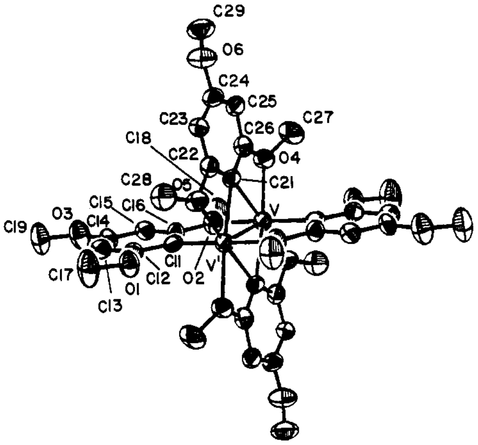

Figure 1. ORTEP view of the $V_2(tmp)_4$ molecule. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

0.080, the error in an observation of unit weight being 2.16. A final difference synthesis showed random fluctuations not exceeding ±0.43 e/Å^3. Final positional parameters are given in Table I. A table of anisotropic thermal parameters is available as supplementary material as are values of observed and calculated structure factor amplitudes.

Results and Discussion

Figure 1 shows an ORTEP plot of the entire molecule and defines the atom-numbering scheme. Pertinent bond distances and angles are listed in Table IIA while the less important data are available as supplementary material (Table IIB). The molecules reside on crystallographic centers of inversion.

The arrangement of the 2,4,6-trimethoxyphenyl ligands about the two vanadium atoms is entirely analogous to that found in the $V_2(dmp)_4$ molecule.[9] There are two ligands that are bidentate and form conventional three-atom bridges between the two metal atoms; the other two ligands are of the curious tridentate type where the phenyl ring bridges the two vanadium atoms and one methoxy oxygen atom is coordinated to each of the metal atoms.

There is a small but statistically real difference between the V≡V bond length observed here, 2.223 (2) Å, and that found previously in the 2,6-dimethoxy compound, 2.200 (2) Å, viz., 0.023 (3) Å. Such a change, while small, is probably too large to be accounted for purely by packing forces or other extramolecular factors. It may, therefore, most reasonably be attributed to the presence of the additional methoxy group in the para position, which could have a significant effect on the ring carbon atom that lies over the V≡V bond. This, in turn, evidently weakens the bond slightly.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $V_2(tmp)_4 \cdot 2THF$, 83830-97-1.

Supplementary Material Available: Tables of structure factors, additional bond distances and angles (Table IIB) and thermal parameters (Table III) (13 pages). Ordering information is given on any current masthead page.

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Phosphazenes. 1. Reactions of Hexachlorocyclotriphosphazene with Methyllithium

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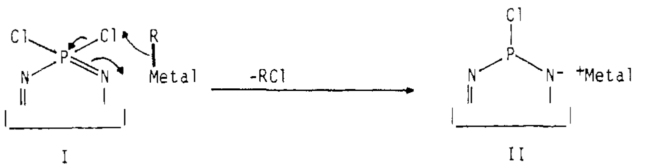
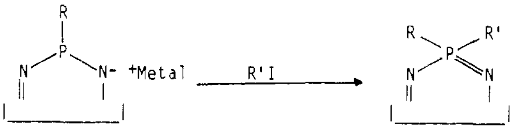
Reactions of organometallic reagents with chlorophosphazenes have received considerable attention in the last few years. However, only recently has some understanding

Scheme I



Scheme II



of the mechanisms of these reactions been achieved. It has been discovered that organocopper and Grignard reagents react with hexachlorocyclotriphosphazene (I) via a metal–halogen exchange pathway.[1-3] The final products from these reactions depend on the particular metal involved. For Grignard reagents, the final products are bis(cyclotriphosphazenes)[2] whereas organocopper reagents yield stable metallophosphazenes.[1]

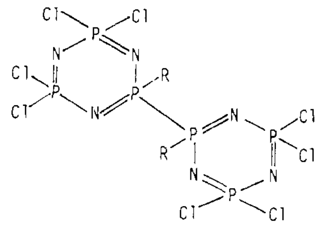
In this work we have investigated the reactions of hexachlorocyclotriphosphazene (I) with methyllithium. This study was undertaken in order to answer several questions. First, can alkylated cyclic phosphazenes be prepared by the reactions? A previous report on this reaction suggested that alkylation did not occur, but no mention was made of the actual reaction products.[4] Also, similar reactions of hexafluorocyclotriphosphazene[5] and poly(difluorophosphazene)[6] with organolithium reagents appear to lead to good yields of substituted products. Second, do these reactions proceed via a metal–halogen exchange reaction analogous to that of Grignard reagents, and if not, what is the reaction mechanism?

Results and Discussion

Initially it was thought that the reactions of hexachlorocyclotriphosphazene with methyllithium would proceed in a manner analogous to that of organocopper or Grignard reagents, that is, by the metal–halogen exchange pathway, and work was undertaken to verify this idea.

There are several key observations to this metal–halogen exchange reaction. The first, and probably most important, is that when this pathway is operative, chloromethane is evolved from this reaction mixture.[1] This arises by the process shown in Scheme I.

The second key observation is that in the case of Grignard reagents the metallophosphazene (II) reacts further to form bis(cyclotriphosphazene) compounds of type III.[2]



III

The final observation is alkyl halide trapping of the metallophosphazene as shown in Scheme II. The products from these reactions contain one alkyl group from the organometallic reagent and one alkyl group from the added alkyl halide.[3,7] With these key observations in mind, a study of the reactions of $N_3P_3Cl_6$ with methyllithium was initiated.

Scheme III

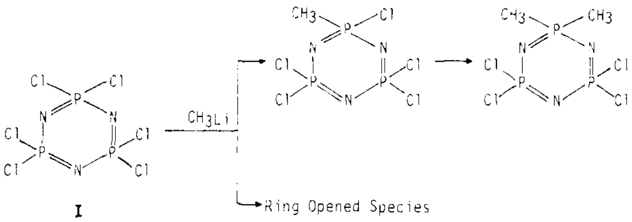


Table I. Yield of Cyclic Phosphazenes (mg) from the Reactions of I with CH_3Li

solvent	−60 °C	0 °C	+20 °C	reflux
THF	280	360	385	420
Et_2O	270	370	390	400
THF/TMEDA	90	95	105	110
Et_2O/TMEDA	85	95	100	100

The Overall Reaction. When hexachlorocyclotriphosphazene (I) was allowed to react with methyllithium under a variety of reaction conditions, acyclic "ring-opened" phosphazenes and small amounts of monomethyl- and dimethyl-substituted chlorocyclotriphosphazenes were produced. The general reaction is summarized in Scheme III. The structures of the cyclic compounds were confirmed by ^1H and ^{31}P NMR and mass spectrometry. These spectra were identical with those previously reported for these compounds.[7,8] The acyclic compounds were found to be low molecular weight linear phosphazenes and were insoluble in most organic solvents except tetrahydrofuran and diethyl ether. They were fairly hygroscopic and reacted exothermically with water and other protic solvents. They decomposed without melting at 280 °C in an open capillary. The infrared spectrum of the material (KBr pellet) consisted of a strong band in the 1200-cm^{-1} region, characteristic of the P=N stretch. There were weaker bands at 1300, 950, and 870 cm^{-1}. The peak at 1300 cm^{-1} is found to occur in many methylated phosphazenes.[7] The ^1H NMR spectrum (THF-d_8 solution) showed a broad, uncharacteristic set of resonances between 1.2 and 2.5 ppm. The ^{31}P NMR spectrum (THF-d_8 solution) showed another broad, ill-defined set of resonances between 15 and 40 ppm. The molecular weight was found to be ~950 in diethyl ether. These data indicate that the ring-opened species is probably a matrix formed by ring cleavage, which is followed by ring substitution by these short linear molecules. This possibility will be discussed in a later section.

The reactions between hexachlorocyclotriphosphazene and methyllithium were run in both tetrahydrofuran and diethyl ether at −60, 0, and 20 °C and at reflux. The variation of the solvent had very little effect on the product distribution. However, at higher temperatures slightly more of the cyclic products were observed. The yields of the various cyclic products are listed in Table I. Yields of the acyclic products were difficult to estimate due to the presence of magnesium halides but were assumed to represent the rest of the phosphazene present.

Several attempts were made to check for evidence of metal–halogen exchange, as well as other possible reaction pathways. First, gas evolution from each reaction was monitored; none was observed. Second, alkyl halide trapping experiments with ethyl iodide or bromide were carried out. No ethyl group

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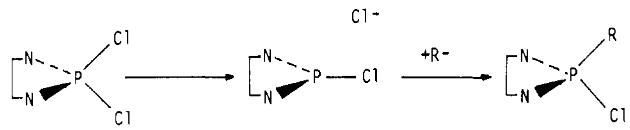
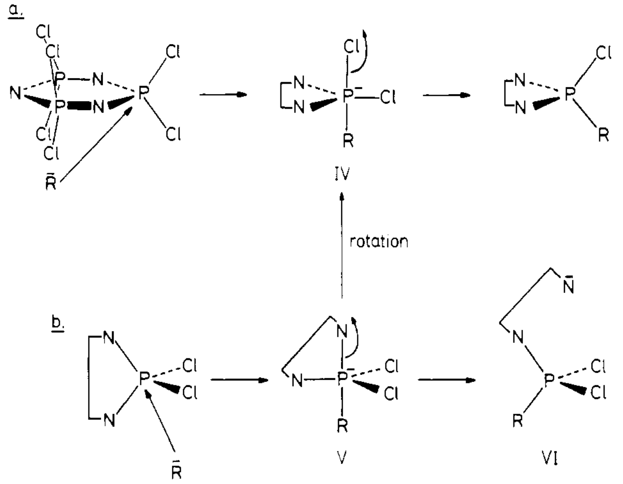
Scheme IV



Scheme V

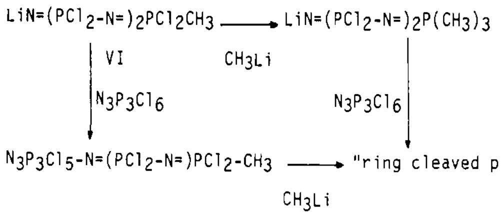


incorporation into either the cyclic or acyclic products was observed by ^{1}H NMR. Finally, all the reactions were repeated in the presence of tetramethylethylenediamine (TMEDA). This reagent was added in an attempt to complex the lithium ion. It has been suggested that binding this metal to a backbone nitrogen atom is in some way responsible for the skeletal cleavage.[6] However, in all the reactions where TMEDA was present, the yield of cyclic products decreased markedly.

The Reaction Mechanism. From these results, several possible mechanistic pathways can be ruled out. First, metalation of a P–CH_3 group can be eliminated.[9] No methane was evolved. Second, the absence of methyl chloride or ethane (possibly produced by trapping of "nascent" methyl chloride with methyllithium) and the lack of ethyl group incorporation into any of the final products clearly rule out a metal–halogen exchange pathway. The only other realistic possibility that exists, therefore, is a simple nucleophilic attack by the organometallic reagent at phosphorus. This type of reaction can proceed via two different mechanistic pathways—S_N1 or S_N2. Both possibilities can be considered. The S_N1 pathway would proceed as shown in Scheme IV. This reaction involves simple ionization of halogen followed by rapid attack of the organometallic reagent on the phosphazenium cation. It would appear unlikely that the reaction would proceed solely along these lines, as it is known that the rate of formation of the phosphazenium cation is extremely slow. This is clearly demonstrated by the slow rate of arylation of $N_3P_3Cl_6$ by Friedel–Crafts reactions.[10]

Attack by the alkyl group via an S_N2 type pathway could occur by the two possible routes shown in Scheme V, analogous to that observed in simple phosphate ester hydrolysis.[11] Pathway a involves attack by the alkyl group axial to a halogen. This would lead to the formation of intermediate IV. Loss of the axial chloride ion from this species would yield substituted products. The intermediate formed by this mode of attack is expected to be fairly stable as the N–P–N bond angle in these species would be ~120°, similar to the normal N–P–N bond angle found in $N_3P_3Cl_6$.[12] The actual formation of this intermediate, however, seems unfavorable both electronically and sterically, as the incoming alkyl anion must pass close to two chlorine atoms. This is considered to be a very hindered mode of attack. Pathway b, however, provides a completely unhindered mode of attack for the alkyl group on the phosphazene ring. Approach of the anion axial to ring nitrogen would lead to the formation of intermediate V. In this species one ring nitrogen is axial, the other is equatorial, and the N–P–N bond angle would be close to 90°, clearly a strained conformation.[11] To relieve this strain, intermediate V could undergo pseudorotation to intermediate IV or undergo loss of the axial nitrogen atom to yield compound VI. This seems to be the preferred pathway and readily accounts for the high yields of ring-cleaved products.[11] When the reactions were run at higher temperatures, slightly more cyclic products were observed. These results can be explained in two ways: (a) the S_N1 process would be faciliated at higher temperatures and (b) rotation of intermediate V to IV would be easier at higher temperatures. The presence of TMEDA, however, would render the organometallic reagent more nucleophilic and thus favor the S_N2 pathway b.

Scheme VI



Ring cleavage does not appear to occur after methyl substitution. This was demonstrated by the reaction of methylpentachlorocyclotriphosphazene[8] with methyllithium, which led to high yields of 1,1-dimethyltetrachlorocyclotriphosphazene.[7] Also, cleavage due to metalation of a P–CH_3 group can be ruled out by the fact that no methane was generated.[9]

Evidence for a Ring-Opening Reaction. For support of the postulate of the ring-opening mechanism, degradative acid hydrolysis experiments were performed on the ring-opened material. Treatment with 2 N HCl at 150 °C in a sealed tube yielded $(CH_3)_3P{=}O$, $(CH_3)_2P(O)OH$, $(CH_3)P(O)(OH)_2$, and H_3PO_4. $(CH_3)_2P(O)OH$, $(CH_3)P(O)(OH)_2$, and H_3PO_4 are all expected products from the hydrolysis of either a cyclic or linear phosphazene that contains some degree of methyl group incorporation. The $(CH_3)P{=}O$, however, can result only from a ring-cleavage product (i.e., VI) where the terminal phosphorus atom is further substituted with methyl groups after cleavage. These linear species (VI) can also react through the $=N^-Li^+$ end of the chain. Addition to another P—Cl bond would yield a matrix composed of cross-linked rings or short linear chains. This type of material would have no distinct ^{31}P NMR resonances. Both these possible types of reaction are shown in Scheme VI.

In conclusion, it appears that the reactions of hexachlorocyclotriphosphazene with methyllithium does not proceed by metal–halogen exchange but rather by nucleophilic attack at phosphorus, leading to high yields of ring-cleaved products.

Experimental Section

Material. Hexachlorocyclotriphosphazene (I) was supplied by the Ethyl Corp. and was purified by sublimation followed by recrystallization from *n*-hexane. Methyllithium was obtained from the Aldrich Chemical Co. Tetrahydrofuran and diethyl ether were distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium–benzophenone ketyl drying agent. All reactions were carried

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out under an atmosphere of dry nitrogen.

General Procedure. All of the experiments were carried out in a similar manner. The following is a typical procedure: Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) was dissolved in THF (150 mL). The methyllithium solution (22.4 mL, 0.028 mol) was slowly added over a period of $\sim$20 min. The reaction mixture was allowed to stir overnight. Removal of the solvent under vacuum and filtration of the products dissolved in CH_2Cl_2 through neutral alumina gave the cyclic products. The yields are listed in Table I. For reactions involving TMEDA, the phosphazene (5.0 g, 0.014 mol) and TMEDA (8.45 mL, 0.056 mol) were first dissolved in the solvent and then the organometallic reagent was added as before. For reactions involving ethyl bromide, the phosphazene (5.0 g, 0.010 mol) and ethyl bromide (2.09 mL, 0.028 mol) were dissolved in the solvent and the above procedure repeated.

Acid Hydrolysis. The "ring-cleaved" products from the above reactions were all hydrolyzed in the same manner. The following is a typical procedue: A 1.0-g sample of the material was placed in a glass ampule with ethanol (30 mL) and 2 M HCl (30 mL). The ampule was then cooled to −196 °C, evacuated, and sealed and was then heated at 150 °C for 24 h. After this time, the ampule was allowed to cool at room temperature and opened, and the solvent was removed in vacuo. Sublimation of the solid residue at 80 °C (0.5 mm) yielded $\sim$0.1 g of $(CH_3)_3P{=}O$ (identified by its mass spectrum and ^{31}P NMR). Extraction of the sublimator residue with toluene gave a mixture that proved to be $(CH_3)_2P(O)OH$, $CH_3P(O)(OH)_2$, and H_3PO_4 (identified by mass spectrometry and ^{31}P NMR).

Acknowledgment. We thank the taxpayers of Virginia for support of this work.

Registry No. Hexachlorocyclotriphosphazene, 940-71-6; methyllithium, 917-54-4.

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Structural Effects on Polarographic Reduction of Substituted Dihydro(dimethylamine)(pyridine)boron(1+) Cations in Acetonitrile

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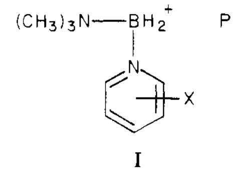
Received June 25, 1982

The polarographic reduction of trimethylamine-*N*-pyridylboronium hexafluorophosphates (I) (or dihydrido(tri-



I

methylamine)(pyridine)boron(1+) hexafluorophosphates) is investigated in this paper, particularly from the point of view of effects of substituents on the reduction process. Such substituent effects were first treated qualitatively by the electronegativity rule by Shikata and Tachi.[3] More recently a linear free energy relationship was used for quantitative treatment of substituent effects in organic compounds on the basis of the modified Hammett equation:[4] $\Delta E_{1/2} = \rho\sigma_X$. This study is, to our knowledge, the first attempt to extend such an approach to compounds containing boron. The study has been carried out in acetonitrile, diminishing the role of proton transfers and resulting in a stabilization of the products of the one-electron uptake.[5]

Experimental Section

Compounds Ia–Is (Table I) were prepared according to ref 6. Spectroscopically pure acetonitrile dried over 4A molecular sieves was used as a solvent. Tetrabutylammonium perchlorate (G. F. Smith Chemical Co.) was used as delivered.

Polarographic curves were recorded with a Sargent XV polarograph using a capillary electrode with the following characteristics: m = 3.54 mg s^{-1}, t_1 = 6.6 s (in open circuit). The side arm of the electrolytic H-cell, filled with agar gel saturated with sodium chloride, was separated from the solution investigated by a medium-porosity sintered-Pyrex disk.

Solutions containing 0.25 mM boronium compound and 0.05 M tetrabutylammonium perchlorate in acetonitrile were freshly prepared by weighing. Such solutions were stable for at least 24 h. Half-wave potentials were measured with use of log $[i/(i_d - i)]$ vs. E plots, against a calomel reference electrode containing a saturated aqueous solution of sodium chloride. All values of half-wave potentials were corrected for the iR drop with use of measurements of resistance by means of a conductoscope.

The temperature of the solution was kept at 25 ± 1 °C. Solutions were purged by nitrogen passed through a heated copper furnace for 15 min. The temperatures of the gas and furnace were controlled so as to minimize variations in evaporation of the solvent.

Results

Most substituted trimethylamine-*N*-pyridylboronium hexafluorophosphates (I) studied are reduced in a single wave, which was proved by mercury pressure to be diffusion controlled. A comparison of limiting currents (i_d, Table I) indicates that most of the compounds studied are reduced by the same number of electrons. Calculation of diffusion coefficients by using the Ilkovič equation indicates that n = 1. The values of half-wave potentials, i_d/C, and αn_a were practically independent of concentration (Table II).

Only acetyl- (Ii) and benzoylpyridine (Ih) derivatives are reduced in two waves, one of them corresponding to the reduction of the carbonyl group. The shape of the plot of log $[(i_d - i)/i]$ vs. E indicates that for compounds Ib, If, Ig, Ij, and Is the process is close to reversible and for all others irreversible. Limiting currents for the 3-chloro- (Ic) and acetylpyridine (Ii) derivatives are significantly lower than those that would correspond to a one-electron process. An even more marked decrease was observed for the 3-methoxy-5-cyano derivative (Il). When maxima appeared on the limiting current, they were suppressed by using methylene chloride as cosolvent. The waves of the 4-methoxypyridine derivative (Ir) were so affected by maxima that measurement of the limiting current was impossible.

Discussion

The one-electron uptake leads to a formation of a radical, which may be followed by dimerization similar to that reported[7] for *N*-alkylpyridinium compounds or by cleavage of the bond between the boron atom and either the pyridine or the amine nitrogen. Even if the fate of the primary electrode product is not known, it is possible to use the polarographic data for structural correlations using the modified Hammett equation.[4]

For the application of the modified Hammett equation for the treatment of polarographic half-wave potentials for meta-

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