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PHOSPHINEBORANE ANALOGS OF TRIMETHYLSILYL AMIDES

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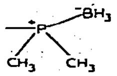
Summary

The reaction of $(CH_3)_2(BH_3)PCl$ with the lithium salts of acetamide, *N*-methyl acetamide, and *N*-methyl formamide produced the $N(CH_3)_2(BH_3)P$-monosubstituted amides. Attempts to employ the same procedure for the preparation of the bis-acetamide, the acetanilide and the *N*-methyl benzamide derivatives were unsuccessful. Variable temperature NMR spectroscopy revealed the presence of rotational isomers for the formamide with a population of 0.85 for the major rotamer which on the basis of the ^{31}P-formyl proton coupling constants was assigned the structure where the $(CH_3)_2(BH_3)P$ group is *trans* to carbonyl oxygen. The free energies of activation were determined to be 16.2 and 17.3 kcal/mol. For the other derivatives only one isomer could be detected down to —60°C. The compounds are similar to the trimethylsilyl analogs in structure and rotational populations, but the lower rotational barrier in the phosphineborane formamide derivative suggests a greater destabilization of the polar ground state amide resonance structure by the formal positive charge on phosphorus.

Recent studies [1,2] of the surprisingly stable compound $(CH_3)_2(BH_3)PCl$ indicate that while many of its reactions are quite similar to those of the isoelectronic silicon compound, $(CH_3)_3SiCl$, there are some interesting differences. For example, the primary amine, $(CH_3)_2(BH_3)PNH_2$, can be readily prepared as a stable compound and can then be converted to the air-and-water-stable isoelectronic analog of hexamethyldisilazane. In addition to chemical differences such as these there is one major physical difference, the compounds are considerably less volatile than the silicon isoelectronomers ($[(CH_3)_2P(BH_3)]_2NH$, m.p. 164°C; $[(CH_3)_3Si]_2NH$, b.p. 126°C). This difference can be accounted for by the greater polarity of the P—B bond suggested by the Lewis formula



but the distribution of electron density in phosphineboranes is still uncertain [1].

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Because of the dramatic effect of the trimethylsilyl group on amide-imidate tautomerism [3] and the conformations and rotational barriers of amides [4,5] we anticipated that a comparative study of the phosphineborane analogs would lead to a better understanding of the different electronic effects of these isoelectronomers. We have therefore studied the reaction of $(CH_3)_2(BH_3)PCl$ with the lithium salts of a variety of amides and have characterized the *N*-$(CH_3)_2$-$(BH)_3P$-substituted amides that resulted.

Experimental

All procedures were carried out under a nitrogen atmosphere using oven-dried glassware and dry reagents. Dimethylchlorophosphineborane was prepared according to the method of Schmidbaur and Weiss [2] from dimethylchlorophosphine (Strem Chemical Co.) and $BH_3 \cdot THF$ (Aldrich Chemical Co.). The phosphineborane was not isolated but was added in the THF solution to the lithium salts of the appropriate amides at room temperature. After the precipitated LiCl had settled (usually overnight), the solution was removed from the precipitate by syringe, and the solvent was removed by vacuum. The résidue was sublimed to give the product whose physical and spectral characteristics are listed in Table 1.

Lithium salts of the amides were prepared by treatment of the appropriate amide in THF with a solution of butyllithium in hexane at 0°C. After stirring for 1 h the solution was allowed to warm to room temperature for 1 h and was then treated with dimethylchlorophosphineborane as indicated above.

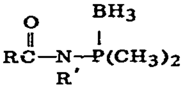
NMR and IR spectra were recorded on Perkin-Elmer R32 (90 MHz) and 621 spectrophotometers, respectively.

Results and discussion

The reaction of the lithium salts of *N*-methyl acetamide and *N*-methyl formamide with dimethylchlorophosphineborane produced the desired dimethylphosphineborane derivatives in reasonable yields. The reaction of the lithium salts of acetanilide and *N*-methyl benzamide produced mixtures that could not be iden-

TABLE 1

PHYSICAL AND SPECTRAL CHARACTERISTICS OF *N*-$P(CH_3)_2(BH_3)$ AMIDES

 $R\overset{O}{\overset{\|}{C}}-\underset{R'}{N}-\overset{BH_3}{\overset{\mid}{P}}(CH_3)_2$		M.p. (0°C)	yield (%)	^{1}H chemical shifts (ppm) [b]			
				$P(CH_3)_2$	BH_3	R	R'
R	R'						
H	CH_3	80—85	60	1.55(d) [c]	1.4(qd)	9.45 [c]	2.88(d) [c]
CH_3	H	74—79	60 [a]	1.65(d)	1.4(qd)	[e]	2.03(d)
CH_3	CH_3	69—71	65	1.46(d)	1.4(qd)	1.92(d)	2.90(d)

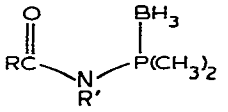
[a] Prepared from lithium salt of acetamide. [b] Downfield from TMS in CH_2Cl_2; all $J(^{31}P—^1H)$ in $P(CH_3)_2$ 11 Hz; $J(^{31}P—^1H)$ in $N(CH_3)$ of formamide 7 Hz for major rotamer, 11 Hz for minor, 11 Hz in N—CH_3 acetamide. [c] Resonance of major rotamer; for minor rotamer see text. [e] Obscured.

tified but the absence of the $P(CH_3)_2$ doublet in the ^1H NMR spectra of these mixtures is clear evidence that the desired compounds were not produced.

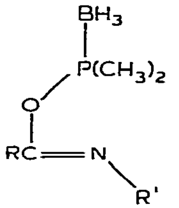
Several attempts to prepare the bis-phosphineborane acetamide, from the reaction of 2 moles of BuLi with 1 mole acetamide followed by reaction with $(CH_3)_2(BH_3)PCl$ and the reaction of $[(CH_3)_2(BH_3)P]_2NLi$ (prepared according to Schmidbaur and Weiss [2]), with acetyl chloride, resulted only in the formation of the mono-$(CH_3)_2(BH_3)P$-substituted acetamide. The attempted conversion of this to the bis derivative via reaction of its lithium salt with $(CH_3)_2(BH_3)PCl$ was also unsuccessful.

The physical and spectral characteristics of the aliphatic amide derivatives are presented in Table 1. All of the compounds are white sublimable solids that contain small amounts of impurity which produced a small multiplet upfield of the $P(CH_3)_2$ doublet in the NMR. This impurity is probably a result of a small amount of impurity CH_3PCl_2 in the commercial $(CH_3)_2PCl$ or the sensitivity of $(CH_3)_2PCl$ to reaction with the atmosphere. Attempts to purify the starting material by distillation and the products by recrystallization were not successful.

The infrared spectrum of each amide contains an intense peak in the characteristic B—H stretching region (ca. 2390 cm^{-1}), a peak in the carbonyl region at 1690—1700 cm^{-1}, but no absorption in the P—O stretching region (1000—1100 cm^{-1}) [6]. The mono-acetamide derivative also contains an NH absorption at 3395 cm^{-1}. The infrared spectra therefore suggest the amide (A) rather than imidate (B) structure for these compounds.



(A)

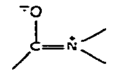
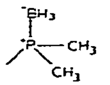


(B)

The NMR spectra contain a doublet (*J* 11 Hz) at 1.4—1.6 ppm for the $P(CH_3)_2$ protons, and a 1/1/1/1 quartet of broad, barely resolved doublets (partly obscured by the impurity mentioned above) centered at ca. 1.4 ppm which can be attributed to the splitting of the BH_3 proton by both phosphorus ($I = 1/2$) and boron-11 ($I = 3/2$). The NMR spectra of the acetamide derivatives also contain doublets (*J* 1 Hz) for the acetyl-methyl group, presumably a result of coupling to ^{31}P.

Below 30°C the spectrum of the N—CH_3 formamide derivative exhibits two doublets for both the $P(CH_3)_2$ and NCH_3 groups with the lower field doublet in each case being considerably less intense (13% of the major doublet). At 35°C the two N—CH_3 doublets coalesce while the $P(CH_3)_2$ doublets with their greater separation (0.39 ppm relative to 0.17 ppm for the NCH_3 doublets measured at 0°C) do not coalesce until 50°C. The formyl proton also appears as two peaks, a broad singlet at 9.5 ppm and a less intense doublet (*J* 9 Hz) at 9.1 ppm. Because both NCH_3 peaks are coupled to the phosphorus both doublets must be a result of $P(CH_3)_2(BH_3)$ groups attached to nitrogen (moreover, the IR spectrum has no peak in the P—O region, vide supra). Therefore, the two sets of resonances for each group are due to rotational isomers of the amide form.

Because the less intense, higher field formyl resonance has the greater coupling to phosphorus, the less populated isomer must have the phosphorus *trans* to the formyl hydrogen. (The greater *trans* coupling across the CON linkage is well documented [7]). The major isomer therefore contains the $P(CH_3)_2(BH_3)$ group *trans* to the carbonyl oxygen which is in agreement with the conformational preferences found for the trimethylsilyl analog [4] and other tertiary formamides [7]. The population of the major isomer (0.85) is very similar to that found for *N*-methyl-*N*-trimethylsilyl formamide (0.87), but the free energies of activation (16.2, 17.3 kcal/mol) as calculated by the method of Shanan-Atidi and Bar-Eli [8], are somewhat lower than those of the trimethylsilyl analog (18.5, 19.8 kcal/mol [4]).

Barriers to rotation in amides are known to be a function of the size and the inductive and resonance effects of the groups attached to nitrogen [7,9]. The barrier-lowering effect of the trimethylsilyl group has previously been attributed to $(p-d)\pi$ interaction between the nitrogen lone pair and the silicon *d*-orbitals in the transition state for the rotational process [4]. The lower barrier of the $P(CH_3)_2(BH_3)$ derivative could be attributed to (a) a greater size of the $P(CH_3)_2$-(BH_3) group relative to the $Si(CH_3)_3$ group, which would destabilize the ground state, (b) a higher effective electronegativity of the phosphorus group which would destabilize the polar resonance structure  or (c) greater $(p-d)\pi$ interaction between nitrogen and phosphorus in the transition state. The similar structural parameters found for the isoelectronic species $[(CH_3)_3Si]_2N^-$ [10] and $[(CH_3)_2(BH_3)P]_2CH^-$ [11] suggest that the size of the two isoelectronic groups may not be very different and consequently the lower barrier is probably not due to the size effect. The lower barrier could be attributed, however, to either the higher effective electronegativity or greater $(p-d)\pi$ interactions in the phosphorus analog that the resonance structure  implies. Although the actual charge distribution in the P—B bond is uncertain, the lower barrier can be most simply attributed to destabilization of the polar amide resonance structure by the more electronegative $P(CH_3)_2(BH_3)$ group.

The absence of additional peaks in the $P(CH_3)_2$ and NCH_3 regions of the NMR spectra of the acetamide derivatives from −60 to 120°C could be ascribed to very low barriers to rotation, accidental equivalence of chemical shifts of the rotamers, or essentially 100% population of one rotamer. Because of similar observations for the trimethylsilyl and other alkyl acetamides and the known barrier to rotation in *N*-methyl-*N*-trimethylsilylacetamide (ca. 15 kcal/mol [4]), the last explanation (100% abundance of one isomer) is probably the most likely.

Acknowledgements

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