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BORON-NITROGEN COMPOUNDS

LX *. THE REACTION OF (2-PYRIDYLAMINO)DIPHENYLBORANE WITH ALDEHYDES AND KETONES

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Summary

(2-Pyridylamino)diphenylborane reacts cleanly with aldehydes or ketones in a 1,2-addition of the 2-pyridylamino and diphenylboryl fragments of the aminoborane across a carbonyl group. The 1 : 1 molar reaction proceeds smoothly and with good yields; the resultant products are stable in air indicating fourfold coordination at the boron. This assumption is also borne out by spectroscopic data.

Introduction

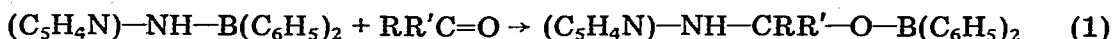
Two preparative routes for the synthesis of (pyridylamino)boranes $(C_5H_4N)NH-BR_2$, have recently been established [1,2] and preliminary studies illustrated the usefulness of these species in aminoboronation reactions, i.e., the addition of the two fragments $(C_5H_4N)NH$ and BR_2 , respectively, across multiple bonds. In the present work a detailed accounting is given for the interaction of (2-pyridylamino)diphenylborane with representative aldehydes and ketones.

One of the features of (2-pyridylamino)diphenylborane is the relative stability of the compound toward hydrolytic attack [2], which is in startling contrast to the behavior of the structurally quite similar (phenylamino)diphenylborane, $(C_6H_5)NH-B(C_6H_5)_2$. It has been reasoned that this increase in hydrolytic stability of the (pyridylamino)borane is due to internal coordination of the pyridine nitrogen with the boron, which event would provide the latter with a fourfold coordination and thus would tend to stabilize the species. It was hoped that a similar situation would hold true for the products of a 1,2-addition of (2-pyridylamino)diphenylborane across a carbonyl group and thus

* For part LIX see ref. 3 and for part LXVIII see ref. 4.

would provide an entrance to a class of organic boron derivatives exhibiting relative inertness to hydrolysis.

In the present work (2-pyridylamino)diphenylborane was reacted with an excess of acetaldehyde, benzaldehyde, acetone and cyclohexanone, respectively. In all cases a 1 : 1 molar interaction was observed, which can be illustrated by the following equation:



Experimental

All reactions and transfers were carried out under an argon atmosphere. Solvents were dried and distilled before use by conventional methods. Melting points (uncorrected) were determined using a Mel-Temp block. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 11377.

Infrared spectra were recorded on KBr discs of the materials using a Perkin-Elmer Model 621 spectrometer employing standard operating conditions. Proton magnetic resonance spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal reference. Boron-11 NMR spectra were recorded at 19.3 MHz on a HA-60IL instrument. Mass spectral data were obtained using a Perkin-Elmer-Hitachi RMU-8 instrument.

(2-Pyridylamino)diphenylborane was prepared according to the previously described procedure [2].

Reaction of (2-pyridylamino)diphenylborane with acetaldehyde (I)

A sample of (2-pyridylamino)diphenylborane (6.53 g, 25.3 mmol) was placed in a 150 ml 3-necked flask filled with argon. The flask was then equipped with a water cooled reflux condenser (10°C). A magnetic stirring bar and 80 ml of freshly distilled acetaldehyde were added. The system was isolated from the atmosphere on one side by a mercury bubbler and on the other side by an argon inlet. A slow passage of argon was maintained throughout the reaction.

Stirring was begun and the mixture was brought to gentle reflux using a heating mantle. After 2 h most of the solid (2-pyridylamino)diphenylborane had dissolved and the solution had turned slightly yellow. Refluxing was maintained for a total of 20 h. After 20 h a large amount of nearly transparent crystals had collected on the sides of the reaction flask. Heating was stopped and the excess acetaldehyde was removed under vacuum (20–30 Torr). The remaining yellowish solid was crushed and slurried with 50 ml of hot heptane and was collected on a glass frit. The solid thus obtained weighed 7.63 g after drying under vacuum (10⁻¹ Torr); the theoretical weight for a 1 : 1 molar interaction is 7.64 g.

The solid was then dissolved in 25 ml of CH₂Cl₂ (dried over P₄O₁₀ and distilled on a vacuum manifold). Heptane was added dropwise (ca. 50 ml) to the clear solution until a turbidity developed. This mixture was allowed to stand for 30 min and a colorless solid precipitated, which was collected by filtration and was washed with 25 ml of heptane. The heptane wash was added to the filtrate. The residue was dried under vacuum (10⁻¹ Torr) and weighed 3.21 g, melting point 168–170°C.

The filtrate was cooled to 0°C with stirring. After several hours a white solid was collected by filtration and weighed 1.64 g after washing and vacuum drying. The melting point and infrared spectrum were identical to the first fraction collected at room temperature. Total yield: 63.3%.

Anal. Found: C, 75.28; H, 6.30; N, 9.30; B, 3.91. $C_{19}H_{19}N_2BO$ calcd.: C, 75.55; H, 6.34; N, 9.27; B, 3.58%.

The highest peak observed in the mass spectrum is at $m/e = 302$ (with a relative intensity of 1.5% as compared to the base peak at $m/e = 78$) corresponding to the parent ion.

Reaction of (2-pyridylamino)diphenylborane with benzaldehyde (II)

A sample of (2-pyridylamino)diphenylborane (5.58 g, 21.6 mmol) and 75 ml of freshly distilled benzaldehyde were reacted in a manner analogous to the synthesis of I. The mixture was heated to 50°C. After 30 min a clear and colorless solution was obtained but heating was maintained for a total of 2 h. After cooling the solution to room temperature the mixture was filtered under argon to remove a small amount of suspended matter. The filtrate was treated with 250 ml of hexane without obtaining a precipitate. The mixture was then cooled to 0°C with vigorous stirring. After 1 h a considerable amount of colorless precipitate had collected and the mixture was filtered under argon. The collected (on a glass frit) solids were washed with two 25 ml portions of hexane. After drying under vacuum (20–30 Torr) the solid weighed 7.26 g (theoretical, 7.86 g for a 1 : 1 molar interaction) and smelled strongly of benzaldehyde. The solid was dried at 55°C, 10^{-1} Torr for 2 h. At the end of this drying the odor of benzaldehyde was gone. The dried sample weighed 6.33 g (80% yield), melting point 154–158°C.

Anal. Found: C, 79.35; H, 5.93; N, 7.68; B, 2.77. $C_{24}H_{21}N_2BO$ calcd.: C, 79.16; H, 5.81; N, 7.68; B, 2.96%.

The highest peak observed in the mass spectrum is at $m/e = 364$ (with a relative intensity of 2.2% as compared to the base peak at $m/e = 78$) corresponding to the parent ion.

Reaction of (2-pyridylamino)diphenylborane with acetone (III)

A sample of (2-pyridylamino)diphenylborane (5.2 g, 20.2 mmol) and 50 ml of reagent grade acetone (dried over anhydrous $MgSO_4$) were reacted in an analogous manner to that described in the synthesis of I. The reaction mixture was heated to gentle reflux. After 30 min the solution was clear and colorless; shortly thereafter a colorless solid began to precipitate. The reaction was stopped after 2 h and the solid was collected by filtration under argon and was washed with two 25 ml portions of hexane. After drying under vacuum (10^{-1} Torr) at room temperature the sample weighed 3.32 g, melting point 189–190°C. The filtrate was evaporated to dryness and an additional crop of 1.87 g of a slightly yellow solid was obtained, melting at 174°C (with decomposition). After recrystallization of the latter from hot acetone 0.40 g of material melting between 187–190°C and exhibiting an infrared spectrum identical to the major fraction was obtained (total yield: 58.4%).

Anal. Found: C, 76.08; H, 6.73; N, 8.76; B, 3.31. $C_{20}H_{21}N_2BO$ calcd.: C, 75.97; H, 6.69; N, 8.86; B, 3.42%.

The highest peak observed in the mass spectrum is at $m/e = 316$ (with a rela-

tive intensity of 3% as compared to the base peak at $m/e = 78$) corresponding to the parent ion.

Reaction of (2-pyridylamino)diphenylborane with cyclohexanone (IV)

A sample of (2-pyridylamino)diphenylborane (4.84 g, 18.8 mmol) and 50 ml of freshly distilled cyclohexanone were combined in a manner analogous to the synthesis of I. This mixture was stirred and was heated to 60°C. The solution was slightly blue-black in color and most of the (2-pyridylamino)diphenylborane was initially insoluble. After a total reaction time of 5 h the solution was almost clear and blue-black in color. The mixture was allowed to cool to room temperature and was filtered to remove suspended matter. Hexane was added (ca. 75 ml) until a precipitate began to form. The mixture was stirred for 30 min at 0°C and was then filtered. Solids were collected on a glass frit under argon and washed with two 25 ml portions of hexane. After drying under vacuum (10^{-1} Torr) for 1 h at room temperature the colorless material weighed 3.43 g, melting point 181–182°C.

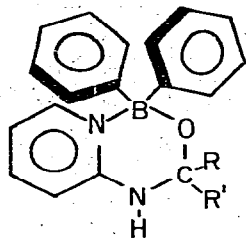
The filtrate was treated with an additional 100 ml of hexane and was cooled to 0°C with stirring for several hours. A colorless precipitate weighing 1.25 g (after washing and drying), melting point 181–183°C, was collected by filtration under argon to give a total yield of 71.5%.

Anal. Found: C, 77.60; H, 7.11; N, 7.61; B, 3.05. $C_{23}H_{25}N_2BO$ calcd.: C, 77.54; H, 7.07; N, 7.85; B, 3.03.

The highest peak observed in the mass spectrum is at $m/e = 356$ (with a relative intensity of 1% as compared to the base peak at $m/e = 279$) corresponding to the parent ion; the base peak corresponds to the parent minus phenyl ion.

Results and discussion

The 1,2-addition of (2-pyridylamino)diphenylborane across the carbonyl group of aldehydes and ketones appears to be a general reaction as is evidenced by the products obtained when the cited aminoborane is reacted with a sampling of aldehydes and ketones. Most likely the resultant materials have the coordinated cyclic structure depicted below:



- I: R = H; R' = CH₃
 II: R = H; R' = C₆H₅
 III: R = R' = CH₃
 IV: R, R' = (CH₂)₅

The 1,2-addition compounds I–IV are slightly soluble in polar organic solvents but are insoluble in water. They appear to be stable when exposed to the atmosphere though no detailed investigation of this feature has yet been undertaken.

The suggested structure involving tetracoordinate boron is based on a variety of data. In the mass spectra of compounds I–IV parent ions are observed in all cases but are of low intensity. The first set of peaks of significant intensity be-

low the parent ion always corresponds to the loss of a phenyl group from the parent ion P. Subsequent fragmentation of the P minus 77 ions seems to follow two major patterns. One is the loss of a HNCRR' moiety to give a set of ions centered at $m/e = 182$ that is readily assigned to the $[(C_5H_4N)B(O)(C_6H_5)]^+$ species. This latter ion is common for the mass spectra of all four addition compounds and thus supports the contention that the 1,2-addition has occurred in the manner indicated in eq. 1, but also that compounds I–IV have, as a structural element, a boron bond to a pyridyl group as illustrated above. This structure involving four-coordinate boron is further substantiated by the fact that compounds I–IV are not readily attacked by moisture; their infrared spectra remain unchanged after exposure of samples to normal laboratory atmosphere for five days and no weight or other changes are observed during that period. An alternate breakdown of the P minus 77 ions involves the loss of a C_6H_5BO fragment whereby the $[(C_5H_4N)NHCRR']^+$ ions are formed. These latter also appear prominently in the mass spectra; their observation supports the assumption that the aminopyridine moiety is kept intact during the 1,2-aminoboration process and thus lends further credence to the reaction as outlined in eq. 1. The suggested major fragmentation pattern is depicted in Fig. 1.

The infrared spectra of the compounds show the NH stretching mode as a sharp singlet of medium intensity within a narrow frequency range ($\nu(NH)$ for I = 3378 cm^{-1} , II = 3376 cm^{-1} , III = 3365 cm^{-1} , IV = 3377 cm^{-1}). This observation disputes a possible four-coordination of the amino-nitrogen. Other features of the infrared spectra include the typical B–phenyl stretching modes near 1440 cm^{-1} and the observation of a fairly intense broad absorption in the $1360\text{--}1380\text{ cm}^{-1}$ frequency range normally considered to be indicative of B–O bonding. However, attempting to present a more detailed assignment of the multi-line spectra of such polyatomic species as I–IV seems to be a vain undertaking.

Proton NMR data on compounds I–IV are summarized in Table I. The single N-bonded proton was not observed in any case but the other data are in reasonably good agreement with the values expected for the proposed structures.

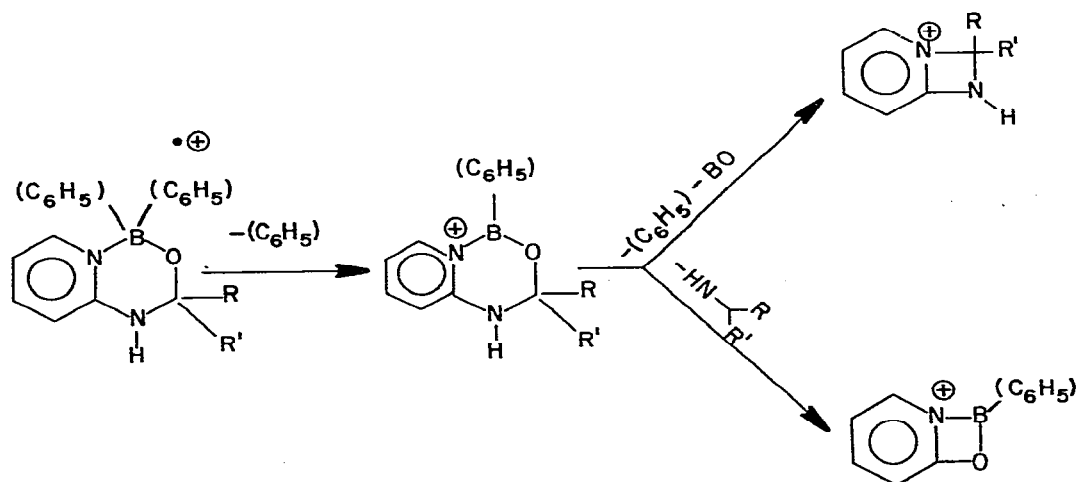


Fig. 1. Suggested major fragmentation pattern of the 1 : 1 reaction products of (2-pyridylamino)diphenylborane with carbonyl compounds.

TABLE I
 PROTON CHEMICAL SHIFT DATA (δ) FOR COMPOUNDS I-IV ^a

Com- pound	Solvent	Aromatic protons		Aliphatic protons	
		δ (ppm)	RI (%)	δ (ppm)	RI (%)
I	acetone- <i>d</i> ₆	8.75 m	16.1	4.88q ^b	1
		7.15 s		1.33d ^b	2.8
II	tetrahydrofuran	7.32 m	18.6	5.85 s	1
		7.20 s			
		6.72 s			
		6.55 s			
		6.45 s			
III	acetone- <i>d</i> ₆	7.75 m		1.30 s	
		7.42 m			
		7.13 m			
		6.52 m			
IV	acetone- <i>d</i> ₆	7.25 m	14.6	1.50 m	10
		7.18 s			

^a TMS as internal reference; abbreviations: RI = relative intensity; s = singlet; m = multiplet; d = doublet; q = quartet. ^b $J(\text{C-H}) = 5.5 \text{ Hz}$.

Boron-11 NMR spectra were obtained on compounds I, II and IV in tetrahydrofuran solution using external $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ as reference. The observed chemical shifts of 1.4 (I), 1.8 (II) and 1.3 (IV) ppm downfield from the reference also support the concept of the presence of tetracoordinated boron in these compounds and thus lend additional credence to the suggested structure.

Acknowledgements

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