Journal of Organometallic Chemistry, 117 (1976) 1—11

BORON—NITROGEN COMPOUNDS

LXI *. STUDIES ON (2-PYRIDYLAMINO)DIPHENYLBORANE AND SOME RELATED SPECIES

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(Received February 27th, 1976)

Summary

(2-Aminopyridine)-triphenylborane, (2-H_2N—C_5H_4N)B(C_6H_5)$_3$, has been prepared from its acid—base pair constituents; pyrolysis of the compound yields *B*-triphenyl-*N*-tris(2-pyridyl)borazine, [—BC_6H_5—N(2-C_5H_4N)—]$_3$. An intermediate in the transamination of (dimethylamino)diphenylborane with 2-aminopyridine to yield (2-pyridylamino)diphenylborane, (2-C_5H_4N)NH—B(C_6H_5)$_2$, has been isolated and was identified to be a 1 : 1 molar adduct of (dimethylamino)diphenylborane with 2-aminopyridine. Somewhat related to this 1 : 1 adduct is a material that is obtained as initial product of the interaction of (2-pyridylamino)diphenylborane with water, which can be formulated as a 1 : 1 : 1 adduct of (2-pyridylamino)diphenylborane, (hydroxy)diphenylborane and 2-aminopyridine; pyrolysis of this species yields (diphenylboryl)(2-pyridylamino-phenylboryl) oxide, (C_6H_5)$_2$B—O—BC_6H_5—NH(2-C_5H_4N), for which a coordinated cyclic structure is suggested. This same diboryl oxide is obtained from the interaction of (2-pyridylamino)diphenylborane with molecular oxygen and also by the reaction of the cited aminoborane with acetophenone via oxygen abstraction from the latter. (2-Pyridylamino)diphenylborane 1,2-aminoboronates one CO double bond of carbon dioxide; this reaction is analogous to the reaction of (2-pyridylamino)diphenylborane with aldehydes or ketones as described previously.

Introduction

(2-Pyridylamino)diphenylborane, (2-C_5H_4N)NH—B(C_6H_5)$_2$, is a rather unique aminoborane species: In contrast to the chemically closely related (phenylamino)diphenylborane the cited (pyridylamino)borane is quite insensitive to atmospher-

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* For part LX see ref. 2.
* NMR values are expressed in δ.

ic moisture at room temperature [1]. This observation has led to the assumption that (2-pyridylamino)diphenylborane contains four-coordinate boron; a structure with internal back-donation from the pyridyl nitrogen to the boron has been suggested for the molecule [1]. Also, (2-pyridylamino)diphenylborane has been used for the 1,2-aminoboronation of the carbonyl group of various aldehydes and ketones and the reaction appears to be of general scope [2]. However, when acetophenone is reacted with (2-pyridylamino)diphenylborane, oxygen is abstracted from the ketone as is outlined below. These and some other observations have prompted the present study of the (2-pyridylamino)diphenylborane molecule and related species.

Results

Several (2-pyridylamino)diorganylboranes, $(2\text{-}C_5H_4N)NH{-}BR_2$, have been prepared by a condensation process [3] (eq. 1) or a transamination procedure [1] (eq. 2) and similar ligand exchange reactions [3].

$$(C_5H_4N)NH_2 + BR_3 \rightarrow (H_2N{-}C_5H_4N)BR_3 \rightarrow RH + (C_5H_4N)NH{-}BR_2 \qquad (1)$$

$$(C_5H_4N)NH_2 + R'_2N{-}BR_2 \rightarrow R'_2NH + (C_5H_4N)NH{-}BR_2 \qquad (2)$$

(2-Pyridylamino)diphenylborane has previously been prepared according to eq. 2 [1] ($R' = CH_3$, $R = C_6H_5$) as well as by a ligand exchange reaction between (ethoxy)diphenylborane and (2-pyridylamino)dibutylborane [3].

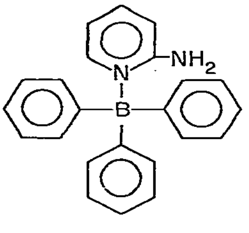
The reaction of 2-aminopyridine with triphenylborane at or near room temperature readily proceeds to yield a 1 : 1 adduct according to the first step of eq. 1. However, pyrolysis of the complex does not proceed in strict accordance with the second step of eq. 1, i.e., stopping at the loss of one benzene molecule. Rather, at the temperature required to decompose the adduct to yield benzene and (2-pyridylamino)diphenylborane, the latter is thermally unstable and decomposes with the formation of *B*-triphenyl-*N*-tris(2-pyridyl)borazine, $[{-}BC_6H_5{-}N(2\text{-}C_5H_4N){-}]_3$. Indeed, under vacuum, pure (2-pyridylamino)diphenylborane is stable only to 134°C; at this temperature the compound evolves benzene with the formation of the cited borazine. Prolonged heating of $(2\text{-}H_2N{-}C_5H_4N)\text{-}B(C_6H_5)_3$ in toluene at only 110°C also produces the cited borazine rather than (2-pyridylamino)diphenylborane.

At room temperature (2-pyridylamino)diphenylborane is not attacked by moisture or oxygen when exposed to the atmosphere for a period of several days [1]. However, in hot THF solution the compound reacts with molecular oxygen to give the species of the composition $(C_6H_5)_2B{-}O{-}B(C_6H_5){-}NH(2\text{-}C_5H_4N)$. This latter compound (which can be viewed as an aminoborane or as a diboryl oxide) is also obtained in another fashion: A THF solution of (2-pyridylamino)-diphenylborane reacts with one half molar equivalent of water near 63°C to yield the double adduct $[2\text{-}H_2N{-}C_5H_4N](C_6H_5)_2B{-}NH(2\text{-}C_5H_4N)[B(OH)\text{-}(C_6H_5)_2]$. The double adduct is thermally stable to 115°C; at this temperature it decomposes with the formation of benzene, 2-aminopyridine, and the diboryl oxide cited above, i.e., $(C_6H_5)_2B{-}O{-}B(C_6H_5)NH(2\text{-}C_5H_4N)$. This latter compound is also formed in formidable quantities when (2-pyridylamino)diphenylborane is reacted with either an excess of acetophenone in the absence of solvent, or with acetophenone in 1 : 1 molar ratio in THF solution. No 1,2-aminoboronation product similar to the ones obtained from the interaction of (2-pyridylamino)diphenylborane with other ketones [2] is observed. On the other hand, (2-pyridylamino)diphenylborane aminoboronates carbon dioxide at elevated temperatures according to eq. 3:

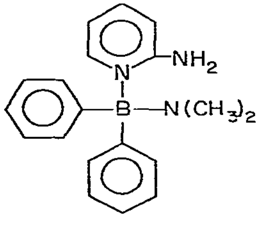
$$(C_5H_4N)NH{-}B(C_6H_5)_2 + CO_2 \rightarrow (C_5H_4N)NH{-}CO{-}O{-}B(C_6H_5)_2 \qquad (3)$$

Discussion

2-Aminopyridine offers two potential donor sites when reacting with a borane to form an amine—borane. The observation of two sharp N—H stretching absorptions at 3451 and 3325 cm^{-1}, respectively, in the infrared spectrum of the complex obtained by the reaction of triphenylborane, $B(C_6H_5)_3$, with 2-aminopyridine suggests that the annular nitrogen serves as donor in the resultant compound. This observation is in agreement with the fact that complexing of 2-aminopyridine with tris(*o*-alkoxyphenyl)boranes [4] also occurs via the annular nitrogen atom of the aminopyridine as is the case for the 1 : 1 adducts obtained from 2-aminopyridine and trialkylboranes [3]. Hence, the adduct of 2-aminopyridine with triphenylborane has to be formulated as (2-aminopyridine)-triphenylborane, $(H_2N{-}C_5H_4N)B(C_6H_5)_3$, I. This structure is also in better agreement with the relatively high thermal stability of the compound than would be a species in which the amino group acts as the donor site.



(I)

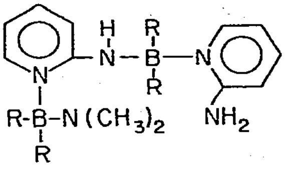


(II)

(2-Aminopyridine)-triphenylborane, $(H_2N{-}C_5H_4N)B(C_6H_5)_3$, is thermally quite stable. When heated under vacuum it sublimes though some decomposition occurs. However, the pyrolysis process leads directly to *B*-triphenyl-*N*-tris(2-pyridyl)borazine, $[{-}BC_6H_5{-}N(2\text{-}C_5H_4N){-}]_3$, and the expected intermediate (2-pyridylamino)diphenylborane, $(C_5H_4N)NH{-}B(C_6H_5)_2$, is not observed. Indeed, the experimental data show that the latter compound is thermally not stable beyond 134°C but decomposes with the formation of benzene and *B*-triphenyl-*N*-tris-(2-pyridyl)borazine.

Occasionally, difficulties are encountered in the preparation of (2-pyridylamino)diphenylborane via the transamination of (dimethylamino)diphenylborane with 2-aminopyridine according to eq. 2 above. Such difficulties are evidenced by low yields or impure products and mostly arise when the reaction mixture is either not heated for a sufficient period of time or the reaction temperature is too low; for a revised procedure see the experimental section. The earlier experimental difficulties may readily be explained by the following.

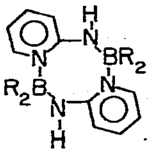
The stronger coordinating ability of the annular nitrogen of 2-aminopyridine as compared to that of the amino nitrogen results in the formation of an initial complex, II, which would be expected to release dimethylamine with the formation of the (2-pyridylamino)diphenylborane. It is possible that once some (2-pyridylamino)diphenylborane is formed, this compound coordinates with additional (dimethylamino)diphenylborane and 2-aminopyridine to give the intermediate III, R = C_6H_5. This requires that II dissociates in hot hexane to some extent to give the original Lewis acid—base pair. Another possibility for the production of III involves the condensation of two molecules of II accompanied by the loss of dimethylamine. However, attempts to isolate III by monitoring the evolution of dimethylamine from a suspension of II in hot hexane were unsuccessful. An infrared spectrum of the reaction mixture recorded after evolution of approximately one half of the theoretical quantity of dimethylamine indicated the presence of only starting material and (2-pyridylamino)diphenylborane.



(III)

Both II and III contain tetracoordinate boron which occurrence would tend to impair a ready progress of the transamination and the experimental data indicate that both species seem to play a significant role in the transamination of (dimethylamino)diphenylborane with 2-aminopyridine. The complex II, of course, has its analogue in (2-aminopyridine)-triphenylborane, I, but, as outlined below, III also has an analogue, V, which was isolated and identified.

(2-Pyridylamino)diphylborane reacts with water in hot THF to form a double adduct $[H_2N—C_5H_4N](C_6H_5)_2B—NH(C_5H_4N)[(OH)B(C_6H_5)_2]$. Even in hot THF this adduct is stable toward further hydrolysis, suggesting the presence of only tetracoordinated boron in the complex. The structure of the adduct is substantiated by the infrared spectrum of the compound. One broad O—H stretching mode is observed at 3483 cm^{-1} and three sharp N—H valence vibrations are recorded at 3409, 3393 and 3379 cm^{-1}, respectively. In conjuction with the hydrolytic stability of (2-pyridylamino)diphenylborane at room temperature, the cited data can be interpreted to suggest the existence of (2-pyridylamino)diphenylborane as a cyclic dimer, IV (R = C_6H_5).

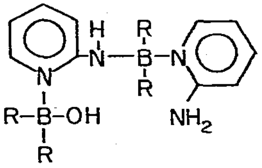


(IV)

An alternate structure would be that of a coordination polymer, $[(2\text{-}C_5H_4N)\text{-}NH—B(C_6H_5)_2]_n$. However, a dimer involving coordination of the amino group to the boron atom of the second moiety can be ruled out. First of all, earlier data

[4] as well as the present work show the annular nitrogen of the pyridylamine to be the stronger donor site. Moreover, the observation of one strong and sharp infrared absorption at 3376 cm^{-1} indicates the amino nitrogen to be three-coordinate in consonance with structure IV.

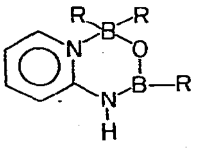
Attack of one H_2O molecule on IV results in cleavage of the eight-membered B—N—C heterocycle to yield V. The open structure of V may well involve less steric strain than is encountered in IV and may thus be responsible for the enhanced hydrolytic stability of V as compared to that of IV.



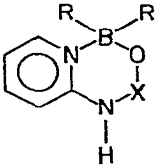
(V)

However, pyrolysis causes a breakdown of V. Benzene is formed and 2-aminopyridine is given off to yield the diboryl oxide $(C_6H_5)_2B—O—B(C_6H_5)—NH(2\text{-}C_5H_4N)$. This species may be formulated as a coordinated heterocycle, VI. The same coordinated heterocycle is formed when oxygen is bubbled through a suspension of (2-pyridylamino)diphenylborane in benzene near 60° C.

Compound VI exhibits a surprising hydrolytic stability even though it contains one trigonal boron atom. Upon exposure of VI to atmospheric moisture, no changes in the infrared spectrum or the melting point of the compound are observed. However, when VI is treated with water in hot THF, some water is absorbed as is evidenced by a weight increase and minor changes in the infrared spectrum of the compound. The shift of ν(NH) of VI from 3411 to 3283 cm^{-1} upon interaction with moisture seems to indicate weak bonding of H_2O at the amino nitrogen site. Indeed, drying of hydrated VI under vacuum at elevated temperatures quantitatively reverts the material to VI. Structure VI is closely related to that of the products described earlier [2] resulting from the interaction of (2-pyridylamino)diphenylborane with aldehydes or ketones (VII, X = CRR′) and also with carbon dioxide (VII, X = CO) as described in the experimental section. These observations seem to suggest a considerable inherent stability for the heterocyclic system VII in which a boron atom is coordinated with the annular pyridine nitrogen.



(VI) R = C_6H_5



(VII) R = C_6H_5

As mentioned above, aldehydes and ketones readily interact with (2-pyridylamino)diphenylborane and the overall process can be described as a 1,2-aminoboronation of a carbonyl group (cf. eq. 3). However, the reaction of (2-pyridylamino)diphenylborane with acetophenone proceeds quite differently and VI is obtained by abstraction of oxygen from the acetophenone as a major product of the reaction. The simultaneous formation of (2-aminopyridine)-triphenylborane suggests that extensive rearrangement reactions occur, but no ready explanation of this observation can be forwarded at the present time.

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, NY.

Infrared spectra were recorded on KBr discs of the materials using a Perkin—Elmer Model 621 spectrometer employing standard operating conditions. Proton nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal reference *. Boron-11 nuclear magnetic resonance spectra were recorded at 19.3 Hz on a HA-60IL instrument using $(C_2H_5)_2O \cdot BF_3$ as external standard. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-8 spectrometer.

(2-Aminopyridine)-triphenylborane (I)

A sample of 2-aminopyridine (11.39 g, 121 mmol) was placed in a 500 ml three-necked flask, equipped with a stirrer, a dropping funnel and an adapter for maintaining an atmosphere of argon. The system was flushed with argon and 100 ml of dry and peroxide free THF were added. To this mixture a slurry of 25.18 g (104 mmol) of triphenylborane in 50 ml of THF was added. A slightly exothermic reaction occured but the temperature did not rise above 35°C. The mixture was stirred for 1 h and THF was removed by water aspirator vacuum. The remaining colorless solid was washed with three 20 ml portions of hexane to remove unreacted 2-aminopyridine. After drying of the residue under vacuum (10^{-1} Torr at 50°C) 32.5 g (97 mmol, 93% yield) of colorless crystals, m.p. 156—158°C, of (2-aminopyridine)triphenylborane were obtained. On heating a mixture of the latter with THF for 3 h no decomposition is observed and the (2-aminopyridine)-triphenylborane is recovered essentially quantitatively.

The ^{11}B NMR spectrum of the compound (in THF) shows a singlet at +2.1 ppm relative to $(C_2H_5)_2O \cdot BF_3$. The ^1H NMR spectrum shows a broad singlet at 5.57 ppm relative to TMS which is assigned to the amino protons; in addition, three sets of aromatic multiplets centered at 6.48, 7.22 and 7.88 ppm are observed. The mass spectrum of the material is consistent with that of a mixture of the free Lewis acid—base pair; no peak corresponding to the parent compound is observed.

Pyrolysis of (2-aminopyridine)-triphenylborane

A sample (4.59 g, 13.6 mmol) of (2-aminopyridine)-triphenylborane was heated to between 145—181°C under vacuum for 1.25 h. A large amount of colorless solid (1.93 g) sublimed above the level of the heating bath and 0.47 g of a liquid was trapped at liquid nitrogen temperature. The sublimate was identified as (2-aminopyridine)-triphenylborane, the liquid as benzene (6.0 mmol). The residue (1.45 g) appeared as a yellowish glass (after cooling to room temperature) and exhibited an infrared spectrum analogous to that of the product of the thermal decomposition of (2-pyridylamino)diphenylborane, which was identified to be *B*-triphenyl-*N*-tris(2-pyridyl)borazine, $[-BC_6H_5-N(2\text{-}C_5H_4N)-]_3$ (see below).

Thermal stability of (2-aminopyridine)-triphenylborane in toluene at 110°C

A sample of (2-aminopyridine)-triphenylborane (4.03 g, 12 mmol) was heated to 110°C in dry toluene for 24 h under an argon atmophere, whereby the initially insoluble material dissolved as the solution was warmed. After cooling to room temperature a colorless solid (1.06 g, 49% yield, m.p. 315—320°C) was obtained and was collected by filtration. This solid exhibits an infrared spectrum identical to that of *B*-triphenyl-*N*-tris(2-pyridyl)borazine.

(2-Pyridylamino)diphenylborane and related species

(2-Aminopyridine)(dimethylamino)diphenylborane (II)

A sample of 2-aminopyridine (13.77 g, 146.5 mmol) was placed in a 500 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser; 250 ml of hexane and 30.50 g (145.9 mmol) of (dimethylamino)diphenylborane [1] were added, dry argon was passed through the system and the mixture was warmed to reflux using an oil bath. After approximately 1 h a clear but slightly yellow solution was obtained, shortly thereafter a colorless sandy-like precipitate was formed. After a total reaction time of 3—4 h the reaction mixture was cooled to room temperature and the precipitate was collected. It was washed with two 25 ml portions of hexane and was dried under vacuum to yield 33.53 g of a material, m.p. 97—100°C.

The infrared spectrum of this material is not identical with that of (2-pyridylamino)diphenylborane and the ^1H NMR spectrum gives evidence for the presence of a $N(CH_3)_2$ group (singlet at 2.14 ppm) besides showing a complex multiplet centered at 7.10 ppm. The data of the elemental analysis substantiate a composition $C_{19}H_{22}N_3B$, indicative of a 1 : 1 molar adduct formed from 2-aminopyridine and (dimethylamino)diphenylborane; structure II is assigned to the material.

Analysis: Found: C, 75.01; H, 7.43; N, 13.65; B, 3.76. $C_{19}H_{22}N_3B$ calcd.: C, 75.27; H, 7.32; N, 13.85; B, 3.57%.

(2-Pyridylamino)diphenylborane

Compound II (29.52 g) was covered with 250 ml of dry hexane and the mixture was refluxed for 48 h with stirring. After cooling to room temperature the colorless solid was collected by filtration, was washed with 50 ml of THF and was dried in vacuum to yield 24.88 g (99%) of (2-pyridylamino)diphenylborane, m.p. 154—156°C, identical (IR, mass spectrum) to the material described previously [1,3].

Thermal stability of (2-pyridylamino)diphenylborane; preparation of B-triphenyl-N-tris(2-pyridyl)borazine

A sample of (2-pyridylamino)diphenylborane (4.62 g, 16.5 mmol) was slowly heated under vacuum. The first increase in pressure was observed at 134°C and the sample was heated to 180°C and was kept at that temperature until the formation of volatile material had ceased (ca. 30 min). The volatile material (condensed at —196° C) was identified as benzene (1.02 g, 13.1 mmol); a small amount of colorless sublimate (0.15 g, 1.6 mmol) was identified as 2-aminopyridine. The residue (3.16 g) was recrystallized from benzene to yield colorless crystals of *B*-triphenyl-*N*-tris(2-pyridyl)borazine, m.p. 315—320° C. This material crystallizes from hot benzene with incorporation of two molecules of benzene per molecule of borazine. This conclusion is based on the elemental analysis of the recrystallized product (see below) and on infrared data. The infrared spectrum of the purified product shows additional absorption bands attributable to benzene which are not observed in the spectrum of the crude *B*-triphenyl-*N*-tris(2-pyridyl)borazine. These bands disappear, however, if the purified material is heated in vacuum above 100°C.

Analysis: Found: C, 77.98, H, 5.69, N 11.88, B, 4.93. $C_{33}H_{27}N_6B_3 \cdot 2C_6H_6$ calcd.: C, 77.63; H, 5.65, N, 12.06, B, 4.66%.

The mass spectrum of the compound shows *m/e* 540 as the highest and base peak of the spectrum, corresponding to the cited borazine.

Reaction of (2-pyridylamino)diphenylborane with molecular oxygen

A sample of (2-pyridylamino)diphenylborane (2.54 g, 9.84 mmol) was reacted with excess oxygen by bubbling the gas through a benzene suspension of the aminoborane at 61—62° C. After 1 h all solid has dissolved and the mixture was dark brown in color. Hexane (ca. 175 ml) was added and a brownish solid precipitated. This solid (0.87 g, ca. 49% yield) is impure (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI). The filtrate contains a complex miture of materials. After removal of the solvent the mass spectrum of the residue shows a very intense peak at *m/e* 196, believed to be due to the loss of a phenyl group from a species $(C_6H_5)_2B—O—NH(NC_5H_4)$, but no pure material could be isolated from the mixture.

Reaction of (2-pyridylamino)diphenylborane with water; formation of (hydroxy)-diphenylborane-(2-pyridylamino)diphenylborane-(2-aminopyridine), V.

A mixture of water (7.8 mmol) and (2-pyridylamino)diphenylborane (4.05 g, 15.7 mmol) in 75 ml of THF (freshly distilled from Na/benzophenone) was heated to 63° C. After 30 min the reaction mixture was clear and colorless but heating was continued for a total period of 2.5 h. Hexane (ca. 150 ml) was added but no precipitate was formed. The mixture was concentrated by vacuum evaporation and a colorless precipitate was collected by filtration, was washed and was dried to yield 3.33 g (79%) of a material, m.p. 143—144° C. The mass spectrum of the material shows the highest peak at *m/e* 346. The fragmentation pattern of this ion corresponds closely to that expected for bis(diphenylboryl)oxide, $(C_6H_5)_2B—O—B(C_6H_5)_2$, calculated parent ion *m/e* 346. However, the elemental analysis data suggest the formulation of the material as a double adduct, V, formed from (2-pyridylamino)diphenylborane with (hydroxy)diphenylborane, $HOB(C_6H_5)_2$, and 2-aminopyridine, in a 1 : 1 : 1 molar ratio.

Analysis: Found: C, 76.22, H, 6.20; N, 10.18; B, 3.98. $C_{34}H_{32}N_4B_2O$ calcd.: C, 76.44; H, 6.04; N, 10.48; B, 4.05%.

The infrared spectrum of this compound clearly shows an O—H valence mode near 3500 cm^{-1} as well as three N—H stretching vibrations in the 3409-3379 cm^{-1}

region; structure V is suggested for the compound, (hydroxy)diphenylborane-(2-pyridylamino)diphenylborane-(2-aminopyridine). The ^{11}B NMR spectrum of the material (in THF) supports this assumption: Only one but broad singlet is observed for the two boron nuclei in similar environment centered at —1.8 ppm.

Pyrolysis of (hydroxy)diphenylborane-(2-pyridylamino)diphenylborane-(2-aminopyridine); formation of (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI)

A sample of V (2.36 g, 4.42 mmol) was pyrolyzed under vacuum. The first increase in pressure was observed at 115°C; the pressure increased rapidly at ca. 125°C. The sample softened at ca. 133°C and was heated to a maximum temperature of 172°C, which was maintained until no additional volatiles were produced (ca. 10 min). The volatile material (condensed at —196°C) was identified as benzene. A colorless solid that sublimed out of the pyrolysis vessel was identified as 2-aminopyridine whereas the non-volatile residue, m.p. 229—233°C, was identified as (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI) formed in essentially quantitative yield as based on boron.

Analysis: Found: C, 76.11; H, 5.90; N, 7.86; B, 5.81. $C_{23}H_{20}N_2B_2O$ calcd.: C, 76.30; H, 5.57; N, 7.73; B, 5.97%.

The ^{1}H NMR spectrum of the material (in $DCCl_3$ with internal TMS as reference) exhibits 4 sets of multiplets between 8.01—6.27 ppm downfield from TMS. The ^{11}B NMR spectrum (in THF) shows the expected two resonance signals. The one observed at —2.8 ppm is assigned to the boron of the diphenylboryl moiety and supports the suggested (see structure VI) four-coordinate environment. The signal for the trigonal boron is observed at —9.9 ppm indicating weak coordination with the solvent. Unfortunately, the compound is not sufficiently soluble in non-coordinating solvents to permit the recording of the spectra in the latter nor to permit the determination of solution molecular weight data.

The mass spectrum of the compound shows the highest *m/e* values in the *m/e* 361 region but in very low intensity; intense peaks appear in the *m/e* 285 region. Exposure of the material to the atmosphere for 24 h does not give any change in the infrared spectrum or the melting point.

Hydrolytic stability of (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI)

A sample of (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (1.30 g, 3.59 mmol) was treated under argon in THF with ca. 10.8 mmol of H_2O at 63°C for 24 h. The solvent was removed by vacuum evaporation and 1.40 g of colorless solid, m.p. 225—230°C, was recovered.

The infrared spectrum of this solid is very similar to that of the starting material, VI, the major difference being a shift in the N—H stretching mode from 3411 to 3283 cm^{-1}; the mass spectrum shows a fragmentation pattern identical to that of the pure compound, VI.

The sample was dried between 100—120°C under vacuum for 1 h. The infrared spectrum of the dried sample is identical to that of the pure starting material.

Reaction of (2-pyridylamino)diphenylborane with acetophenone

Formation of (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI)

A sample of (2-pyridylamino)diphenylborane (6.78 g, 26.3 mmol) and 50 ml of freshly distilled acetophenone were placed in a three-necked flask equipped for reflux and magnetic stirring. The system was isolated from the atmosphere on one side by an argon inlet and on the other side by a mercury bubbler connected to the argon outlet from the top of the reflux condenser. A slow stream of argon was passed through the system during the reaction. The mixture was heated to 60° C for 5 h. During this time the (2-pyridylamino)diphenylborane slowly dissolved and the solution changed from slightly yellow to yellow-orange in color. After cooling to room temperature the solution was filtered under argon to remove a small amount of suspended matter. The filtrate was mixed with 200 ml of hexane but no precipitate was formed; on cooling to 0°C two liquid phases developed. A 25 ml portion of CH_2Cl_2 was added with stirring and the mixture was cooled to —10° C. A colorless solid was formed and after standing for 1 h the mixture was filtered under argon. The solid, m.p. 231—233° C, was collected on a glass frit and after washing with hexane it was dried under vacuum (10^{-1} Torr/50° C) for 1 h (1.54 g, 33% yield). Infrared and mass spectral data show the material to be identical with the (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI) as described above.

The filtrate from the reaction was concentrated by removing the hexane and CH_2Cl_2 under vacuum. The remaining viscous material was vacuum distilled and the distillate was identified as acetophenone; the residue was a sticky yellow oil (4.87 g) which was not investigated further.

Reaction of (2-pyridylamino)diphenylborane with acetophenone in tetrahydrofuran

A mixture of (2-pyridylamino)diphenylborane (4.97 g, 19.3 mmol) and acetophenone (2.47 g, 20.6 mmol) in 50 ml of THF was warmed to gentle reflux. The solution was clear and colorless after one hour but the reaction was continued for a total of 7.5 h. After cooling to room temperature THF was removed under vacuum and a viscous liquid remained. Fractionation of this liquid under vacuum (10^{-2} Torr/60° C) yielded acetophenone (1.9 g, 15.8 mmol) and a viscous yellow residue which was treated with 50 ml of hexane and 10 ml of THF. This solvent mixture extracted the material responsible for the yellow color and a colorless solid remained which was collected by filtration under argon (1.66 g after washing and drying) and was identified as (diphenylboryl)(2-pyridylamino-phenylboryl) oxide (VI) (45% yield). Evaporation of the filtrate gives 3.06 g of a mixture consisting primarily of (2-aminopyridine)-triphenylborane.

Reaction of (2-pyridylamino)diphenylborane with carbon dioxide (VII, $X = CO$)

A sample of (2-pyridylamino)diphenylborane (1.65 g, 6.4 mmol) was reacted with an excess of CO_2 at 65°C in 50 ml of dry benzene by bubbling the gas through the mixture for 23 h. A colorless solid was collected by filtration, was washed with hexane and was dried to give 0.83 g (43% yield) of a material, m.p. 202—203° C, identified as VII, $X = CO$.

Analysis: Found: C, 71.54; H, 4.90; N, 9.36; B, 3.44. $C_{18}H_{15}N_2BO_2$ calcd.: C, 71.56; H, 5.00; N, 9.27; B, 3.58%.

An additional 0.45 g of material (m.p. 219—225° C) can be obtained from the filtrate; it constitutes a mixture of (diphenylboryl)(2-pyridylamino-phenylboryl) oxide and the compound described above. The infrared spectrum of the compound exhibits an intense C=O stretch at 1709 cm^{-1} and a very weak N—H mode at 3395 cm^{-1}.

The mass spectrum of the compound shows a low intensity peak at *m/e* 302, corresponding to the parent ion of a 1 : 1 molar interaction product of (2-pyridylamino)diphenylborane with carbon dioxide. The fragmentation pattern shows the loss of a phenyl group as evidenced by a peak at *m/e* 225. The parent minus phenyl ion then loses a mass of 43 to give a peak at *m/e* 182 thought to correspond to the $(C_6H_5)BO(NC_5H_4)^+$ ion.

The ^{11}B NMR spectrum of the compound (in THF) shows a singlet at —3.0 ppm indicative of tetra-coordinate boron; the ^{1}H NMR spectrum exhibits only a multiplet structure in the aromatic region.

Acknowledgements

This work was supported by the Kentucky Tobacco and Health Research Institute. The authors are also grateful to Reilly Tar and Chemical Corporation, Indianapolis, Indiana, for a generous gift of 2-aminopyridine.

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