Journal of Organometallic Chemistry, 149 (1978) 271—277

BORON—NITROGEN COMPOUNDS

LXXI *. PREPARATION AND PROPERTIES OF (2-PYRIDYLAMINO)DIETHYLBORANE

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(Received October 4th, 1977)

Summary

(2-Pyridylamino)diethylborane has been obtained in good yield and purity by the reaction of triethylborane with 2-aminopyridine in 2/1 molar ratio in the absence of solvent. Carbon-13 NMR data suggest that at room temperature and below the compound exists in at least two forms; only at higher temperatures does the normal aminoborane form become exclusive. Pyrolysis of the compound leads to the formation of *B*-triethyl-*N*-tri-2-pyridylborazine, $[-BC_2H_5-N(2-C_5H_5N)-]_3$.

Introduction

Recent studies involving the aminoboronation of unsaturated organic substrates with (2-pyridylamino)diphenylborane [2,3] and the properties of the cited species [4] have prompted a search for aminoboranes of similar structure but which are more reactive towards small gaseous molecules and exhibit better solubilities in common organic solvents than (2-pyridylamino)diphenylborane. In this context, the preparation of (2-pyridylamino)diethylborane has been studied. Previously [5,6], a synthesis of (2-pyridylamino)dialkylboranes according to equation 1 has been described.

$$C_5H_4N\text{-}2\text{-}NH_2 + BR_3 \rightarrow (2\text{-}C_5H_4N)NH\text{-}BR_2 + RH \quad (1)$$

$R = n\text{-}C_3H_7, n\text{-}C_4H_9, i\text{-}C_4H_9$

However, our attempts to utilize the literature procedure [6] for the preparation of (2-pyridylamino)diethylborane were unsuccessful nor could a pure (2-pyridylamino)di-n-propylborane be obtained. Substantial modifications of the original

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* For part LXX see ref. 1.

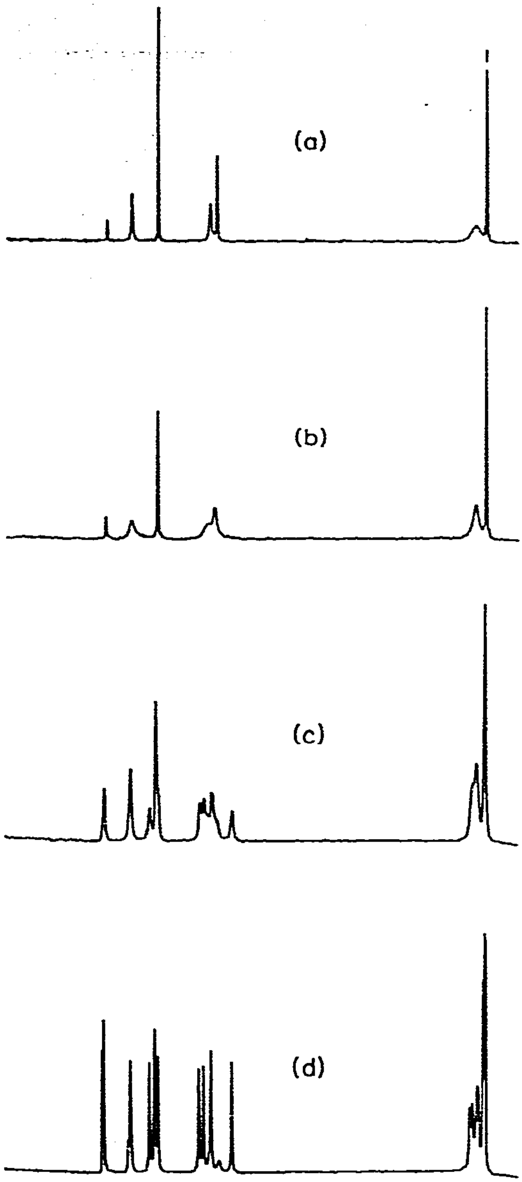
method [6] were required in order to obtain the latter compound in reasonable purity. Utilizing these modifications it is possible to prepare the desired (2-pyridylamino)dialkylboranes.

Results and discussion

The reaction of 2-aminopyridine with a slight stoichiometric excess of tri-n-propylborane in tetrahydrofuran following the literature procedure [6] was found to yield a material having the same infrared spectrum as that reported but mass spectral data indicated a mixture containing but a small amount of (2-pyridylamino)di-n-propylborane and a large quantity of one or more unidentified compounds. However, reaction in the absence of solvent and using a 2/1 molar ratio of trialkylborane and 2-aminopyridine yields (2-pyridylamino)di-n-propylborane as the major product, though even repeated distillation does not give a completely pure material. Utilizing these same modifications triethylborane and 2-aminopyridine give a 73% yield (based on 2-aminopyridine) of (2-pyridylamino)diethylborane.

At room temperature, pure (2-pyridylamino)diorganylboranes seem to exist in complex forms [4,6]. An associated species is reasonably well established for (2-pyridylamino)diphenylborane [4] and intermolecular hydrogen bonding is suggested to prevail for (2-pyridylamino)dialkylboranes [6]. The ambient temperature ^{11}B NMR spectrum of (2-pyridylamino)diethylborane (1/1 solution by volume in cyclohexane) exhibits a strong resonance signal at 48 ± 2 ppm in addition to a second signal near −1 ± 2 ppm. Both values correspond closely to the data reported for the di-n-propyl and di-n-butyl derivatives [6]; the high field signal disappears at elevated temperature. These observations suggest the existence of at least two species at room temperature, one of which contains tetracoordinated boron. The presence of at least two species at room temperature and below is also verified by ^{13}C NMR data.

At ambient temperature and in $CDCl_3$ (1/1 by volume) solution (spectrum b in Fig. 1) the ^{13}C resonance signals of (2-pyridylamino)diethylborane assigned to atoms 6, 5 and 3 of the pyridine ring [7] and which are observed at 147.0, 116.7 and 114.4 ppm, respectively, are unusually broad and suggest a complex system that is observable on the ^{13}C NMR time scale. Previous work has shown that high-temperature recording of ^{13}C NMR spectra of organoboron compounds is a useful technique for resolving multiplet resonance signals that are collapsed in ambient temperature spectra [8]. Indeed, a broadening of the resonance signal of the boron-attached carbon atoms of (2-pyridylamino)diethylborane at 12.5 ppm is observed on recording of the ^{13}C NMR spectrum of the compound at 52°C (spectrum a in Fig. 1). On the other hand, low-temperature recording of organoboron compounds has been shown to result in the loss of fine structure but the intensity of signals not observable at ambient temperature may be increased sufficiently in order to be recognized [8]. However, on recording the ^{13}C NMR spectrum of (2-pyridylamino)diethylborane at lower than ambient temperature (spectra c and d in Fig. 1), the exact opposite is observed. Instead of the expected (for a pure monomeric species) sharpening of the resonance signals of the boron-bonded carbon atoms a multiplet structure is appearing. Concomitant with this process the singlet of the CH_3 carbon atoms of the boron-



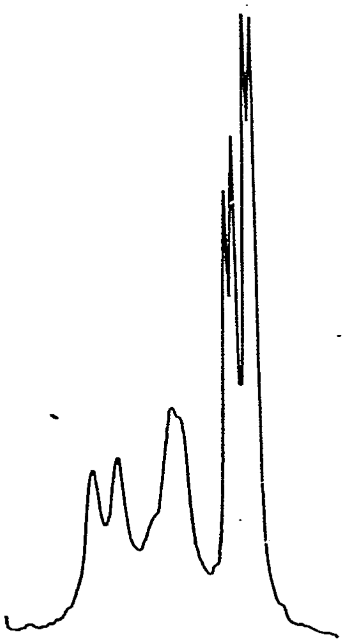


Fig. 1. The ^{13}C NMR spectrum of (2-pyridylamino)diethylborane at various temperatures: (a) = +52°C; (b) = +30°C; (c) = +5°C; (d) = −25°C.

Fig. 2. The ^{13}C resonance signals of the boron-bonded ethyl groups of (2-pyridylamino)diethylborane at −25°C.

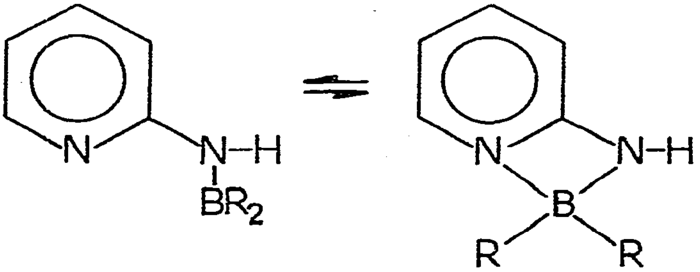
bonded ethyl groups (δ 8.00 ppm at +52°C) splits into a doublet of doublets as is illustrated in Fig. 2, and the signals of the pyridyl carbon atoms separate into two groups of signals each representing five carbon atoms. Since the depicted spectra are proton-noise decoupled and the ^{11}B quadrupole coupling has been shown to become thermally decoupled, the additional peaks that are observed in the low-temperature spectra must be due to the observation of non-equivalent carbon atoms. This can occur either through intermolecular association or by low-temperature enhancement of a second monomeric species that is less favored at elevated temperatures.

The ^{13}C NMR spectra of solutions of (2-pyridylamino)diethylborane in $CDCl_3$ or hexadeuterobenzene show no dependency on the concentration over a range of approximately 5 to 50% by weight. Rather, all spectra correspond closely to the features as illustrated in Fig. 1. (Note: The low-concentration spectra are, however, of relatively poor quality). Furthermore, cryoscopic molecular weight determinations on an approximately 9×10^{-3} molal solution of (2-pyridylamino)-diethylborane in benzene suggest that at the freezing point of the solution only a monomeric species with a molecular weight of about 167 (calculated for the monomeric compound: 162) is present. These data tend to suggest that intramolecular processes are responsible for the unusual spectroscopic behavior as described above.

The infrared spectrum of neat (2-pyridylamino)diethylborane (recorded at room temperature) exhibits a strong band at 1641 cm^{-1}. Analogous absorptions in the spectra of (2-pyridylamino)dialkylboranes were assigned to an associated species since they disappear on recording of the spectra at elevated temperatures [6]. On the other hand, a band of similar shape and intensity is observed in a wide variety of 2-aminopyridine derivatives, e.g., $[-BC_6H_5-N(2\text{-}C_5H_4N)-]_3$ (1626 cm^{-1}), $(C_6H_5)_2B-O-BC_6H_5-NH-(2\text{-}C_5H_4N)$ (1631 cm^{-1}), $(C_6H_5)_2B-O-CHCH_3-NH-(2\text{-}C_5H_4N)$ (1638 cm^{-1}), and $[-BC_2H_5-N(2\text{-}C_5H_4N)-]_3$ (1632 cm^{-1}), where intermolecular association appears to be unlikely. Moreover, the NH stretching region of the spectra of (2-pyridylamino)dialkylboranes features more than one absorption. Finally, the UV spectrum of (2-pyridylamino)-diethylborane (ca. 10^{-5} *M* solution in cyclohexane) exhibits absorption maxima at 233 and 290 nm; the spectrum is very similar to that of 2-aminopyridine in methanol (maxima at 234 and 296 nm).

Summarizing the present experimental data on (2-pyridylamino)diethylborane and the earlier work [6] on additional (2-pyridylamino)dialkylboranes, the following conclusions can be reached: Except where steric factors seem to become important, (2-pyridylamino)dialkylboranes exist in more than one species at room temperature and below. One of the species contains tetracoordinate boron but the species with boron in trigonal environment is more abundant and becomes exclusive at elevated temperatures. The data also suggest that only monomeric species are involved.

These observations find a reasonable explanation by assuming intramolecular rearrangement of a monomeric species as is indicated by structures I and II.



(I) (II)

Structure II resembles the dimeric aminoboranes, $(R_2NBR'_2)_2$, where dimerization has been linked to a strongly basic nitrogen [9]. Since the pyridyl nitrogen of 2-aminopyridine is the stronger donor site [10] the formation of an intramolecular donor—acceptor bond in the (2-pyridylamino)dialkylboranes as illustrated in II would not be surprising. Moreover, it has been shown that the tendency of aminoboranes to dimerize is strongly influenced by steric factors, which can become even more significant than inductive or mesomeric effects [11]. This would closely parallel the observations made for the (2-pyridylamino)-dialkylboranes. One of the major differences between the latter and the dimeric aminoboranes is the four-coordination of all annular atoms in $(R_2NBR'_2)_2$ species. On the other hand, the four-membered ring system $(—NR—BR'—)_2$ containing only trigonal annular atoms is also well known [12] and II would seem to fall in between the two series of four-membered ring systems containing only annular boron and nitrogen.

As is expected for an aminoborane derived from a primary amine, the pyrolysis of (2-pyridylamino)diethylborane yields *B*-triethyl-*N*-tri-(2-pyridyl)borazine with the elimination of ethane.

Experimental

All reactions and transfers were carried out under an argon atmosphere. Solvents were dried by conventional methods and distilled before use. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 11377.

Infrared spectra were recorded on the neat materials using a Perkin—Elmer Model 621 spectrometer employing standard operating conditions. Mass spectral data were obtained on a Perkin—Elmer-Hitachi RMU-7 spectrometer. A Varian CFT-20 NMR spectrometer was used to obtain the ^{13}C NMR data; all spectra were recorded using identical instrument setting. ^1H NMR spectra were recorded on a Varian T-60 instrument and ^{11}B NMR spectra were recorded on a Varian HA-100 spectrometer at ambient temperature. All chemical shift data are reported in ppm with positive values indicating downfield from the reference.

2-Aminopyridine was obtained from Reilly Tar and Chemical Corporation, Indianapolis, Indiana; triethylborane and tri-n-propylborane were purchased from Callery Chemical Co., Callery, Pennsylvania.

Reaction of triethylborane in a 2/1 molar ratio with 2-aminopyridine in the absence of solvent; preparation of (2-pyridylamino)diethylborane

A sample of 2-aminopyridine (17.17 g, 182.5 mmol) was placed in a three-neck 150 ml flask and 35.76 g (265.0 mmol) of triethylborane was added over a 20 minute interval through a pressure-compensating addition funnel. The flask contents slowly liquified during the addition of the trialkylborane and stirring was begun as soon as possible. Subsequently, the temperature was raised slowly by use of an oil-bath until gas evolution became rapid (65°C) and a temperature of 65 to 70°C was maintained until gas evolution ceased abruptiy (approximately 2.5 h, 80% of ethane collected). After cooling the reaction mixture to about 40°C excess triethylborane was removed under reduced pressure. The residue was distilled at 5×10^{-2} Torr to give 21.26 g of a fraction boiling from 57 to

61°C (corresponding to a 72% yield of (2-pyridylamino)diethylborane based on 2-aminopyridine).

Analysis: Found: C, 66.47; H, 9.37; B, 6.50; N, 17.06. $C_9H_{15}N_2B$ calcd.: C, 66.70; H, 9.33; B, 6.67; N, 17.28%.

The ^1H NMR spectrum of the compound in C_6D_6 (TMS as internal reference) exhibits several broad bands in the aromatic region with maxima at 8.06, 7.03, 6.93, 6.47 and 5.87 ppm, and a broad singlet for the ethyl protons at 0.92 ppm (downfield from TMS) with relative intensities of 1/1.9 (calcd.: 1/2). The infrared spectrum (neat liquid, NaCl plates) shows absorptions (frequencies in cm^{-1}) at 3420(sh), 3408w, 3384w, 3276w, 3244vw, 3059vw, 3024vw, 2954vs, 2911s, 2874s, 2835w, 1641vs, 1602m, 1595(sh), 1577s, 1570m, 1532vs, 1497s, 1462(sh), 1448m, 1427vs, 1390vs, 1366w, 1354w, 1327m, 1313m, 1275m, 1242m, 1209vs, 1165w, 1140(sh), 1093m, 1067m, 1050m, 1032w, 995vw, 932w, 920w, 870w, 855(sh), 837w, 787m, 763m, 747m.

The mass spectrum of the compound obtained at 15 and 70 eV shows a parent ion at *m/e* 162 and the ready loss of an ethyl group to give the base peak at *m/e* 133.

Pyrolysis of (2-pyridylamino)diethylborane

A sample of the (2-pyridylamino)diethylborane (6.00 g, 37 mmol) was heated under vacuum (10^{-1} Torr) and refluxed without noticeable decomposition at an oil-bath temperature of 100°C. The system was then filled with argon and the temperature of the heating bath was increased to 150°C at which setting gas evolution became noticeable; it became rapid at a bath temperature of 180°C. Further heating to a final bath temperature of 230°C resulted in the formation of approximately 23.5 mmol of ethane after 2 h. The remaining glassy solid was recrystallized from methylene chloride/hexane to give 1.2 g of yellowish air-sensitive needles, melting point 85 to 87°C. The mass spectrum of this product showed a parent peak at *m/e* 396 as calculated for *B*-triethyl-*N*-tri-2-pyridylborazine. Ready loss of an ethyl group gives a peak at *m/e* 367 and the base peak of the spectrum is observed at *m/e* 265. Proton NMR and infrared data indicated that the recrystallized product is contaminated with an impurity containing NH bonds.

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 and to Professor H. Nöth, University of Munich, Germany, for the recording of ^{11}B NMR spectra.

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