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CONVERSION OF TRIS(ISOPROPYLAMINO)BORANE TO POLYBORAZINES. THERMAL DEGRADATION TO BORON NITRIDE

F. GUILHON,* B. BONNETOT, D. CORNU and H. MONGEOT

Laboratoire de Physicochimie Minérale Ib, Université Claude Bernard Lyon I,
43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France

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Abstract—Thermolysis of tris(isopropylamino)borane (**1**) and its reaction with ammonia were investigated. Compound **1** exhibited good thermal stability resulting in almost complete evaporation during its thermogravimetric analysis under Ar up to 1000°C. Refluxing of **1** for 42 h at 250°C produced its conversion into the expected *B,B′,B″*-tris(isopropylamino)-*N,N′,N″*-triisopropylborazine (**2**), and into the new intermediate $[(NHPr^i)_2B]_2NPr^i$ (**3**), both found in low concentrations. Reaction of **1** with ammonia at room temperature resulted in spontaneous transamination, cyclization and polycondensation reactions leading first to *B,B′,B″*-tris(isopropylamino)borazine (**4**), and subsequently to polyborazines. In spite of the high carbon content of **1**, its pyrolysis at 1000°C under NH_3 led to the formation of boron nitride containing less than 1% carbon.

Boron nitride is a well known, technologically important non-oxide ceramic which is primarily found in a hexagonal crystalline modification, *h*-BN, that resembles graphite. Whilst it is easily obtained in powder form from the pyrolysis of simple inexpensive reagents more difficulties are encountered in producing fibres, films and foams. These forms are accessible by an alternative route, which is the pyrolysis of polymers that contain boron and nitrogen.[1] The polymer precursors that have attracted the greatest interest are the borazine derivatives that were expected to lead to borazine backbone polymers. Paine and Sneddon[2] recently published a review on these interesting boron nitride precursors: borazine rings can be joined by either B—B or B—N linkages (polyphenylene analogues) or by NR or NH bridge groups. Borazine rings can also be pendant groups of the polymer. We were interested in the second type of polymer. Early work on this chemistry[3-6] showed that NH or NR bridge formation requires the presence of NH_2 or NHR groups on the boron atoms of monomeric borazine derivatives. Narula *et al.*[7] and later Kimura *et al.*,[8] in order to favour polycondensation reactions and to obtain carbon-free sources of BN, studied the aminolysis of $(NMe_2BNH)_3$ and $(NEt_2BNH)_3$. Replacement of NR_2 groups by NH_2 led to the formation of monomeric or polymeric species with low carbon content and finally afforded excellent boron nitride precursors.

In previous work we demonstrated $B(NHMe)_3$ to be a very interesting product for the preparation of borazine based polymers.[9] It was converted by simple heating, first to $(NHMeBNMe)_3$ and then to a viscous polymer by polycondensation reactions with the formation of NMe bridge groups. Finally, it proved to be an easy to process precursor for the formation of boron nitride matrices and coatings.[10]

In the present work we studied the pyrolysis chemistry of hindered tris(isopropylamino)borane. Bulky isopropyl groups were expected to be more stable with respect to cyclization and polycondensation reactions. The initial steps of aminoborane thermolysis were then monitored by ^{11}B, ^1H and ^{13}C NMR spectroscopy. In order to find a simpler route to polymers with low carbon contents, we have also investigated the aminolysis of $B(NHPr^i)_3$, at room temperature. Poly-

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* Author to whom correspondence should be addressed.

merization mechanisms involved were determined both by NMR and IR spectroscopic studies. Finally, a thermogravimetric analysis and a bulk pyrolysis of $B(NHPr^i)_3$ under NH_3 up to 1000°C were performed.

EXPERIMENTAL

Materials and methods

Standard inert-atmosphere techniques were used in the synthesis and manipulations. All products were manipulated in an efficient dry-box. Solvents were all dried on activated molecular sieves (Merck 4 Å) before being used. NMR spectra were obtained with a Brüker AM 300 spectrometer at 96.28 MHz for ^{11}B with $Et_2O \cdot BF_3$ as an external reference (positive values downfield) and using CCl_4 solution. They were obtained at 300 MHz for ^1H and 75 MHz for ^{13}C in $CDCl_3$ solution with TMS as internal reference, or in CCl_4 solution with C_6D_6 as external reference. Abbreviations used in NMR are: s = singlet; d = doublet; h = heptet; m = unresolved multiplet, b = broad, sh = shoulder. The infrared spectra were obtained as Nujol or poly(chlorotrifluoroethylene) oil mulls in a hermetic cell with CsI windows on a Perkin–Elmer 840 spectrometer. Abbreviations used in IR are: s = strong, m = medium, w = weak. Thermogravimetric analyses were performed on a Setaram model B70 instrument. Electron impact (EI) mass spectral data (70 eV) were obtained on a Fisons model 70E spectrometer under standard operating conditions. Elemental analyses were obtained from the Service Central d'Analyse CNRS-Vernaison.

Preparation of $B(NHPr^i)_3$

Isopropylamine (Aldrich, neat, 99% purity) and N 25 boron trichloride (Alphagaz) were used as received. In a typical experiment a solution of BCl_3 (73.7 g, 0.63 mol) in pentane (150 cm^3) was added dropwise to a stirred and cooled (−80°C) solution of isopropylamine (228.2 g, 3.86 mol) in pentane (350 cm^3) in a 2-l reaction flask. The reaction was highly exothermic and large amounts of a white solid (isopropylamine hydrochloride) precipitated from the transparent solution. This mixture was allowed to warm up, then was filtered and the white solid was washed with 500 cm^3 of pentane. Pentane was removed from the filtrate and 50.6 g (yield, 43.7%) of **1** containing about 2% (molar) of *B,B′,B″*-tris(isopropylamino)-*N,N′,N″*-triisopropylborazine, (**2**) was collected. This crude product was the starting material for subsequent experiments. $B(NHPr^i)_3$: NMR data (CCl_4, δ/ppm): ^{11}B: 22.4 (lit. 22.4[11] in C_6H_6; 23.3[12] in C_6H_6); ^1H: 1.26 (d, $J_{HCCH} = 6.3$ Hz, CH_3), 1.53 (bd, $J_{HCNH} = 9.7$ Hz, NH), 3.24 (m, CH) [lit.[12]: 1.04 (d, $J_{HCCH} = 6.1$ Hz, CH_3), 1.31 (d, $J_{HCNH} = 9.7$ Hz, NH), 3.05 (CH), in CCl_4]; ^{13}C: 27.47 (CH_3), 42.04 (CH).

Pyrolysis of $B(NHPr^i)_3$

In a one-necked flask equipped with a reflux condenser, 5 g (27 mmol) of **1** were heated for 20 h at 120°C and then refluxed for 42 h at 250°C. The flask was evacuated (100 mmHg) to remove the volatile monoisopropylamine formed. The composition of the mixture was monitored by ^{13}C, ^1H and ^{11}B NMR spectroscopy. After partial removal of unreacted **1** by vacuum evaporation (22°C, 10^{-2} mmHg), the lighter species were tentatively distilled: the brown viscous mixture was heated at 100°C under 10^{-3} mmHg pressure, volatiles being condensed under cooling with liquid nitrogen. Both the residue and the condensate were studied by NMR spectroscopy. The ^{11}B NMR spectrum of the condensate is shown in Fig. 1. $(NHPr^iBNPr^i)_3$ and the reaction intermediate, $[(NHPr^i)_2B]_2NPr^i$, appeared to be the main compounds formed. Corresponding mass spectroscopic data showed the presence of **2**: the M^+ ion was detected [*m*/*z* (rel. int.), 378(3)]. The expected isotope pattern was observed, but neither **1** nor **3** could be positively detected owing to the complexity of the spectrum.

$(NHPr^iBNPr^i)_3$ (**2**): NMR data (CCl_4, δ/ppm): ^{11}B: 28.0; ^{13}C: 25.96 (CH_3(cyclic)), 27.87 (CH_3 (amino)), 45.99 (CH(cyclic)), 43.87 (CH(amino)); ^1H: 1.41 (d, $J_{HCCH} = 6.8$ Hz, CH_3(cyclic)), 1.30 (d, $J_{HCCH} = 6.2$ Hz, CH_3(amino)), 2.14 (bd, $J_{HCNH} = 10.8$ Hz, NH), 3.67, (h, CH(cyclic)), 3.58 (m, CH(amino)).

$[(NHPr^i)_2B]_2NPr^i$ (**3**): NMR data (CCl_4 δ/ppm): ^{11}B: 25.6; ^{13}C: 27.49 (CH_3(amino)), 42.60 (CH(amino)), 25.94 (CH_3(bridge)), 45.89 (CH(bridge)); ^1H: 1.23 (d, $J_{HCCH} = 6.3$ Hz, CH_3(amino)), 1.87 (d, $J_{HCNH} = 10.1$ Hz, NH), 3.45 (m, CH(amino)).

The thermogravimetric analysis of **1** (150 mg) under Ar (0.1 l min^{-1}, 0.5°C min^{-1}) up to 1000°C showed a significant weight loss (89%) over the first 300°C. The gas evolution was complete below 600°C (93% weight loss). The black, powdered residue obtained was in too small an amount to carry out any chemical analysis.

Reaction of B-*trichloroborazine with monoisopropylamine and triethylamine*

B-Trichloroborazine was prepared by the hot-tube method of Brown and Laubengayer[13] by reacting BCl_3 with NH_4Cl. It was purified by sublimation

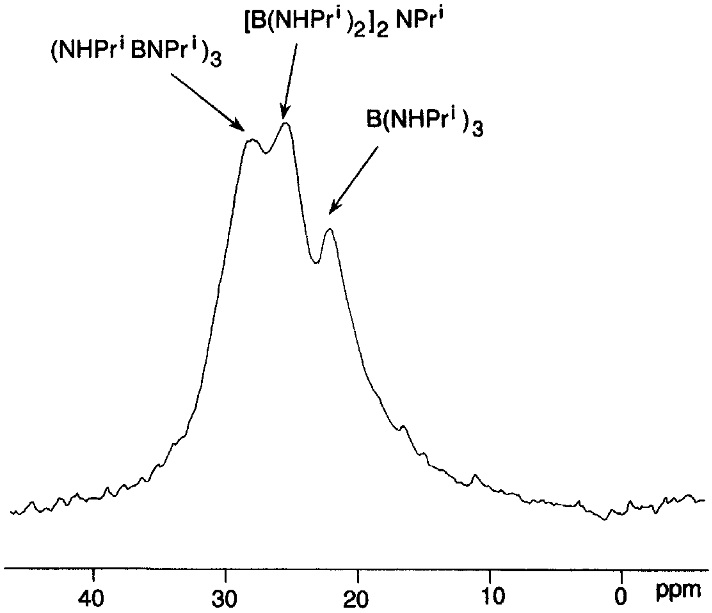


Fig. 1. ^{11}B NMR spectrum of the distillate of the mixture obtained by pyrolysis of B(NHPr^i)$_3$.

in vacuo. To a stirred solution of *B*-trichloroborazine (1.28 g, 6.9 mmol) in toluene (40 cm^3), a solution of monoisopropylamine (1.465 g, 24 mmol) and triethylamine (2.47 g, 24.4 mmol) in toluene (40 cm^3) was added dropwise, at room temperature. A white solid (1.35 g) rapidly precipitated which was filtered off and evaporated to dryness. It was identified by IR spectroscopy as triethylamine hydrochloride, its spectrum being in line with the one from the literature. After evaporation of the obtained solution (1.5 mmHg), 1.5 g (85.7% yield) of a viscous clear yellow liquid was recovered. According to its ^{11}B, ^{1}H and ^{13}C NMR spectra it was indentified as the expected *B,B′,B″*-tris (isopropylamino)borazine containing traces of the corresponding dimer, [$N_3H_3B_3$(NHPr^i)$_2$]$_2$NPr^i. Due to the NHPr^i substituent effect a broad singlet rather than a doublet[14] was observed for the proton bonded to the nitrogen of the borazine ring.

(NHPr^{i}BNH)$_3$ (**4**): NMR data (δ/ppm): ^{11}B: 25.11 (toluene), 25.01 (CCl_4); ^{1}H (CCl_4): 3.32 (m, CH), 2.57 (NH(borazine)), 1.74 (d, $J_{\mathrm{HNCH}} = 9.8$ Hz, NH), 1.25 (d, $J_{\mathrm{HCCH}} = 6.32$ Hz, CH_3); ^{13}C (CCl_4): 42.26 (CH), 27.36 (CH_3). Mass spectrum: Calc. for $[M-CH_3]^+$ *m*/*z* 235 (16), 236 (67), 237 (100), 238 (20); Obsd *m*/*z* 235 (18), 236 (70), 237 (100), 238 (10).

[$N_3H_3B_3$(NHPr^i)$_2$]$_2$NPr^i could be detected but was not fully characterized because of its small concentration: NMR data (CCl_4, δ/ppm): ^{1}H: 3.32 (m, CH), 3.09 (1 = 1, NH(borazine)), 2.76 (1 = 2, NH(borazine)), 1.88 (d, $J_{\mathrm{HNCH}} = 9.9$ Hz, NH(amino)), 1.41 (d, $J_{\mathrm{HCCH}} = 6.25$ Hz, CH_3(bridge)), 1.24 (d, $J_{\mathrm{HCCH}} = 6.28$ Hz, CH_3(amino)); ^{13}C: 42.01 (CH(amino)), 27.24 (CH_3(amino)), 24.87 (CH_3(bridge)). Mass spectroscopic data also suggested the presence of the dimer. The two largest peaks of the isotopic distributions corresponding to the ions $[M]^+$ and $[M-CH_3]^+$ were detected: *m*/*z* (rel. int.), $[M]^+$ 444 (0.5), $[M-CH_3]^+$ 429 (0.1).

The IR spectrum of **4** presented the prominent bands that are characteristic of *B,B′,B″*-tris (dialkylamino)borazines.[15,16] IR (cm^{-1}): 3420w, 3440sh (νNH); 2968s, 2937w, 2873w (νCH); 1507vs, 1465sh (νBN, CH_3 asym. deformation); 1382-1365w(d) (*gem*-dimethyl doublet); 1193s (NH in-plane deformation); 1123w (νCN); 696–686w(d) (BN out-of-plane deformation); 607w, (asymmetric BN side-chain deformation). As observed by Gerrard *et al.*,[15] the νCN band was shifted to lower frequencies ($\Delta\nu = 39$ cm^{-1}) compared to that found for the parent amine.

Aminolysis of B(NHPr^i)$_3$

Compound **1** (3.96 g, (21.4 mmol) was introduced into a 100-cm^3 reaction flask. After cooling with liquid nitrogen, NH_3 (291 cm^3 under 680 mmHg pressure, 10.7 mmol) was condensed into the flask. The mixture was allowed to warm to room temperature and was vigorously stirred as soon as it started to melt. Volatiles were successively condensed and allowed to warm three times to give, finally, a slightly white mobile liquid. The low viscosity was caused by the presence of monoisopropylamine. After its removal at reduced pressure a viscous product was obtained (sample **a**). This procedure was repeated twice with the same amount of NH_3 (samples **b** and **c**) finally leaving a very viscous, white residue. According to IR spectroscopic analysis, monoisopropylamine was the only volatile product formed. Composition of the mixture was monitored by IR (see Fig. 2) and NMR spectroscopy. Analytical results for sample **c**: B, 14.0; N, 34.1; H, 10.1; C, 40.8%.

TGA of **1** were recorded: a 150 mg sample was maintained for 2 h at room temperature (isotherm at 25°C) in a stream of nitrogen (0.1 l min^{-1}) which was then replaced by an ammonia flow. Under nitrogen atmosphere a weak constant weight loss was observed due to vaporization of **1** (2% per hour). Replacing nitrogen by ammonia (0.1 l min^{-1}) resulted in a rapid weight loss reaching a maximum of 39.5% in 35 min. A second sample was slowly heated (1°C min^{-1}) up to 1000°C under ammonia (0.1 l min^{-1}). The thermogram showed that the weight loss was initially rapid (42.0% in 40 min) and then continued at a decreasing rate to reach a maximum of 85%. This treatment led to the formation of a white powdered residue whose infrared spectrum showed a strong broad absorption centred at 1408 cm^{-1} and a sharp weak band at 810 cm^{-1}, both typical of boron nitride.[1] The presence of residual N—H and C—H bonds was revealed, respectively, by a weak band at 3430 cm^{-1} and three weak sharp bands in the 2900 cm^{-1} region. Furthermore, the XRD spectrum displayed two broad diffractions centred at $2\theta = 24.9°$ and $2\theta = 42.5°$ usually obtained with boron nitride of low crystallinity.[17]

Aminolysis of B,B′,B″-*tris(isopropylamino)*-N,N′,N″-*triisopropylborazine* (**2**)

Following exactly the same procedure as before the aminolysis of the distillation residue (about 2 g of a mixture containing mainly **2**) previously obtained by pyrolysis of **1** was undertaken with 10.7 mmol of ammonia (291 cm^3 under 680 mmHg pressure). A spontaneous reaction occurred below 0°C and monoisopropyalmine was characterized by IR spectroscopy as the unique volatile product formed. After removal of Pr^iNH_2 at reduced pressure a dark brown viscous residue was collected and studied by IR and NMR spectroscopy. *B,B′,B″*-Triamino-*N,N′,N″*-triisopropylborazine was one of the main compounds formed. Polymeric species were also present in the mixture according to the numerous signals in the NMR spectra. The IR spectrum presented the prominent bands that are characteristic of homologous *B,B′,B″*-triamino-

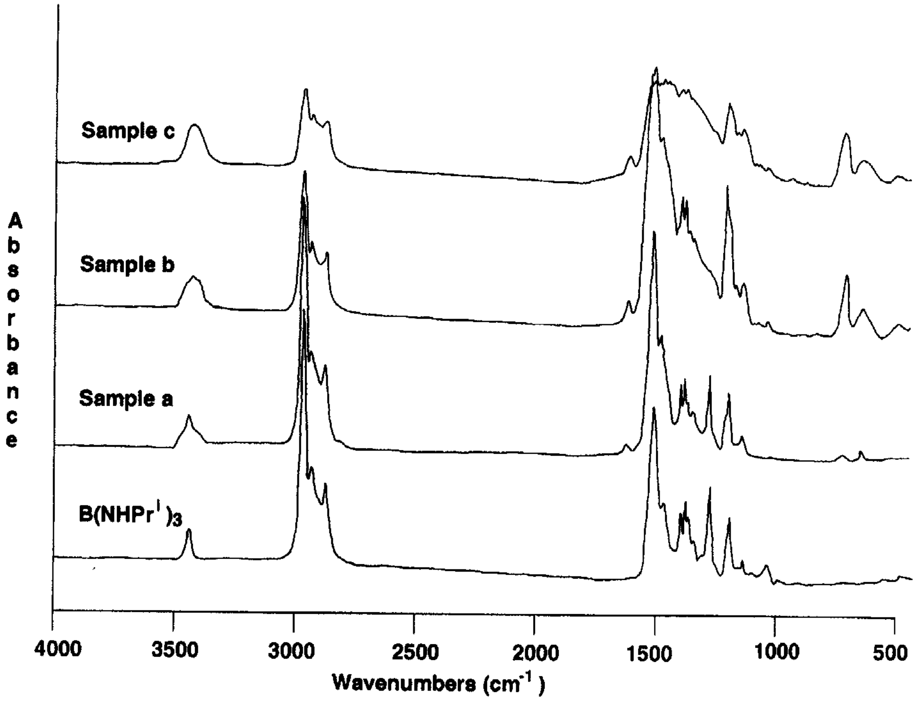


Fig. 2. Infrared spectra of B(NHPr^i)$_3$ and of its reaction products with NH_3. **a**: 21.4 mmol of **1** with 10.7 mmol of NH_3, **b**: 21.4 mmol of **1** with 21.4 mmol of NH_3, **c**: 21.4 mmol of **1** with 32.1 mmol of NH_3.

N,N′,N″-trimethylborazine.[18,19] IR (cm^{-1}) : 3552w (νNH asym., lit.: 3540), 3470w (νNH sym., lit.: 3460), 1608s, sharp (NH_2 deformation mode, lit.: 1608), 1183m, sharp (N–Pr^i; lit.: 1154 for N–CH_3), 715–710w doublet (BN ring deformation, lit.: 710–698). In both cases no band was observed in the 600 cm^{-1} region which would be expected for the BN side-chain deformation mode.

$(NH_2BNPr^i)_3$: NMR (CCl_4, δ/ppm) : ^{11}B : 26.07; ^{13}C : 44.48 (CH), 24.47 (CH_3) ; ^1H : 2.24 (NH_2), 3.65 (h, CH), 1.46 (d, J_{HCCH} = 7.0 Hz, CH_3).

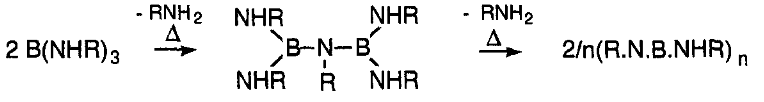
Bulk pyrolysis of **1** *under ammonia*

Compound **1** (2.5 g) was maintained for 12 h at room temperature under a flow of NH_3 (10 cm^3 min^{-1}) in a tube furnace. The temperature was then raised to 1000°C at a rate of 1°C min^{-1}, held at this temperature for 2 h then cooled to room temperature. The IR spectra of the white powdery solid obtained (0.37 g, 14.8% yield) showed two absorptions typical of boron nitride[1] centred at 1408 and 807 cm^{-1}. A medium broad band centred at 3429 cm^{-1} (νNH) and three very weak sharp bands at 2966, 2930 and 2859 cm^{-1} (νCH) were also observed. The XRD profile displayed two broad diffractions centred at $2\theta = 24.9°$ and $2\theta = 42.5°$ showing the presence of low crystallinity boron nitride.[17] The residue contained small amounts of carbon according to its elemental analysis. Found: B, 38.3; N, 53.2; H, 1.8; C, 0.7; O, 6.4. Calc. for BN: B, 43.6; N, 56.4%.

RESULTS AND DISCUSSION

Thermolysis of $B(NHPr^i)_3$ *under reflux conditions*

In previous work[9] we thoroughly characterized borazine, $(NHMeBNMe)_3$, and diborazine, $[(BNHMe)_2(NMe)_3]_2NMe$, by NMR spectroscopy, which easily and rapidly formed in the initial steps of the thermolysis of $B(NHMe)_3$, confirming Aubrey and Lappert's findings.[3] They postulated that simple heating of tris(alkylamino)boranes, $B(NHR)_3$, resulted in their conversion to borazine, $(RNHBNR)_3$, followed by association of borazine rings with elimination of primary amine, RNH_2. The mechanism of the borazine formation was proposed by Lappert and Majumdar[20,21]



(1)

I

II

Evidence for this mechanism rested mainly on the isolation of diborylamines (**I**) as reaction intermediates, although these species were only isolable under sterically favourable conditions. Only diborylamine (**I**) with R = Bu^t was mentioned in the literature.[20–22] The nature of R is of importance; indeed, more or less forcing thermal conditions are required to form the borazine from the aminoborane.[3] Moreover, a cyclic dimer (**II**, $n = 2$) was obtained if R = Bu^t by heating $[(NHBu^t)_2B]_2NBu^t$.[20,21] No homologue of **II** with $n = 2$ was reported in the literature.

Our attempts to convert $B(NHPr^i)_3$ into the corresponding borazine revealed its greater thermal stability than the methyl compound.[9,10] This was due to steric hindrance. After heating **1**, for 42 h at 250°C, the mixture still contained about 60% of aminoborane. After evacuation of **1** and further distillation a residue and a condensate were obtained. The ^{11}B NMR spectrum of the residue exhibited a unique broad peak at δ 28.0 with a shoulder at δ 25.6 and the condensate spectrum showed three peaks at δ 28.0, 25.6 and 22.4. The signal at δ 28.0 can be assigned to boron atoms of the heavier species, borazine (**2**) and polyborazines. As was observed in recent work on methyl borazines[9] the corresponding inequivalent boron environments were not resolved. Compound **2** was fully characterized by one-dimensional ^{13}C NMR spectroscopy, but only the two-dimensional ^1H–^1H and ^1H–^{13}C correlated NMR spectroscopy techniques (COSY) allowed full assignment of the particular chemical shifts of the protons. Numerous other small peaks were observed belonging to oligomeric and polymeric species but none of them could be characterized.

The condensate containing the lighter species exhibited a peak at δ 22.4 due to the remaining aminoborane. The most intense signal at δ 25.6 was assigned to the reaction intermediate, **3**. ^1H NMR data provided compelling evidence for the presence of this new species. Its spectrum exhibited a characteristic CH_3 doublet at δ 1.23, slightly shifted from that of aminoborane (δ 1.24 in the same spectrum) showing the almost equivalent environment of the two CH_3 groups. The 2D ^1H–^1H NMR technique allowed the unambiguous assignment of signals corresponding to CH (δ 3.45, m) and to NH (δ

1.87, d). This NH signal was located between the NH signals of the aminoborane and the borazine. The different spectra have not allowed us to determine the chemical shifts of the hydrogen nuclei belonging to the N–Pr^i bridge group. The carbon nuclei signal assignment was acheived using ^1H–^{13}C correlation NMR spectroscopy data and according to relative intensities of the different peaks in the one-dimensional ^{13}C NMR spectrum. The cyclic dimer (**II**, R = Pr^i) was not present in the reaction medium, or its concentration was too low to be detected. Due to its lowest molecular mass, it should be at least as volatile as compounds **2** and **3** and it should exhibit ^1H, ^{13}C and ^{11}B NMR spectra resembling those of borazine. No such signals were observed in the spectra of the condensate and the residue.

In excellent agreement with previous results, the thermogram of **1** under Ar exhibited a steep weight loss of 89% below 300°C, mainly due to volatilization of aminoborane (T_{eb} = 37°C under 1 mmHg[3]). This observation supported the expectation that **1**, at relatively low temperature, should not be involved in cyclization and polycondensation reactions leading to heavier and non-volatile species. As for the weak gradual weight loss (4%) observed above 300°C, it corresponded to cyclization of remaining aminoborane followed by polymerization and decomposition reactions. The very small quantity of the black residue thus obtained undoubtedly contained large amounts of carbon.

Synthesis of B,B′,B″-*tris*(*isopropylamino*)*borazine*

B,B′,B″-Tris(isopropylamino)borazine (**4**) was expected to be one of the main products formed by aminolysis of **1**. Pure samples were synthesized from trichloroborazine and monoisopropylamine according to the classical reaction

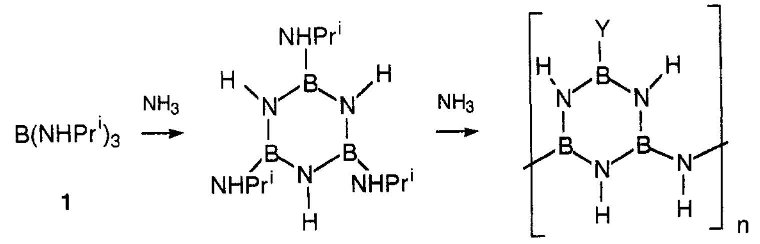
$$(HNBCl)_3 + 6\,RR'NH \longrightarrow (RR'NBNH)_3 + 3\,RR'NH.HCl \qquad (2)$$

The reactions with secondary amines[23,24] are more straightforward than with primary amines because no polymerization can occur via NH of amino groups. Only *B,B′,B″*-tris(methylamino) borazine derived from a primary amine, CH_3NH_2, was reported in the literature.[25] Using triethylamine as reactant for hydrogen chloride elimination, the reaction with isopropylamine was nearly quantitative and **4** was fully characterized by ^{13}C, ^1H and ^{11}B NMR and IR spectroscopy.

Aminolysis of B(NHPr^i)$_3$

B(NHPr^i)$_3$ (**1**) reacted spontaneously with NH_3 at room temperature to give, mainly, *B,B′,B″*-tris (isopropylamino)borazine (**4**), and then polyborazines.

The first experiment consisted of the direct reaction of **1** with ammonia in a 2 : 1 ratio (sample **a**, Fig. 2). In the light of the ^{13}C, ^{11}B and ^1H NMR spectra only small amounts of **1** reacted to form mainly *B,B′,B″*-tris(isopropylamino)borazine (**4**) and monoisopropylamine. Sample **b**, obtained after further addition of NH_3, gave almost the same IR spectrum as compound **4**. Upon addition of a large quantity of ammonia (sample **c**), most of the bands of the last IR spectrum broadened, especially those characteristic of borazine rings in the 600 and 700 cm^{-1} regions. This can be ascribed to polycondensation reactions between borazine rings of compound **4**, through the formation of NH bridge groups. According to the literature[18] the corresponding νNH band appeared at 3400 cm^{-1}. We observed a band at 3440 cm^{-1} (NH amino groups) in this region with two shoulders at 3467 cm^{-1} (NH cyclic groups) and 3406 cm^{-1} (NH bridge groups) whose intensities increased until all these absorptions collapsed to give a broad peak centred at 3428 cm^{-1}. All the ^{11}B NMR spectra showed a new broad peak centred at δ 25.1, which grew and broadened on increasing the amount of ammonia involved in the reaction. It was assigned to both the boron atoms of **4** and of polyborazines. This observation supported the idea that the borazine rings were preserved as the unit structure of the condensates. ^{13}C NMR spectra were consistent with the above results. The first spectrum (sample **a**) exhibited two weak signals at δ 42.32 and 27.36, corresponding to compound **4**, in addition to the two strong signals of compound **1**. These two weak peaks became the two main peaks in the spectra of samples **b** and **c**. Nevertheless, many other small signals appeared around these two signals. They can be assigned to NHPr^i groups located in different environments because of the formation of intermolecular bonds. ^1H NMR spectra confirmed these conclusions: in spite of their complexity owing to the presence of numerous overlapping signals. Compound **4** was characterized as the major compound of sample **b** and was detected in sample **c**. Furthermore, almost



1

4

Polyborazine : Y = NHPr^i, NH$_2$

(3)

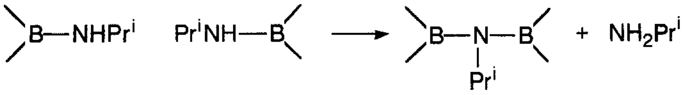
all the new sharp doublets observed for samples **a**, **b** and **c** corresponding to methyl groups appeared in the region δ 1.2–1.4. They can be assigned to methyl groups belonging to NHPr^i groups. This interpretation is consistent with the presence of several broad doublets in the region δ 1.5–2.5 due to the corresponding NH groups. We also observed many new broad singlets in the region δ 2.0–3.0 which can be assigned to different cyclic or bridge NH groups resulting from polycondensation reactions.

The general reaction pathway involved several steps. B(NHPr^i)$_3$ underwent transamination reactions resulting in replacement of NHPr^i groups by lighter and more reactive NH$_2$ groups. Subsequent fast cyclization reactions occurred giving mainly NH cyclic groups. They were followed by further transamination reactions leading to polycondensation of borazine rings with formation of NH bridge groups. These NH cyclic and bridge groups formed by reaction between NH$_2$ and NHPr^i groups with elimination of isopropylamine.

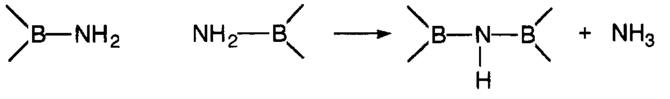
$$\rangle\mathrm{B{-}NHPr^i} + \mathrm{NH_2{-}B}\langle \longrightarrow \rangle\mathrm{B{-}\underset{H}{N}{-}B}\langle + \mathrm{NH_2Pr^i} \qquad (4)$$

This conclusion is based on the following observation: the IR spectra of samples **a**, **b** and **c** exhibited a well-separated weak band, with a constant intensity, at 1606 cm^{-1}. It was assigned to a NH$_2$ deformation mode indicative of B–NH$_2$ groups. Very few (NHR)$_n$B(NH$_2$)$_{3-n}$ compounds are reported in the literature and they are known to be unstable.[26] As a consequence these B–NH$_2$ groups should take their origin in the amine exchange reaction between borazine or polyborazine with ammonia. Gutmann *et al.*[18] found the NH$_2$ deformation mode at 1608 cm^{-1} for *B*,*B*′,*B*″-tris(amino-*N*,*N*′,*N*″-trimethylborazine. We observed it at the same frequency in the IR spectrum of *B*,*B*′,*B*″-triamino-*N*,*N*′,*N*″-triisopropylborazine obtained by aminolysis of compound **2**. Adding more and more NH$_3$ from sample **a** to sample **c** resulted in elimination of increasing amounts of isopropylamine without any significant change in the B–NH$_2$ band intensity. B–NH$_2$ partly substituted borazines and polyborazines then appeared as relatively stable polycondensation intermediates.

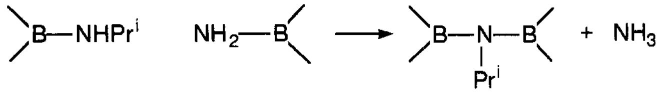
Three other reactions could lead to the formation of borazines and polyborazines, but none of them could be retained as the main condensation reaction. Reaction (5), leading to NPr^i groups and to



$$\rangle\mathrm{B{-}NHPr^i} \quad \mathrm{Pr^iNH{-}B}\langle \longrightarrow \rangle\mathrm{B{-}\underset{Pr^i}{N}{-}B}\langle + \mathrm{NH_2Pr^i} \qquad (5)$$



$$\rangle\mathrm{B{-}NH_2} \quad \mathrm{NH_2{-}B}\langle \longrightarrow \rangle\mathrm{B{-}\underset{H}{N}{-}B}\langle + \mathrm{NH_3} \qquad (6)$$



$$\rangle\mathrm{B{-}NHPr^i} \quad \mathrm{NH_2{-}B}\langle \longrightarrow \rangle\mathrm{B{-}\underset{Pr^i}{N}{-}B}\langle + \mathrm{NH_3} \qquad (7)$$

the formation of isopropylamine did not proceed at room temperature according to the pyrolysis study of **1**. The formation of NH groups by reaction between two NH_2 groups with the elimination of ammonia (reaction (6)) was improbable. Indeed, this mechanism would imply that the amine exchange occurred first on two aminoborane molecules to give two unstable $NH_2B(NHPr^i)_2$, which should then react together to form a dimer, $[(NHPr^i)_2B]_2NH$. Neither of these two intermediates was detected in different NMR spectra, even though the reaction was performed in dilute solution with wery small amounts of NH_3. Reaction (7), between NH_2 and $NHPr^i$ groups with elimination of ammonia, if occurring, concerned negligible quantities of this type of Pr^i group. Such groups should give ^{13}C NMR signals in the regions δ 24.0–25.0 (CH_3) and δ 44.5–46.5 (CH) and ^1H NMR doublets in the region δ 1.35–1.45. Spectra of samples **a**, **b** and **c** exhibited only weak signals corresponding to very few cyclic or bridging Pr^i groups. They were supposed to be mainly due to reaction products of compound **2**, initially present in aminoborane (2 mol%), with ammonia. The disappearance of the four ^{13}C NMR signals in **2** after reaction with NH_3 to give several other weak signals in the same region strongly supported the fact that corresponding borazine rings were directly inserted in polyborazinyl species.

The high carbon content found for sample **c** (40.8%, calc. for **4**: 42.9%) has its origin in the $BNHPr^i$ groups present in the final product. Conversion products of **2** also contribute to this carbon content. Another possible source of carbon could be Pr^i in cyclic or bridging positions which could be formed in low concentration if condensation according to eq. (1) was not perfectly selective.

The thermogravimetric analysis of **1** under NH_3 atmosphere confirmed the extreme reactivity of **1** towards ammonia. Nevertheless, the rapid 39.5% weight loss observed at room temperature was lower than expected (54.6% for the formation of **4**). Actually, the absence of any stirring under these conditions seriously affected the above reactions.

Aminolysis was not observed at temperatures below 250°C in the case of $B(NHMe)_3$.[9] Furthermore, the classical cyclization and polycondensation reactions, which occurred easily with tris(methylamino)borane[9] giving rise to compounds of $(NHRBNR)_3$ type and related polyborazines,[3] is impossible or very slow at temperatures below 250°C. Compared with $B(NHMe)_3$, the high stability of $B(NHPr^i)_3$ with respect to autopolymerization and its high carbon content are counterbalanced by its high reactivity towards ammonia. For this reason boron nitride obtained by pyrolysis of aminoborane contained only very small amounts of carbon (0.7 wt %) in contrast to the carbon content (58.4 wt %) of the precursor. Moreover, the advantage is that reaction of tris(isopropylamino)borane with ammonia leads rapidly to a viscous and processible polymer. Finally, in spite of its high carbon content, $B(NHPr^i)_3$ appeared as a very interesting boron nitride precursor.

REFERENCES

1. R. T. Paine and C. K. Narula, *Chem. Rev.* 1990, **30**, 71 and references cited therein.
2. R. T. Paine and L. Sneddon, *Chemtech.* July (1994), p. 29.
3. D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.* 1959, 2927.
4. R. Toeniskoetter and F. R. Hall, *Inorg. Chem.* 1963, **2**, 29.
5. K. J. L. Paciorek, D. A. Harris and R. H. Kratzer, *J. Polym. Sci., Polym. Chem. Ed.* 1986, **24**, 173.
6. K. J. L. Paciorek, W. Krone-Schmidt, D. H. Harris, R. H. Kratzer and K. J. Wynne, *ACS Symp. Ser.* 1988, **360**, 392.
7. K. N. Narula, R. Schaeffer, A. Datye and T. Paine, *Inorg. Chem.* 1989, **28**, 4044.
8. Y. Kimura, Y. Kubo, N. Hayashi, *J. Inorg. Organomet. Polym.* 1992, **2**, 231.
9. B. Bonnetot, B. Frange, F. Guilhon and H. Mongeot, *Main Group Met. Chem.* 1994, **17**, 583.
10. B. Bonnetot, F. Guilhon, J. C. Viala and H. Mongeot, *Chem. Mater.* 1995, **7**, 299.
11. F. A. Davis, I. J. Turchi and D. N. Greeley, *J. Org. Chem.* 1971, **36**, 1300.
12. H. Nöth, *Chem. Ber.* 1971, **104**, 558.
13. C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.* 1955, **77**, 3699.
14. O. T. Beachley, *Inorg. Chem.* 1969, **8**, 981.
15. W. Gerrard, H. R. Hudson, E. F. Mooney, I. M. Stripp and H. A. Willis, *Spectrochim. Acta* 1962, **18**, 149.
16. W. Gerrard, E. F. Mooney and H. A. Willis, *Spectrochim. Acta* 1962, **18**, 155.
17. J. Thomas, Jr, N. E. Weston and T. E. O'Connor, *J. Am. Chem. Soc.* 1963, **84**, 4619.
18. V. Gutmann, A. Meller and R. Schlegel, *Mh. Chem.* 1963, **94**, 1071.
19. A. Meller and R. Schlegel, *Mh. Chem.* 1964, **95**, 383.
20. M. F. Lappert and M. K. Majumdar, *Proc. Chem. Soc.* 1963, 88.
21. M. F. Lappert and M. K. Majumdar, *Adv. Chem. Ser.* 1964, **42**, 208.
22. A. Meller, *Gmelin Handbuch der Anorganische Chemie, Borverbindungen*, band 22, teil 4, pp. 282–288. Springer-Verlag, Berlin (1975).

23. K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.* 1959, **81**, 3561.
24. W. Gerrard, H. R. Hudson and E. F. Mooney, *J. Chem. Soc.* 1962, 113.
25. J. R. Gould, U.S. Pat. 2,754,177 (1956).
26. D. W. Aubrey, M. F. Lappert and M. K. Majumdar, *J. Chem. Soc.* 1962, 4088.