Simplified synthesis of B-trichloro *N*-trialkylborazines $(ClBNR)_3$, R = Me, Et, and of heterocycles related to 1,3-diaza-2,4-diboranaphthalene $(ClBNC_6H_5)_2$

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Abstract

A 1/1 mixture of the tertiary amine boron trichloride adduct BDMA·BCl_3 (BDMA = *N,N*-dimethylbenzylamine) and the amine hydrochloride RNH_2·HCl (R = Me, Et) was heated in refluxing chlorobenzene to give the B-trichloro *N*-trialkylborazines $(ClBNR)_3$ (R = Me, Et) with very good yield. With NH_4Cl, the same reaction failed to give the related trimeric species $(ClBNH)_3$, the latter compound being obtained in small amounts when the adduct ODMA·BCl_3 (ODMA = *N,N*-dimethyloctylamine) is used instead of BDMA·BCl_3. When applied to $C_6H_5NH_2$·HCl, the same reaction leads to the expected borazine $(ClBNC_6H_5)_3$ with moderate yield (23%), the main compound (77% according to ^1H NMR) being a boron–nitrogen heterocycle derived from 1,3-diaza-2,4-diboranaphthalene $(C_6H_5NBCl)_2$. Attempted isolation of the latter compound by chromatographic methods was unsuccessful. All these derivatives were characterized by high resolution ^{11}B, ^1H and ^{13}C NMR.

Introduction

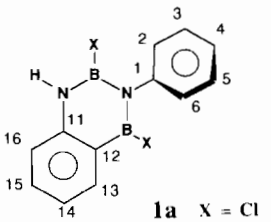
The *N*-trialkyl (aryl) B-trichloroborazines $(RNBCl)_3$ are classically prepared by reaction of the suitable primary amine (or its hydrochloride) with boron trichloride, the resultant adduct $RNH_2 \cdot BCl_3$ being dehydrochlorinated by heating in refluxing aromatic solvents, or by an added tertiary amine (usually triethylamine). The manipulation of gaseous, moisture sensitive boron trichloride, requires a special apparatus; on the other hand, when triethylamine is added, additional impurities are usually formed making the purification of borazines more difficult.

As part of our investigations of the chemical [1] and spectroscopic [2, 3] properties of tertiary amine–boron trihalides adducts, hereafter we report a very clean reaction for the synthesis of chloroborazines

$$BDMA \cdot BCl_3 + RNH_2 \cdot HCl \longrightarrow 1/3(RNBCl)_3 + BDMA \cdot HCl + 2HCl \quad (1)$$

BDMA = *N,N*-dimethylbenzylamine

The tertiary amine boron trichloride adduct used, BDMA·BCl_3, though commercially unavailable, could be readily obtained in a very high purity state [4] allowing a nearly quantitative reaction when $R = CH_3$, C_2H_5. With $R = C_6H_5$, besides the expected trichloroborazine $(C_6H_5NBCl)_3$, the main compound obtained was identified as a diboradiazarobenzene derivative **1a** (Fig. 1). All the compounds were thoroughly characterized by means of high resolution ^{11}B, ^{13}C and ^1H NMR spectroscopy.



1a X = Cl
1b X = Me
1c X = Et

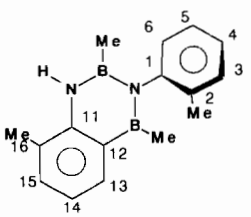


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Fig. 1. Boron–nitrogen heterocycles derived from diazadiboranaphthalene.

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Experimental

Physical measurements

NMR spectra were obtained with a Brüker AM 300 spectrometer at 96.28 MHz for ^{11}B with $BF_3 \cdot Et_2O$ as external reference (positive values downfield), at 300 MHz for ^1H and 75 MHz for ^{13}C, the deuteriated solvent ($CDCl_3$) being also used as reference instead of TMS because of the presence of signals around 0 ppm. Abbreviations used in NMR: dd = doublet of doublets; td = triplet of doublets; b = broad; *i* = ipso; *o*, *m*, *p* = *ortho*, *meta*, *para* atoms. The number in brackets refers to the relative intensity of primary carbons. IR spectra were realized as nujol mulls, the sample being ground in an efficient dry box. Melting points were measured in sealed tubes filled in a dry box.

Materials

All reactions were performed under an atmosphere of dry argon

Preparation of $(CH_3NBCl)_3$

In a typical run, to a solution of 10 g (39.6 mmol) of BDMA · BCl_3 in 50 ml of chlorobenzene were added 2.7 g (40 mmol) of finely ground methylamine hydrochloride $CH_3NH_2 \cdot HCl$ previously dried overnight at 150 °C and the mixture was refluxed for 6 h with vigorous stirring. After cooling and filtration, the resulting solution was evaporated to dryness to yield 2.83 g (ρ = 95% according to (1)) of white crystalline material. The reaction was easily monitored by ^{11}B NMR spectroscopy: thus, besides the broad peak at 31.1 ppm in benzene solution pertaining to the chloroborazine (lit. [5] 31.2, C_6H_6), only traces of BDMA · BCl_3 could be detected (very small peak at 10.2 ppm) with small amounts of BCl_4^- the latter displaying a sharp signal near 6.8 ppm (lit. [6] 6.5 ppm, CH_2Cl_2). By pouring the solution on a Florisil column (SiO_2/MgO: 85/15), an analytical sample was readily obtained (F = 159–160 °C, measured in sealed tubes filled in a dry box, lit. 162–164 °C [7]). Let us add that the ^{11}B NMR signal of this sample usually displays a small peak at 23.6 ppm attributed to $B(NHCH_3)_3$ (lit. 24.2 ppm, C_6H_6 [8]), the related signal having disappeared after the chromatographic step.

Preparation of $(C_2H_5NBCl)_3$

In a quite similar manner, to 10 g (39.6 mmol) of BDMA · BCl_3 in 50 ml of chlorobenzene were added 3.26 g (40 mmol) of $C_2H_5NH_2 \cdot HCl$ with vigorous stirring. After 5 h reflux and filtration 3.25 g (92%) of crystalline material were recovered leading, after pouring onto a Florisil column, to a pure sample of the expected borazine. (F = 54–55 °C, lit. 57–59 °C [7]; δ ^{11}B = 31.2 ppm, CH_2Cl_2, lit 31.4 ppm, C_6H_6 [5]).

If a large excess of $C_2H_5NH_2 \cdot HCl$ (9 mol instead of 1) was used the main signal observed in ^{11}B NMR at 24 ppm was attributed to the trisamino borane $B(NHC_2H_5)_3$ (lit. 23.7 ppm, C_6H_6 [8]).

Reaction of BDMA · BCl_3 with NH_4Cl

To a solution of 10 g (39.6 mmol) of BDMA · BCl_3 in chlorobenzene was added 3.20 g (59.8 mmol) of finely ground NH_4Cl. After refluxing for 24 h, and filtration the ^{11}B NMR spectrum only displayed signals belonging to the starting material (75%) and to BCl_4^- (25%). The use of a higher boiling solvent such as *o*-xylene did not allow isolation of the expected $(HNBCl)_3$. However, when commercially available ODMA · BCl_3 (ODMA = *N*,*N*-dimethyloctylamine) was used instead of BDMA · BCl_3, in one case small amounts of $(HNBCl)_3$ could be recovered by sublimation and compared with an authentic sample by IR spectroscopy [9].

Reaction of BDMA · BCl_3 with $C_6H_5NH_2 \cdot HCl$

To a solution of 10 g (39.6 mmol) of BDMA · BCl_3 in chlorobenzene was added 5.18 g (40 mmol) of $C_6H_5NH_2 \cdot HCl$ under the same conditions as earlier. After 6 h reflux, cooling and filtration, 4.35 g (80% according to reaction (1)) of a slightly yellow oil were recovered that appeared to be a mixture of the expected trimer $(C_6H_5NBCl)_3$ (23%) with the heterocycle **1a** (77%). Attempted separation of both compounds with a Florisil column failed, the latter compound being destroyed on the column. ^{13}C NMR: **1a** 146.93, 143.50, 135.74(1), 133.65(1), 128.73(2), 127.66(2), 126.31(1), 121.44(1), 119.9(b), 116.53(1). Trimer: 143.86, 129.63(2), 128.41(2), 126.35(1) with a small amount of BDMA · HCl and BDMA · BCl_3 as impurity (Fig. 2). ^1H NMR: complex aromatic pattern with protons at 8.07(dd), 7.49(td), 6.99(dd) and 7.06(dd) ppm and a broad signal near 6.94(NH?) ppm. ^{11}B NMR: two broad peaks of unequal height at 28 and 39.5 ppm with a shoulder near 31.4 ppm.

Methylation of the product mixture BDMA · BCl_3 + $C_6H_5NH_2 \cdot HCl$

To the above mixture was added dropwise a suspension of 9.98 g (60 mmol) of CH_3MgI. After being refluxed for 1 h, the mixture was cooled with an ice bath and quenched with a solution of NH_4Cl in water according to the standard procedure [10]. Addition of methanol to the diethyl ether solution gave 0.51 g (11%) of white crystals that appeared to be pure $(C_6H_5NBMe)_3$ according to its melting point 265–266 °C (lit. 264–269 °C [11]) and ^{13}C NMR spectrum [12] (δ ^{13}C = 148.67, 128.67(m), 128.22(*o*) and 124.72(*p*), $CDCl_3$*). In one

*The correct assignment for the different carbon atoms was deduced from the ^1H coupled spectrum, using the well established fact that $^2J(^{13}C-^1H)$ is much smaller than $^3J(^{13}C-^1H)$ in aromatic compounds.

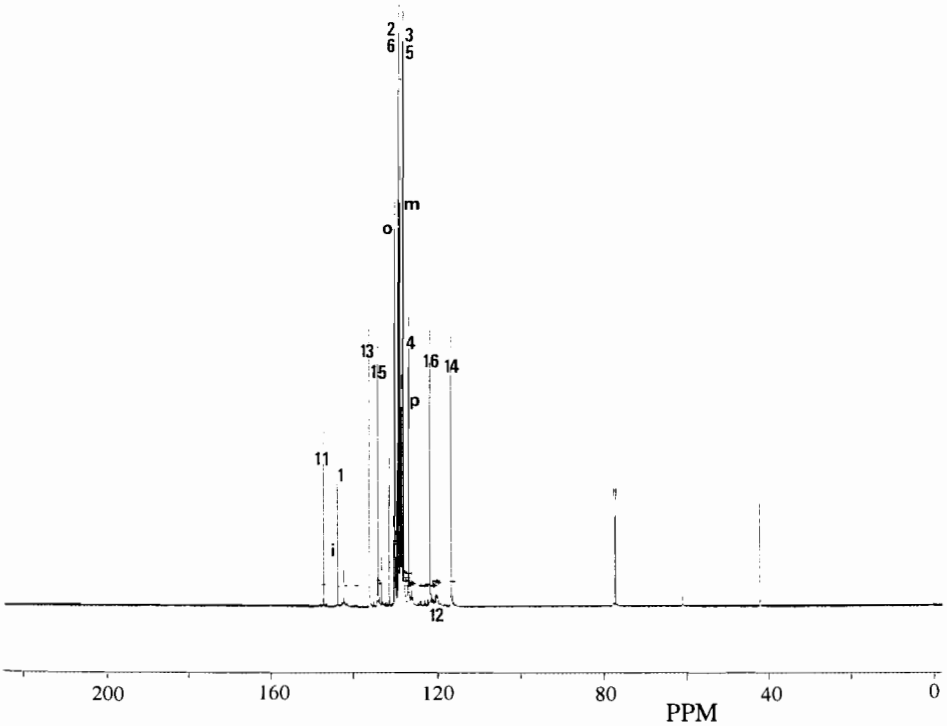

Fig. 2. ^{13}C NMR spectrum of the mixture containing **1a** with $(C_6H_5NBCl)_3$: δ ^{13}C (ppm) = 143.86(i), 129.63(*o* or *m*), 128.41(*m* or *o*) and 126.35(*p*). For the former compound, see text. Additional peaks near 40 and 60 ppm correspond to small amounts of BDMA·BCl_3 and BDMA·HCl. Solvent $CDCl_3$, NS = 539, AQ = 1.769, SW = 18518.519.

case, the slurry was carefully hydrolyzed at −50 °C by dropwise addition of methanol leading, after the usual work-up, to a mixture containing aniline, $(C_6H_5NBMe)_3$ with probably a small amount of **1b** and additional unidentified materials. Attempted separation with a Florisil column was unsuccessful.

Results and discussion

The above reaction (1) is interesting for the preparation of N-trialkyl B-trichloroborazines $(RNBCl)_3$ (R = Me, Et). The presence of BCl_4^- in the early stage of the reaction and its slow decrease, as monitored by ^{11}B NMR spectroscopy, suggest the initial formation of BCl_4^-,RNH_3^+. Thus, consistent with this observation, a possible path may result from dehydrochlorination of the latter by the tertiary amine used to give the adduct $BCl_3 \cdot RNH_2$ which further leads to the trimeric borazine; if the amine hydrochloride is in excess, the trisaminoborane $B(NHR)_3$ (R = Me, Et) is obtained instead. BCl_4^-,NH_4^+ cannot be dehydrochlorinated by BDMA whereas ODMA is only slightly more efficient, the use of Et_3N leading to good yields of $(HNBCl)_3$ [13]. Clearly the steric requirements of the tertiary amine, and its softness or hardness according to Pearson's HSAB scale [14], are of prime importance in these reactions.

Quite different results are obtained when $C_6H_5NH_2$,HCl is treated by BDMA·BCl_3. Although neither **1a** nor **1b** could be isolated in pure form, NMR data bring compelling evidence for the presence of a diazadiboranaphthalene derivative. The best proof could be deduced from the ^{11}B NMR spectra where the presence of two broad signals of different halfheight width is quite typical of this kind of compound [15], the borazine derivative giving rise to a single signal at 31.4 ppm overlapping with those two (lit. δ ^{11}B = 31.5 ppm, CH_2Cl_2). More accurate results are deduced from the ^{13}C NMR spectra. Thus, the splitting observed for the ^{13}C chemical shifts of the carbon atoms of the benzo part of the molecule is also strongly indicative of the presence of a diboradiazaronaphthalene cycle, those belonging to the extra phenyl group lying in the same range [16, 17]. In Table 1 the chemical shifts for **1a** and the related compound **2** are listed. In spite of the fact that some of the chemical shifts reported for the former compound **1a** may be reversed, similar trends are observed for both of them. Let us add that in this compound the boron bonded carbon appears as a very broad signal at 119.9 ppm at a significant higher field than the related compound where the same signal was observed near 124 ppm. The chemical shift of this boron bonded carbon, being quite sensitive to the π electronic density at the boron nucleus [18], may be indicative of an increased conjugation in the former

TABLE 1. ^{13}C chemical shifts of **1a** and **2**

Atom	**1a**	**2**
1	143.50	147.1
2	128.73	133.4
3	127.66	130.4
4	126.31	125.3
5	127.66	126.6
6	128.73	127.6
11	146.93	145.0
12	119.9(b)	123.7(b)
13	135.74	133.9
14	116.53	119.6
15	133.65	132.9
16	121.44	122.1

derivative **1a** for which, having no bulky substituent in *ortho* position, a complete planarity is no longer prevented as previously observed during a crystallographic study of **2** [19]. Finally the ^1H NMR spectroscopy brings little additional information because of overlapping signals with the exception of a few deshielded protons: a doublet of doublets is thus observed at 8.07 ppm pertaining most likely to proton 13 (a similar downfield signal, at 7.96 ppm, has been reported for a related compound [20]), other deshielded or shielded protons being attributed with less confidence.

This reaction is, however, quite interesting as it makes possible the synthesis of the parent compound **1a** of the series by means of the complex BDMA·BCl_3 whereas the classical method requires the use of BI_3 [21], a highly reactive material: thus, it turns out that the boron atom in BDMA·BCl_3 is of a softness equivalent to that of the boron in boron triiodide, probably because of specific steric requirement. Thus, the tertiary amine used, not only behaves as an acceptor for the hydrogen chloride but also plays an important role in the orientation of the reaction towards the formation of the heterocycle **1a** instead of the expected chloroborazine. Such examples of an anomalous effect of tertiary amine are quite numerous in boron nitrogen chemistry [21–23]. Further, our failure to isolate pure compounds either with **1a** or **1b** are in line with earlier results in the literature attributing a very poor hydrolytic stability to the related compound **1c** [24]. Unfortunately our attempts to make this reaction general were unsuccessful. When BDMA·BCl_3 reacted with *o*-$CH_3C_6H_4NH_2$,HCl or *o*-$BrC_6H_4NH_2$,HCl no definite compounds could be observed.

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