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Boron–Nitrogen Compounds. XXXIV.[1a] Preparation and Some Properties of 2-Halo-1,3,2-diazaboracycloalkanes

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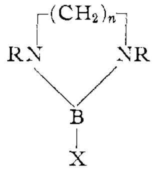
A series of 2-halo-1,3,2-diazaboracycloalkanes has been prepared by (a) the interaction of trialkylamine–trihaloboranes with alphatic α,ω-diamines, (b) displacement of dimethylamino groups of 2-dimethylamino-1,3,2-diazaboracycloalkanes with halogen through interaction with boron trihalides, and (c) a transhalogenation reaction. The 2-halo-1,3,2-diazaboracycloalkanes are thermally rather stable but are very reactive toward moisture and oxygen. The boron-bonded halogen is readily replaced by organic groups through interaction with Grignard reagents. All compounds have a characteristic BN absorption in the 1510–1540-cm^{-1} region of their infrared spectra and the proton magnetic resonance spectra are consistent with their structure. In the mass spectra, the parent peaks P^+ are generally less abundant than the $(P - 1)^+$ peaks.

The first synthesis of heterocyclic σ-bonded boron–nitrogen–carbon compounds was reported by Goubeau and Zappel in 1955.[2] Since that time, several preparative routes have be enexplored to afford the 1,3,2-diazaboracycloalkane system, I.[3] However, with few exceptions, only those derivatives in which X = alkyl or aryl have been described. In particular, derivatives of I with X = halogen are exceedingly rare with only four chloro compounds being known.[4,5] These latter compounds were obtained by treating boron trichloride with the appropriate aliphatic α,ω-diamines in the presence of an excess of triethylamine. With the exception of a Wurtz–Fittig reaction,[4] the chemistry of 2-halo-1,3,2-diazaboracycloalkanes has not been investigated.

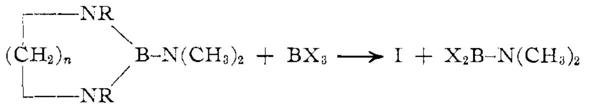

I

The present study concerns the preparation of a series of 2-halo-1,3,2-diazaboracycloalkanes and some of their properties. In a slight modification of the previously described procedure,[4] the preparation of 2-chloro-1,3,2-diazaboracycloalkanes is facilitated when triethylamine–trichloroborane, $(C_2H_5)_3N\cdot BCl_3$, rather than boron trichloride is treated with α,ω-diamines in the presence of an excess of triethylamine providing a smooth reaction according to eq 1; boron tribromide or

$$(C_2H_5)_3N\cdot BX_3 + (C_2H_5)_3N + HRN(CH_2)_nNRH \longrightarrow 2(C_2H_5)_3NHX + I \quad (1)$$

boron triiodide may be used in the place of the chloride. However, in order to reduce side reactions, both nitrogen atoms of the diamine must be secondary. Otherwise, trimerization of I, R = H, occurs readily with the intermolecular elimination of HX and a borazine derivative is obtained along with higher aggregated species. It is worth noting that the reaction described in eq 1 does not work well if boron trifluoride is utilized.

An alternate procedure for the preparation of compounds of type I with X = halogen involves the interaction of 2-dimethylamino-1,3,2-diazaboracycloalkanes[6] with boron trihalides as illustrated by eq 2. Replacement of the boron-bonded exocyclic dimethylamino group can be accomplished with boron trihalides (BCl_3, BBr_3) or with complexes thereof such as trifluoroborane etherate. The reaction works particularly well with the latter whereas when boron triiodide was used, little or no product could be isolated. However, care must be taken to avoid an excess of the boron trihalide; otherwise, B–N ring bonds are attacked and the heterocyclic system may be cleaved.



$$(CH_2)_n(NR)_2B\text{–}N(CH_3)_2 + BX_3 \longrightarrow I + X_2B\text{–}N(CH_3)_2 \quad (2)$$

Halogen exchange between boron trihalides and 2-

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TABLE I

2-HALO-1,3,2-DIAZABORACYCLOALKANES, I

No.	X	R	n	Bp, °C (mm)[a]	% yield (method)	Mol wt[b] Calcd	Mol wt[b] Found	^{1}H nmr data,[c] δ, ppm
1	Cl	CH_3	2	72 (45)	71 (1)	132.4	134	2.96 (s, 6 H); 3.51 (s, 4 H)
2	Br	CH_3	2	81 (44)	32 (2)	176.9	178	3.17 (s, 6 H); 3.73 (s, 4 H)
3	I	CH_3	2	86 (24)	45 (2)	223.9	224	3.43 (s, 6 H); 4.01 (s, 4 H)
4	F	CH_3	3	46 (22)	50 (2)[d]	130.0	130	2.81 (s, 6 H); 2.01 (q, 2 H); 3.06 (t, 4 H)
5	F	C_2H_5	3	55 (11)	70 (2)	158.0	158	
6[e]	F	CH_3		49 (16)	47 (2)	144.0	144	2.80 (s, 6 H); 1.15 (d, 3 H); 2.28 (o, 1 H), 2.89 (d, 4 H)
7	Cl	CH_3	3	100 (40)	57 (1)	146.5	148	3.13 (s, 6 H); 2.27 (q, 2 H); 3.33 (t, 4 H)
8	Cl	C_2H_5	3	66 (10)	74 (1)	174.5	175	
9	Br	CH_3	3	80 (10)	36 (1)[f]	190.9	191	3.35 (s, 6 H); 2.42 (q, 2 H); 3.52 (t, 4 H)
10	I	CH_3	3	59 (3)	25 (1)	237.9	238	3.60 (s, 6 H); 2.61 (q, 2 H); 3.72 (t, 4 H)

[a] Uncorrected. [b] By cryoscopy in benzene and/or by mass spectroscopy (using mass numbers of parent peaks containing ^{37}Cl or ^{81}Br). [c] Neat liquids, external TMS standard. Abbreviations: s, singlet; d, doublet; t, triplet; q, quintuplet; o, octet. [d] An 8% yield by method 3. [e] Bridging hydrocarbon group $-CH_2-CHCH_3-CH_2-$. [f] An 11% yield by method 2.

halo-1,3,2-diazaboracycloalkanes is not an efficient procedure. Though some halogen exchange can be effected in this reaction, boron trihalides readily attack the annular boron–nitrogen bonds resulting in ring cleavage. Attempts to exchange the boron-bonded halogen of I, X = halogen, with either PX_5, PX_3, OPX_3, or SO_2X_2 have been unsuccessful. On the other hand, transhalogenation was accomplished by treating 2-chloro-1,3,2-diazaboracycloalkanes with titanium tetrafluoride.

Careful alcoholysis of 2-halo-1,3,2-diazaboracycloalkanes affords 2-alkoxy derivatives.[5] With Grignard reagents, the halogen is readily replaced by an organic group. By this latter reaction, it has been possible to prepare 1,3,2-trimethyldiazaboracyclopentane, which cannot be prepared by the well-known transamination reaction.[7]

Experimental Section

All diamines used in the present work were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were vacuum distilled before use. Elemental analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra of the materials were recorded on the neat liquids and/or vapor phases on a Perkin-Elmer Model 621 spectrophotometer. Nuclear magnetic resonance spectra were recorded with a Varian HA60-IL and/or Model T-60 spectrometer; mass spectra were provided by the University of Kentucky Mass Spectroscopy Center and were obtained with a Hitachi Perkin-Elmer double-focusing spectrometer, Model RMU-6E.

All experiments were performed under rigorous exclusion of moisture and oxygen in a prepurified nitrogen atmosphere. The cited yields represent only one or two experiments in most cases and no attempt has been made to improve the yields. Analytical data and physical constants of the products are summarized in Table I.

1,3-Dimethyl-2-chlorodiazaboracyclopentane (Typical Experiment, Method 1).—Triethylamine (210 ml, 1.5 mol) was dissolved in 500 ml of dry n-hexane and the solution was cooled in an ice bath. A solution of 61.5 ml (0.75 mol) of boron trichloride in 100 ml of dry n-hexane was added slowly with stirring and a white solid precipitated. The mixture was warmed to room temperature and a solution of 66 g (0.75 mol) of N,N′-dimethylethylenediamine in 300 ml of n-hexane was added slowly. The resultant mixture was refluxed for 3 hr and was filtered. The solids were washed with dry n-hexane and the solvent was stripped off the combined filtrates. The residue was distilled under reduced pressure to yield the desired product.

Refluxing the reaction mixture is not mandatory in preparing the chlorine derivatives. It is required, however, if reasonable yields of the bromine or iodine derivatives are to be obtained. When boron triiodide was employed in the above procedure, benzene was used as the solvent.

1,3-Dimethyl-2-bromodiazaboracyclohexane (Typical Experiment, Method 2).—A solution of 4.5 g (0.029 mol) of 1,3-dimethyl-2-dimethylaminodiazaboracyclohexane[6] in 30 ml of dry n-hexane was cooled in an ice bath and 7.5 g (0.029 mol) of freshly distilled boron tribromide was added dropwise with stirring. When the addition was completed the mixture was kept at ambient temperature overnight. Solvent was stripped off and the residue was distilled under reduced pressure. (Dimethylamino)dibromoborane, bp 54° (20 mm), was collected as by-product besides the desired compound.

1,3-Dimethyl-2-fluorodiazaboracyclohexane (Typical Experiment, Method 3).—1,3-Dimethyl-2-chlorodiazaboracyclohexane (14.7 g, 0.1 mol) was added to a minimum of 6.3 g (0.05 mol) of titanium tetrafluoride (a larger excess of the latter is normally recommended) and the mixture was carefully warmed until an exothermic reaction started. When the reaction subsided the mixture was heated to about 75° for 2 hr. Liquid materials were collected and were rectified under reduced pressure to yield the desired product and titanium tetrachloride.

1,3,2-Trimethyldiazaboracyclopentane (Typical Experiment).—A solution of 0.12 mol of methylmagnesium iodide in ether was added slowly to a solution of 13.3 g (0.1 mol) of 1,3-dimethyl-2-chlorodiazaboracyclopentane in 100 ml of anhydrous ether. The mixture was refluxed for 2 hr and ether was stripped off. The residue was distilled under reduced pressure and was rectified over a 20-cm silver mantle column to give the desired product, bp 122–125° (738 mm), in 32% yield. *Anal.* Calcd for $C_5H_{13}BN_2$: C, 53.6; H, 11.7; B, 9.7; N, 25.0; mol wt, 112. Found: C, 53.3; H, 11.9; B, 9.6; N, 25.0; mol wt (cryoscopic in benzene), 114.

In an analogous procedure the following compounds were prepared from 2-chloro-1,3,2-diazaboracycloalkanes and the appropriate Grignard reagent: **1,3-dimethyl-2-phenyldiazaboracyclopentane**, bp 72–74° (5 mm), lit.[8] bp 73 (3 mm); **1,3,2-trimethyldiazaboracyclohexane**, bp 82–84° (45 mm), lit[7]. bp 30–31° (2 mm); **1,3-dimethyl-2-phenyldiazaboracyclohexane**, bp 71–72° (2 mm), lit.; bp 71–74° (2 mm); **1,3,5-trimethyl-2-phenyl-1,3,2-diazaboracyclohexane**, bp 60° (3 mm). *Anal.* Calcd for $C_{12}H_{19}BN_2$: C, 71.3; H, 9.5; B, 5.4; N, 13.9; mol wt, 202.1. Found: C, 71.0; H, 9.6; B, 5.3; N, 13.8; mol wt (cryoscopically in benzene), 204.

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Discussion

The freshly distilled 2-halo-1,3,2-diazaboracycloalkanes listed in Table I are mobile liquids which are thermally quite stable. However, they must be handled in inert atmosphere. When sealed under vacuum, all compounds can be stored for several months without noticeable decomposition and even the iodine derivatives are not particularly sensitive toward exposure to light. With traces of moisture, all 2-halo-1,3,2-diazaboracycloalkanes react readily and, in the presence of oxygen, they decompose to yield brown solids.

On comparison of the three procedures reported here for the synthesis of 2-halo-1,3,2-diazaboracycloalkanes, it should be emphasized that fluorine derivatives are best prepared by method 2; the latter cannot be recommended for the preparation of iodine compounds. Thus, on the other hand, the latter are readily obtained by method 1 which is not particularly suited for the synthesis of fluorine derivatives. Chlorine and bromine compounds apparently can be obtained in reasonable yields by either of the cited procedures.

It may be noted that (impure) 1,3-dimethyl-2-fluorodiazaboracyclopentane was obtained by both methods 1 and 2. However, this compound dimerizes readily and it was difficult to separate from by-products. No pure material was isolated though mass spectral data revealed the existence of the compound.

Antisymmetric BN stretching modes of all the compounds listed were observed in the 1510–1540-cm^{-1} region of the infrared spectra. This feature may indicate substantial BN π bonding but, in the absence of a normal-coordinate analysis, coupling of CH deformational modes with BN valence vibrations cannot be excluded. This latter event can cause a shift of ν(BN) to higher frequencies and thereby may simulate an unrealistically large BN bond order in these heterocycles.

The proton magnetic resonance spectra of the 2-halo-1,3,2-diazaboracycloalkanes confirm the structure of these compounds. In the spectra of 1,3-dimethyl-2-halodiazaboracyclopentanes (I, $n = 2$) two sharp singlets of an area ratio 3:2 are observed which are due to the N-attached exocyclic methyl groups and to the annular methylene groups. The spectra of the corresponding six-membered heterocycles (I, $n = 3$) exhibit a singlet for the two equivalent methyl groups as well as a triplet and a quintet due to the coupling of protons of the three methylene bridges in the ring. The sharpness of resonance lines is in accordance with previous proton nmr studies on such heterocycles[9] and indicates the planarity of the ring system.

It is of interest to note the trend of the proton chemical shifts of the groups bonded to the nitrogen atoms of the 2-halo-1,3,2-diazaboracycloalkanes. Independent of the ring size, the chemical shifts increase regularly to low field with increasing atomic weight of the boron substituent. This trend cannot be correlated with the change in electronegativity of the halogen atoms (which actually should result in the reverse order). Since boron–halogen π bonding is small as compared to boron–nitrogen π bonding, it can be assumed that the increasing deshielding effect with increasing size of the boron-bonded halogen may be due to steric inhibition of diamagnetism. This event would result from the steric interaction between the sphere of the halogen atoms and the two neighboring methyl groups and appears to be analogous to the deshielding effect observed in the substituted *m*-xylene system.[10] It is unfortunate that parent compounds I, R = H, are not available in order to test this assumption further.

It should be noted that the ratio of chemical shifts $\delta(\mathrm{NC}H_2)/\delta(\mathrm{NC}H_3)$ is relatively constant in the spectra of 1,3-dimethyl-2-halodiazaboracycloalkanes of the same ring size but containing different halogen atoms though variations within the six-membered heterocycles are somewhat larger. This latter observation may be interpreted by a slightly greater interaction of the halogen atoms with the methyl groups in the larger rings (I, $n = 3$) due to their smaller B–N angle. Also, this same effect may be responsible for the lower field resonance of the N–CH_3 groups of the 1,3-dimethyl-2-halodiazaboracyclohexanes as compared to the corresponding five-membered heterocycles though other factors cannot be excluded.

The mass spectra of the 2-halo-1,3,2-diazaboracycloalkanes indicate that the compounds are thermally quite stable up to at least 200°. Under electron impact, all parent peaks P^+ were found less abundant than the $(P - 1)^+$ peaks which are base peaks for most of the compounds. In the absence of sufficient comparative data detailed fragmentation patterns have not yet been studied.

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