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XXIV *. FACILE SUBSTITUTION AND EXCHANGE REACTIONS OF 9-BORABICYCLO[3.3.1]NONANE (9-BBN) AND ITS *B*-SUBSTITUTED DERIVATIVES. SIMPLE CONVENIENT PREPARATIONS OF *B*-HALO DERIVATIVES

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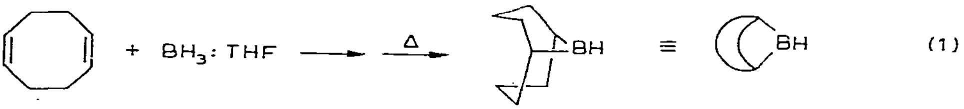
Summary

The exchange and substitution reactions of 9-borabicyclo[3.3.1]nonane (9-BBN) and its *B*-substituted derivatives with various reagents have been studied. The reaction of 9-BBN with halogens and hydrogen halides provides a simple route to *B*-halo-9-BBN's (*B*-X-9-BBN, X = Cl, Br, I). These *B*-X-9BBN's can also be prepared by the facile redistribution reaction between the respective boron trihalides and 9-BBN or *B*-OMe-9-BBN. The alcoholysis of 9-BBN or *B*-X-9-BBN affords *B*-alkoxy-9-BBN in high yield. The exchange reaction between *B*-alkoxy-9-BBN and borane-methyl sulfide affords 9-BBN in quantitative yield. This study reports the simple procedures for the interconversion of a variety of *B*-substituted 9-BBN's.

Introduction

The dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN), is obtained by the hydroboration of 1,5-cyclooctadiene with borane-tetrahydrofuran ($BH_3 : THF$) followed by thermal isomerization (eq. 1) [2].



It has been extensively used for the stereo- and regioselective hydroboration of

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alkenes, alkynes and allenes to provide the corresponding *B*-substituted derivatives [3,4]. 9-BBN is unusually stable for a dialkylborane and possesses unique characteristics. The *B*-substituted 9-BBN's possess a unique property that the 9-BBN moiety acts as a non-participating blocking group in a number of transfer reactions. Thus they are quite different from other trialkylboranes and, therefore, these derivatives find applications as synthetic intermediates [3,5].

Consequently, the preparation of these derivatives is acquiring increasing importance.

Some aspects of the exchange reactions of organoboranes were studied in the past in this laboratory and elsewhere. The exchange reactions of triphenylborane with diborane in stoichiometric ratio affords phenylborane [6]. The facile redistribution of trialkylboranes with aryl borates produces dialkylborinic esters [7]. Similarly, the redistribution reactions of trialkylboranes with boron trihalides provide simple routes to the dialkylhaloboranes or alkyldihaloboranes (eq. 2, 3) [8,9].

$$R_3B + BX_3 \xrightarrow{\text{cat. } B_2H_6} R_2BX + RBX_2 \qquad (2)$$

$$R_3B + 2\ BCl_3 \xrightarrow{\text{cat. } B_2H_6} 3\ RBCl_2 \qquad (3)$$

The dialkylchloroboranes and alkyldichloroboranes have also been prepared via substitution reactions, involving the action of phosphorus pentachloride on the borinate and boronate esters, respectively (eq. 4, 5) [10—13].

$$R_2BOR' + PCl_5 \rightarrow R_2BCl + POCl_3 + R'Cl \qquad (4)$$

$$RB(OR')_2 + 2\ PCl_5 \rightarrow RBCl_2 + 2\ POCl_3 + 2\ R'Cl \qquad (5)$$

In view of the unusual characteristics of the *B*-substituted derivatives of 9-BBN, namely, that the substituent is readily replaceable, leaving the 9-BBN moiety intact in a number of transfer reactions, it was of interest to study the substitution and exchange reactions of some derivatives of 9-BBN.

Results and discussion

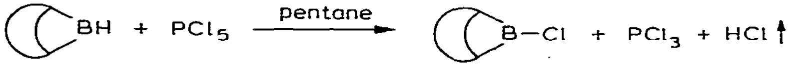
The main objective of this study was to see if the representative *B*-substituted derivatives of 9-BBN undergo the substitution and redistribution reactions to provide simple methods for the interconversion of such derivatives (eq. 6).

(6)

Y = H ; Z = OR , Cl , Br , I
Y = OR ; Z = H , Cl , Br , I
Y = Cl , Br , I ; Z = OR

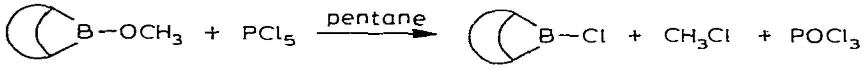
Substitution reactions with phosphorus halides

The lower halides of phosphorus, PCl_3 and PBr_3, do not react with 9-BBN or *B*-OMe-9-BBN even under vigorous conditions such as refluxing for 6 h under neat conditions. However, 9-BBN reacts with PCl_5 in pentane solution to form *B*-Cl-9-BBN (eq. 7).


(7)

The reaction is slow at room temperature (5 h) but is complete within 1 h in refluxing pentane. The product is isolated in good yields by simple distillation following the removal of the solvent and PCl_3. Although a second mole of 9-BBN can be made to react with HCl, no attempt was made in that direction, owing to the difficulty involved in the reaction of 9-BBN with HCl.

The reaction of PCl_5 with *B*-OMe-9-BBN follows the expected route [10], reaching completion in 1 h at room temperature (eq. 8).


(8)

The isolation of *B*-Cl-9-BBN consists of simple distillation after the removal of $POCl_3$. However, analogous reactions with PBr_5 failed to give pure *B*-Br-9-BBN. This agrees with the reports that the reaction of PBr_5 with butyl diphenylborinate failed to give diphenylbromoborane cleanly [14]. The results are summarized in Table 1.

Reaction with halogens and hydrogen halides

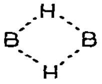
The reaction of boranes with halogens was briefly studied in the past. Köster and Grassberger reacted dialkylboranes with halogens to obtain dialkylhaloboranes [8]. Kinberger and Siebert prepared bromo- and iodo-borane-methyl sulfide complexes ($H_2BX : SMe_2$, $HBX_2 : SMe_2$, X = Br, I) by the reaction of $H_3B : SMe_2$ (BMS) with the respective halogens and hydrogen halides [15]. The preparation of *B*-Br-9-BBN by the action of bromine on 9-BBN was achieved

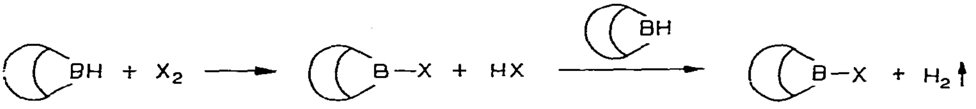
TABLE 1

REACTION OF 9-BBN AND *B*-METHOXY-9-BBN WITH PHOSPHORUS HALIDES

Starting compound	Reagent	Reaction conditions			Yield (%)	B.p. (°C/mmHg)
		Solvent	Temperature (°C)	Time (h)		
9-BBN	PCl_3	pentane	37[a]	24	NR[b]	—
		(neat)	76	8	NR	—
9-BBN	PCl_5	pentane	23	6	—[c]	—
			37[a]	1	86	41—43/0.3
9-BBN	PBr_3	pentane	23	24	NR	—
			37[a]	10	NR	—
9-BBN	PBr_3	cyclohexane	80	10	NR	—
9-BBN	PBr_5	pentane	23	5	—[d]	—
B-OMe-9-BBN	PCl_5	pentane	23	1	75	107—109/45[e]
B-OMe-9-BBN	PBr_5	pentane	23	1	—[d]	—

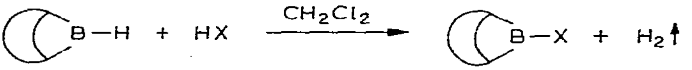
[a] Reaction in refluxing pentane. [b] NR = no reaction. [c] No isolation experiment was carried out. [d] The product was a complex mixture. [e] Distillation was carried out at 45 mmHg to enable the separation of $POCl_3$ and *B*-Cl-9-BBN by fractional distillation.

recently in this laboratory [16]. But all these reports do not represent systematic investigation. It appears that the first step in the reaction is fast, whereas the second step is much more sluggish. In case of the reaction with bromine and iodine, the decolorization occurs within 2 h at room temperature, but the complete disappearance of the  band of 9-BBN in the IR (1560 cm^{-1}) requires about 40 h (eq. 9).



(9)

It has been reported that the substitution reaction of 9-BBN with dry HCl in ether solution leads to *B*-Cl-9-BBN [17]. However, this method cannot be extended for the reaction with HBr and HI, because of the instability of ether towards the acids and the products, *B*-X-9-BBN. Therefore, a general procedure was established for the reaction of 9-BBN with hydrogen halides (eq. 10).



(10)

The experimental conditions and the yields in the individual reactions are given in Table 2.

Reactions with the halides of other metals and non-metals

Having succeeded in the substitution reactions of 9-BBN with HX, X_2 and PCl_5, it was of interest to explore the possibilities of employing the halides of other metals and non-metals for substitution or exchange reactions. The preparation of monohaloborane-trimethylamine by the action of HgX_2 was encouraging (eq. 11) [18].

$$BH_3 : NMe_3 + HgX_2 \xrightarrow[25^\circ C]{Et_2O} H_2BX : NMe_3 \qquad (11)$$

However, 9-BBN failed to react with Me_3SiCl, $SiCl_4$, and the anhydrous halides,

TABLE 2

THE SUBSTITUTION REACTIONS OF 9-BBN WITH HALOGENS AND HYDROGEN HALIDES IN CH_2Cl_2 SOLUTIONS AT ROOM TEMPERATURE

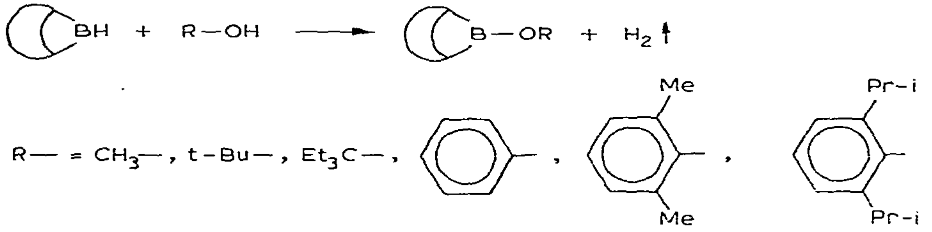
Reagent	Time (h)	Yield (%)	B.p. (°C/mmHg)
Cl_2	40	76	66—67/5
Br_2	36	81	90—92/10
I_2	36	78[a]	106—108/8
HCl	32	79	65—66/5
HBr	28	83	58—60/1
HI	20	83	84—86/2

[a] The first fraction in the distillation was purple in color due to the presence of iodine, which sometimes crystallizes in the condenser.

$AlCl_3$, $ZnCl_2$, $HgCl_2$ and AgI. The reactions were tried under increasingly vigorous conditions, such as pentane at room temperature, refluxing cyclohexane and finally in the case of the liquid halides, refluxing in excess of the halides. But 9-BBN is totally inert towards these halides.

Reaction with alcohols and phenols

The alcoholysis of 9-BBN with a wide variety of alcohols and phenols affords the corresponding *B*-alkoxy-, or *B*-aryloxy-9-BBN in quantitative yield (eq. 12) [19].



(12)

However, the highly hindered phenol, 2,6-di-t-butylphenol, fails to react with 9-BBN under similar conditions [19]. As expected, *B*-halo-9-BBN's also react cleanly with methanol in pentane or CH_2Cl_2 solution, forming *B*-methoxy-9-BBN (eq. 13).

(13)

Redistribution with boron trihalides

The exchange reaction between trialkylborate and boron trichloride has been employed for the preparation of alkoxydichloroborane (eq. 14) [20].

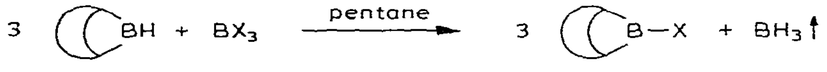
$$B(OR)_3 + 2\ BCl_3 \rightarrow 3\ RO{-}BCl_2 \qquad (14)$$

The preliminary studies by Köster and Grassberger with the disproportionation reaction between dialkylboranes and boron trihalides (eq. 15) were encouraging but incomplete [8].

$$R_2BH + BCl_3 \rightarrow R_2BCl + [HBCl_2] \qquad (15)$$

These workers report the exchange of only one of the three B—X bonds of BX_3 participating in the reaction. In an attempt to explore the possibility of utilizing all of the three B—X bonds for exchange, we undertook to study this reaction in detail.

Our investigations revealed that all three B—X bonds can readily be exchanged to obtain *B*-X-9-BBN's in good yields (eq. 16).



(16)

X = Cl, Br, I

The reaction is carried out in pentane so that the resulting BH_3 escapes from the reaction mixture, thus driving the reaction in the forward direction. The experi-

TABLE 3

REDISTRIBUTION REACTIONS OF 9-BBN AND *B*-METHOXY-9-BBN EITH BORON TRIHALIDES IN PENTANE SOLUTIONS

Starting compound	Reagent	Reaction conditions		Yield (%)	B.p. (°C/mmHg)
		Temperature (°C)	Time (h)		
9-BBN	BCl_3	23	12	76	86—88/17
9-BBN	BBr_3	23	12	—[a]	—
9-BBN	BBr_3	37	1.5	91	109/25
9-BBN	BI_3	37	1	90[b]	70—72/0.4
B-OMe-9-BBN	BCl_3	25	1	92	65—66/0.5
B-OMe-9-BBN	BBr_3	25	1	88	94—95/15
B-OMe-9-BBN	BI_3	37	1	79[b]	70—72/0.2

[a] No isolation experiment was carried out. [b] The starting BI_3 had slight purple color. The product also has this color although the freshly condensed drops are colorless.

mental conditions and the yields for exchange reactions with BX_3 are summarized in Table 3.

Similarly, *B*-OMe-9-BBN also undergoes a redistribution reaction with BX_3 forming *B*-X-9-BBN in good yields (eq. 17).

(17)

X = Cl, Br, I

However, it is necessary to add a small quantity of BX_3 to the product after pumping off methyl borate in order to convert the last traces of the *B*-OMe compound.

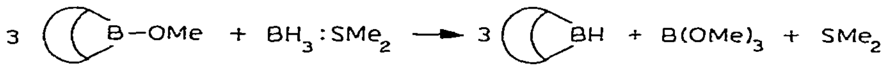
Redistribution with borane-methyl sulfide

Some dialkylboranes were produced in situ by exchange reactions between esters of dialkylborinic acids and lithium aluminum hydride ($LiAlH_4$) or aluminum hydride (AlH_3) [21—23]. Similarly, some monoalkylboranes were obtained from the *B*-alkylcatecholboranes and AlH_3 or $LiAlH_4$ [24]. However, the presence of undesirable side-products greatly limits the application of these methods for the preparation of pure dialkylboranes.

This problem could be successfully solved by the developments of the observation recently made in this laboratory that *B*-butoxy-9-BBN reacts cleanly with BMS producing 9-BBN in quantitative yields (eq. 18) [25].

(18)

We observed that *B*-OMe-9-BBN also undergoes such disproportionation with BMS either in refluxing pentane (0.5 *M* solution) in 2 h, or in THF, or even under neat conditions (eq. 19).



(19)

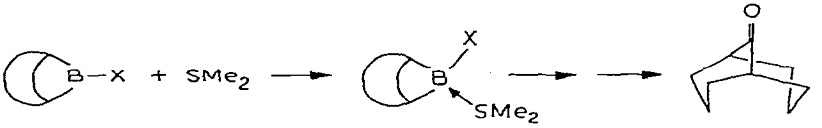
The isolation of 9-BBN involves simply the removal of methyl borate and SMe_2 along with the solvent (THF or pentane). This method provides a convenient preparation of dialkylboranes in pure form from the esters of dialkylborinic acids.

However, the reverse reaction, the redistribution between 9-BBN and methyl borate, does not proceed to give *B*-OMe-9-BBN. In an attempt to facilitate the reaction, the substrates were refluxed in pentane for 10 h so that diborane escapes from the reaction mixture as soon as it is formed. But the reaction does not proceed to any detectable extent.

An attempted disproportionation reaction between the methyl sulfide complex of *B*-chloro-9-BBN (*B*-Cl-9-BBN : SMe_2) and BMS did not reach completion but proceeded only to 15—20% completion as observed by IR and ^{11}B NMR after refluxing for 12 h in pentane. Apart from *B*-Cl-9-BBN : SMe_2 and 9-BBN, the SMe_2 complexes of some partially halogenated borane (probably H_2BCl and $HBCl_2$) were also observed in the ^{11}B NMR spectrum of the material obtained from the pentane extract.

Characterization of the products

The *B*-halo-9-BBN's prepared by various methods have been isolated by distillation in pure form. They are characterized by b.p., ^{1}H NMR and ^{11}B NMR spectral data. These physical constants compared very well with those observed for *B*-X-9-BBN's obtained via hydroboration [26]. In representative cases, the products were converted to their methyl sulfide complexes (*B*-X-9-BBN : SMe_2), and then to bicyclo[3.3.1]nonan-9-one via known reactions (eq. 20) [27].



(20)

These were characterized by their melting points. Typical data are given in Table 4.

TABLE 4

CHARACTERIZATION OF *B*-HALO-9-BBN's (*B*-X-9-BBN) AND THEIR METHYL SULFIDE COMPLEXES

X	Physical properties		SMe_2 Complexes							Yiel of keto
	B.p. (°C/ mmHg)	^{11}B NMR (δ, ppm) [a]	Yield (%)	M.p. (°C)	^{11}B NMR (δ, ppm) [a]	^{1}H NMR [b] (δ, ppm)	Analysis (Found (calcd.) (%))			
							C	H	B	
Cl	41—43/0.3	78.6	87	104—105	18.5	2.26	55.24 (54.97)	9.01 (9.16)	5.09 (4.95)	73(8
Br	58—60/1.0	82.0	91	128—129	12.8	2.30	45.42 (45.66)	7.46 (7.61)	4.28 (4.11)	69(9
I	70—72/0.2	84.2	72	132—133	12.1	2.30	38.92 (38.73)	6.32 (6.46)	3.58 (3.49)	65(7

[a] ^{11}B NMR spectra were recorded in $CDCl_3$ and the positive sign indicates downfield from $BF_3 : OEt_2$ resonan
[b] Chemical shifts of SMe_2 protons. [c] Isolated yields of pure ketone m.p. 155—156°C, lit. m.p. 154—156.5°C [27]. The values in the parentheses indicate GC yields.

9-BBN and *B*-methoxy-9-BBN prepared respectively by redistribution reactions and methanolysis are also characterized by the physical and spectroscopic methods.

Conclusions

This study reveals that the *B*-substituted 9-BBN's undergo facile substitution and disproportionation reactions without participation of the 9-BBN moiety. This enables us to interconvert one derivative into the other by simple steps. It makes *B*-X-9-BBN's (X = Cl, Br, I) available from the readily accessible 9-BBN or *B*-OMe-9-BBN by easy methods, as an alternative to a new synthesis involving the hydroboration of 1,5-cyclooctadiene with the corresponding monohaloborane-methyl sulfide [26]. *B*-Halo-9-BBN's find interesting applications in synthesis [28] and hold great promise for future synthetic use. The preparation of pure 9-BBN from *B*-alkoxy-9-BBN represents the first report of the preparation of a dialkylborane free from undesirable side-products, by redistribution reactions.

Experimental

General comments

The techniques described in Chapter 9 of ref. 29 were used extensively. All glassware was dried at 140°C for at least 4 h, assembled hot, and allowed to cool under nitrogen. The reaction flasks with sidearms capped with rubber septa were assembled under nitrogen before use. All reactions were carried out under a static pressure of nitrogen. The transfers of liquids and solutions of organometallics were done with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or by the double-ended needle technique.

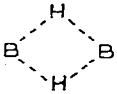
Materials

Technical grade pentane (and hexane) were stirred for one day over concentrated sulfuric acid, treated with anhydrous potassium carbonate, distilled from lithium aluminum hydride and stored in crown capped bottles over 4 Å molecular sieves. Commercial 9-BBN from Aldrich was recrystallized from hexane and the colorless crystalline material (m.p. 151–152°C) was used for all of these reactions. Borane-methyl sulfide (BMS) obtained from Aldrich was used directly. The gaseous reagents, HCl, HBr, HI, Cl_2 and BCl_3, were obtained from Matheson Gas Company; BBr_3 and BI_3 from Ventron, bromine from Fisher Scientific Company, and iodine from Mallinckrodt, were used without further purification. A stock solution of 9-BBN in pentane was standardized and used for most of the reactions.

Analyses

^{11}B NMR spectra were recorded on a Varian XL-100 spectrometer (32.1 MHz) and all chemical shifts are relative to $BF_3 : OEt_2$ (δ 0 ppm); downfield shifts are represented by positive signs. ^1H NMR spectra were recorded on Varian T-60 (60 MHz) spectrometer. All ^1H chemical shifts are relative to tetramethylsilane (δ 0 ppm).

Determination of reaction time by IR

In case of the reactions starting with 9-BBN, the progress of the reaction was followed by IR. The aliquots were withdrawn at definite intervals and the IR spectrum was recorded. The disappearance of the  bridge band at 1560 cm^{-1} indicates the complete uptake of 9-BBN. In the case where 9-BBN is formed, the reaction rate was followed by the increase in intensity of this band.

Determination of reaction time by ^1H NMR

In the conversion of *B*-methoxy-9-BBN to *B*-halo-9-BBN, measured volumes of aliquots were transferred into 25-ml round bottom flasks at fixed intervals of time. Solvent was pumped off at room temperature using water aspirator and $CDCl_3$ was added to the flask; ^1H NMR of this solution was recorded. The completion of the reaction could be inferred from the disappearance of *B*-OCH_3 protons in the spectrum.

Reaction of 9-BBN with PCl_5

(i) Determination of reaction time. In a 50-ml round bottom flask equipped with a magnetic stirring bar and connecting tube, 2.1 g of PCl_5 (10 mmol) was weighed under nitrogen; while stirring vigorously, 24.4 ml of 9-BBN solution in pentane (0.41 *M*, 10 mmol) was added. At definite intervals of time, clear supernatant liquid was withdrawn and IR recorded. It required 6 h for the complete uptake of 9-BBN in the reaction at room temperature. Under refluxing conditions, however, the reaction was complete in 1 h.

The reactions with PBr_5, anhydrous $AlCl_3$, $ZnCl_2$, $HgCl_2$ and AgI were carried out in the same manner.

(ii) Isolation of the product. In a 200-ml round bottom flask equipped with a magnetic stirring bar, a reflux condenser and a connecting tube, 10.4 g of PCl_5 (50 mmol) was weighed under N_2. With stirring, 109 ml of 9-BBN solution in pentane (0.46 *M*, 50 mmol) was added and the contents were refluxed for 1 h. Pentane and PCl_3 were pumped off using a water aspirator and 6.7 g *B*-Cl-9-BBN (86% yield), b.p. 41—43°C/0.3 mmHg was distilled as a colorless liquid. It sometimes solidifies at room temperature.

Reaction of *B*-OMe-9-BBN with PCl_5

(i) Determination of reaction time. In a 50-ml reaction flask, 2.1 g (10 mmol) of PCl_5 was weighed, followed by the addition of 13.3 ml pentane and 6.7 ml of 1.5 *M* pentane solution of *B*-OMe-9-BBN (10 mmol) with vigorous stirring. At definite intervals of time, 4.0 ml aliquots were taken into a 25-ml flask. Solvent was pumped off and ^1H NMR was recorded in $CDCl_3$.

The progress of the reactions of *B*-OMe-9-BBN with BMS, anhydrous $AlCl_3$, $ZnCl_2$, $HgCl_2$ and AgI was followed in the same manner.

(ii) Isolation of the product. To 21 g of PCl_5 (100 mmol) weighed into a 250-ml round bottom flask under N_2 was added 100 ml of pentane, followed by the dropwise addition of 15.2 g (100 mmol) of *B*-OMe-9-BBN with stirring. After 1 h

solvent was pumped off and the product distilled using water aspirator. The first fraction contained 13.2 g (86% yield) of $POCl_3$, b.p. 70—75°C/45 mmHg and then 11.2 g (75% yield) of *B*-Cl-9-BBN distilled as a colorless liquid, b.p. 107—108°C/45 mmHg.

Reaction of 9-BBN with bromine

A 250-ml reaction flask equipped with a magnetic stirring bar, a septum inlet and a cold finger trap (directly fixed on the flask) was charged with 6.1 g (50 mmol) of pure recrystallized 9-BBN and 100 ml of CH_2Cl_2. The cold finger trap was filled with acetone and Dry Ice to prevent the loss of HBr. To the contents of the flask a solution of 1.43 ml (4.4 g, 28 mmol, 10% excess) of Br_2 in 25 ml of pentane was added dropwise. The progress of the reaction was followed by withdrawing 0.2 ml of the solution and recording the IR spectrum. It required 36 h to complete the reaction. The cold finger trap was replaced by a connecting tube and the solvent was pumped off. *B*-Bromo-9-BBN was isolated on distillation as a colorless liquid, 8.1 g (81% yield), b.p. 90—92°C/10 mmHg.

B-Chloro-9-BBN was prepared in the same way, except that Cl_2 (20% excess) was condensed in a graduated tube maintained at —78°C, and was then allowed to distill slowly into the reaction flask containing 9-BBN in CH_2Cl_2. The cold finger trap was filled with a solid/liquid slush bath containing methanol and liquid nitrogen [30]. This maintains a temperature of —98°C (HCl boils at —85°C).

In the case of the reaction of I_2 with 9-BBN, a solution of 50 mmol I_2 in 300 ml CH_2Cl_2 was added.

Reaction of 9-BBN with hydrogen halides

The experimental setup is the same as described for the reaction with halogens. The hydrogen halides are condensed into a graduated tube using an appropriate cooling bath. Thus a liquid N_2/methanol slush bath was used for HCl, acetone/Dry Ice bath for HBr and a —50°C bath prepared by adding a limited quantity of Dry Ice to acetone was used for HI. A measured quantity of liquified hydrogen halide was allowed to distill into the reaction flask.

Following the completion of the reaction as observed by IR, solvent was pumped off and the product distilled under reduced pressure. The yields of *B*-halo-9-BBN's and the boiling points in the individual reactions are given in Table 2.

Methanolysis of B-X-9-BBN

(i) Determination of reaction time. The methanolysis was carried out in CH_2Cl_2 (0.5 *M*) solution by adding methanol to a solution of *B*-X-9-BBN in CH_2Cl_2. The progress of the reaction was followed by NMR as described in the general procedure. The integration of OCH_3 and alkyl protons reveals the relative amounts of *B*-OMe-9-BBN and *B*-X-9-BBN in the reaction mixture. The methanolysis was complete in 1 h at room temperature.

(ii) Isolation of the product. To a solution of 8.7 g of *B*-Cl-9-BBN (55 mmol) in 45 ml of CH_2Cl_2 was added 2.43 ml (60 mmol) of methanol dropwise with stirring at room temperature. After 1 h, the solvent, liberated HCl and the excess

methanol were pumped off and *B*-OMe-9-BBN was distilled and collected as a colorless liquid, b.p. 57—58°C/7 mmHg. The product, 7.7 g, a yield of 92%, was obtained in this reaction.

B-Br-9-BBN and *B*-I-9-BBN afforded 94 and 85% yields of *B*-OMe-9-BBN, respectively.

Reaction of 9-BBN with BBr_3

(i) Determination of reaction time. A 50-ml reaction flask was charged with 22.2 ml of 9-BBN solution in pentane (0.44 *M*, 10 mmol) and 0.38 ml of BBr_3 (3.4 mmol neat liquid) was added dropwise. The progress of the reaction was followed by IR. The reaction mixture was refluxed in order to accelerate the reaction.

The reactions of 9-BBN with PCl_3, PBr_3, $TiCl_4$, $SiCl_4$ and Me_3SiCl were carried out in the same way. In the case of BCl_3 and BI_3, standardized solutions of the reagents in pentane were utilized.

(ii) Isolation of B-Br-9-BBN. To 111 ml of 9-BBN in pentane (50 mmol, 0.45 *M*) was added 1.9 ml (20 mmol, 20% excess) of BBr_3 and the mixture was refluxed for 1.5 h. The solvent was pumped off and the product, 9.1 g (91% yield) of colorless liquid, b.p. 109°C/25 mmHg, was obtained by distillation.

This method was followed for the reaction with BI_3, but in the case of BCl_3, the reaction mixture was stirred at room temperature for 12 h instead of refluxing, in order to avoid the loss of volatile BCl_3.

Reaction of B-OMe-9-BBN with BBr_3

(i) Determination of reaction time. The reaction was carried out in the same manner as described for PCl_5, except that 0.39 ml (3.4 mmol) of BBr_3 was added to 10 mmol of well-stirred solution of *B*-OMe-9-BBN in pentane. The progress of the reaction was followed by ^1H NMR, as already described. Exchange reactions of *B*-OMe-9-BBN with BCl_3 and BI_3 were followed in the same way.

(ii) Isolation of the product. To a solution of 7.6 g (50 mmol) of *B*-OMe-9-BBN in 50 ml of pentane was added 1.9 ml of BBr_3 (20 mmol, 20% excess) and refluxed for 1.5 h. The solvent was pumped off and 0.2 ml of BBr_3 (2 mmol) was added in order to react with trace quantities of unconverted *B*-OMe-9-BBN. After stirring for 0.5 h, the product was distilled, 8.1 g (81% yield) of *B*-Br-9-BBN, b.p. 94—95°C/15 mmHg was obtained as a colorless liquid.

The isolation of *B*-chloro- and *B*-iodo-9-BBN from *B*-OMe-9-BBN was carried out in the same way.

Reaction of B-OMe-9-BBN with BMS

To a solution of 11.7 g (77 mmol) of *B*-OMe-9-BBN in 140 ml of pentane taken in a 250-ml round bottom flask equipped with a reflux condenser, connecting tube and a magnetic stirring bar was added 2.6 ml (26 mmol) of BMS and refluxed. The progress of the reaction was followed by IR. After 2 h, pentane and methyl borate were pumped off and 9.4 g (101% yield) of 9-BBN was obtained as a colorless crystalline solid. The ^1H NMR spectrum indicated the presence of trace amounts of *B*-OMe-9-BBN. Recrystallization from hexane afforded a pure material, m.p. 151—152°C.

Reaction of B-Cl-9-BBN: SMe_2 with BMS

To a suspension of 13.08 g (60 mmol) of *B*-Cl-9-BBN : SMe_2 in 120 ml pentane was added 2.2 ml (22 mmol, 20% excess) of BMS while stirring. The mixture was refluxed for 10 h when IR of the clear supernatant liquid indicated that only 15—20% of the 9-BBN has been formed. The supernatant liquid was decanted and the solvent pumped off from the pentane extract. The ^{11}B NMR spectrum of the product showed that it is mainly the starting *B*-Cl-9-BBN : SMe_2 with 15—20% of 9-BBN and some unreacted BMS along with some partially substituted derivatives of BMS.

Preparation of B-Br-9-BBN : SMe_2 complex

In a 500-ml reaction flask 4.1 g of *B*-Br-9-BBN (20 mmol) was dissolved in 100 ml of pentane. While stirring vigorously at 0°C, 1.8 ml of methyl sulfide (1.48 g, 24 mmol, 20% excess) was added dropwise. The methyl sulfide complex precipitated almost instantaneously. After 0.5 h of stirring, the solvent was decanted, the solid was recrystallized from hexane and dried under aspirator vacuum. There was obtained a colorless crystalline product, 5.8 g (91% yield), m.p. 128—129°C, the ^{11}B NMR spectrum shows a single resonance at δ 12.8 ppm.

The methyl sulfide complexes of *B*-chloro- and *B*-iodo-9-BBN were also prepared and characterized in the same manner. The physical constants and the spectroscopic data are given in Table 4.

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