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BORA-AROMATIC SYSTEMS

VI *. DEHALOGENATION OF ORGANOBORON DIHALIDES IN THE SEARCH FOR BORENES

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Summary

The dehalogenation of various organoboron dihalides (methylboron diiodide, phenylboron dibromide and phenylboron dichloride) by metal reducing agents (potassium, bis(trimethylsilyl)mercury, diethyltin oligomer and hexamethyldistannane) has been examined as a possible approach to the generation of boron(I) or borenoid intermediates. The use of alkynes as a boron(I) trapping agent has been shown to be inadvisable with metals and organoboron dibromides or diiodides. From the reaction of phenylboron dibromide, potassium and diphenylacetylene, none of the previously claimed hexaphenyl-1,4-dibora-2,5-cyclohexadiene could be detected.

The interaction of phenylboron dichloride with various metal agents led to the formation of borenoid intermediates of the type PhBMCl, which showed the tendency to undergo:

(a) alpha-elimination ($M = Me_3SiHg$) to generate phenylborene;

(b) rearrangement ($M = Me_3Sn$) to yield $Ph(Me)BSn(Cl)Me_2$; and

(c) alpha-elimination of PhBMeCl from such latter intermediates to yield Me_2Sn.

Introduction

The recent attention that has been given to the generation and trapping of subvalent boron compounds has prompted us to study the metal reduction of organoboron dihalides, RBX_2, in some detail, in order to learn whether borene

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* For Part V see ref. 1.

(RB) * or borenoid (RBMX) intermediates might be produced. The present study also seeks to reexamine the validity of certain proposed chemical trapping procedures for organoborenes (RB), such as the use of olefins or acetylenes.

Previously reported evidence for the production of subvalent boron intermediates has been obtained by diverse approaches. In pyrolysis reactions of BF_3 and boron conducted at 1800—2000°C the monomeric BF was intercepted by cocondensation of the reaction products with acetylenes at —196°C to yield 1,4-difluoro-1,4-dibora-2,5-cyclohexadienes [4]. The 2,3,5,6-tetramethyl derivactive of such boron heterocycles has been used as a ligand in some nickel(0) complexes, whose crystal structures have recently been determined [5,6]. Chemical trapping of organoborenes themselves has been claimed, or implied, for three different situations: (1) the treatment of phenylboron dibromide with potassium metal in the presence of diphenylacetylene, which procedure led to the isolation of hexaphenyl-1,4-dibora-2,5-cyclohexadiene in 47% yield [7]; (2) the treatment of methylboron dibromide with potassium (admixed with sodium or graphite), in the presence of cyclohexene, and the isolation of 7-methyl-7-borabicyclo[4.1.0]heptane [8]; and (3) the photolysis of tri-1-naphthalenylborane in the presence of cyclohexane or cyclohexene, and the isolation, upon oxidative work-up, of products indicating the presence of cyclohexylboranes (from cyclohexane) or of a 7-borabicyclo[4.1.0]heptane (from cyclohexene) [2]. Furthermore, an anionic complex of C_6H_5B, namely Na^+ $[B(C_6H_5)_2]^-$ is suggested to have arisen from the photochemical elimination of biphenyl from sodium tetraphenylborate [9].

Other attempts to generate and capture subvalent organoboron compounds have encountered serious competition from other reaction pathways. The dehalogenation of alkylboron halides by alkali metals leads instead to geminal diborylalkanes [10,11]. By producing $R_2B^{\bullet}$ intermediates (where R = Et or Ph) in the presence of pyridine bases, relatively stable solvates $[R_2B^{\bullet}Py]$ could be characterized by ESR spectroscopy [12]. On the other hand, the treatment of dimesitylboron fluoride in 1,2-dimethoxyethane with sodium—potassium alloy, which initially was reported to yield the stable dimesitylboryl radical, $(C_9H_{11})_2B^{\bullet}$ [13], has now been shown to produce the trimesitylborane radical anion [14,15]. By contrast, the dechlorination of phenylboron dichloride by sodium in refluxing toluene yields a mixture of $(C_6H_5B)_n$ oligomers, where n = 9—12 [16].

Results

This study of the dehalogenation of boron halides sought new ways to generate $R\underset{\substack{|\\ X}}{B}M$ intermediates, which might undergo alpha-elimination of MX

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* Since RC is a methyne or carbyne, RB could be termed a boryne [2]. But since the emerging ending for a valence two less than the normal valence is -ene (carbene, silene, nitrene, etc.), we suggest that RB be called borylene or borene. Analogous to carbene chemistry [3], boron(I) intermediates could be termed borene intermediates; their higher valent precursors, RBMX, would then be designed as borenoid intermediates.

to yield borenes, RB. As a trapping agent for borenes or other intermediates, diphenylacetylene was used. This alkyne had the advantage of revealing the stereochemistry with which any transient organometallic might have added to the C≡C linkage, by whether *cis*- and *trans*-stilbene would be formed upon protodemetallation. Alkynes, however, proved to be poor trapping agents for reactions involving boron bromides or iodides, since these reagents themselves readily add, in a haloborative manner, to the carbon—carbon triple bond [17, 18].

Organoboron dihalides and potassium metal in the presence of diphenylacetylene

The simultaneous reaction of phenylboron dibromide, potassium and diphenylacetylene, previously reported to yield hexaphenyl-1,4-dibora-2,5-cyclohexadiene, m.p. 146—149°C [7], seemed to be a possible borene reaction worthy of reexamination, especially since the interesting boron heterocycle had been only cursorily characterized. Neither a molecular weight determination nor any chemical structure proof was reported. However, after many attempts to reproduce the results reported in the literature [7], both by strict adherence to the published procedure and by several modifications thereof, we have been uniformly unsuccessful in obtaining the boron heterocycle. The only isolated organoborane fitting the reported melting point and within a reasonable deviation of the elemental analyses was triphenylborane (m.p. 147—148°C), which we obtained by a non-hydrolytic, distillative work-up of the reaction mixture. We are forced to conclude, therefore, that the reported synthesis of hexaphenyl-1,4-dibora-2,5-cyclohexadiene is erroneous *.

In order to learn the actual course of the reaction, a quantitative material accounting was undertaken. Isolation of the potassium bromide showed that it had been formed quantitatively. Column chromatography of the organic products permitted the isolation of over 55% of the boron as phenylboronic anhydride, and after acetolysis, 65—70% of the starting alkyne, 15% of 1,2,3,4-tetraphenylnaphthalene, 5% of *cis*-stilbene and 5% of hexaphenylbenzene.

From these results it is obvious that only a small proportion of the alkyne reacted at all and that most of the phenylboron dibromide simply gave an oligomer of PhB, similar to the findings of previous work [16]. The resulting oligomer could then have served as the source of the triphenylborane obtained by distillation and of the phenylboronic anhydride obtained upon acetolysis [16]. The formation of hexaphenylbenzene and the 1,2,3,4-tetraphenylnaphthalene can be attributed to the known reaction of phenylboron dibromide with the alkyne [19]. Finally, the *cis*-stilbene would have stemmed from a series of reactions similar to that already reported for the sequential bromoboration of diphenylacetylene and the debromination of the adduct by lithium metal [18] (eq. 1). Protodemetallation of II would yield *cis*-stilbene **.

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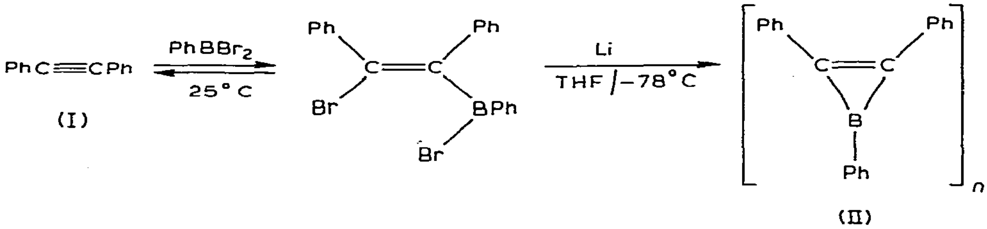
* After communicating our several failures in reproducing the published procedures to Professor Michael Lappert, we learned of the similar inability of several of his co-workers (inter alios, Dr. N.F. Travers) to reproduce these results.

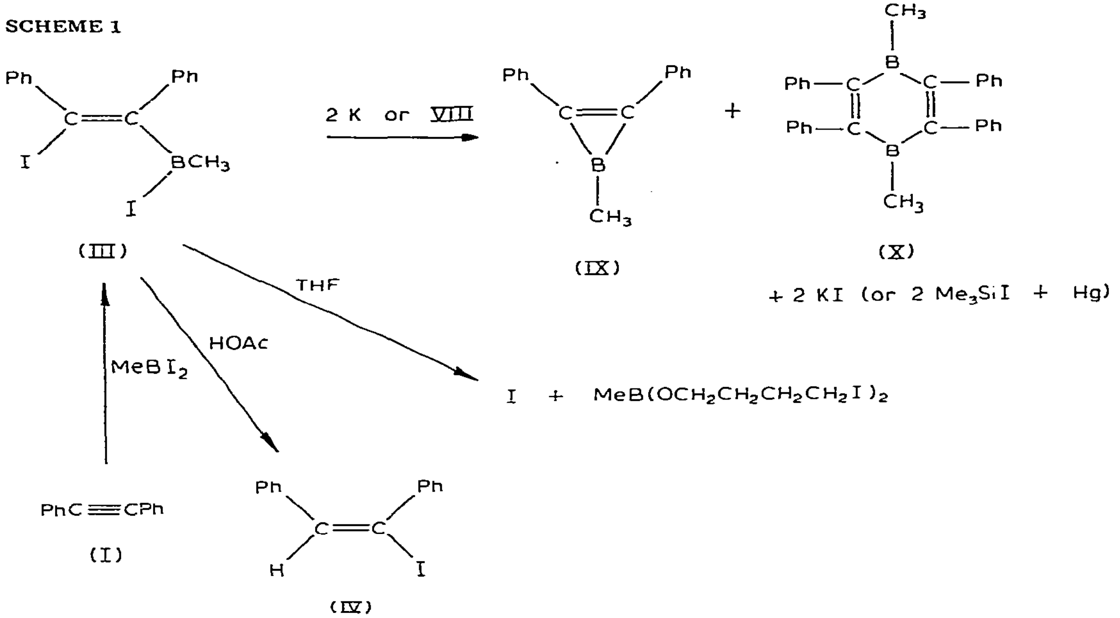
** Since II could not be isolated, the value of n is unknown. But the presence of *cis* vicinal carbon—boron bonds was deduced from the isolation of *cis*-1,2-dideuteriostilbene upon treating II with *O*-deuterioacetic acid [18].



(1)

Study of the reaction of methylboron diiodide with diphenylacetylene and potassium metal confirmed the greater ease of the stepwise process shown in eq. 1 over any borene pathway. The alkyne first underwent a rapid and complete iodoboration to yield principally one geometric isomer, III. Hydrolysis of III gave a mixture of the stilbenes (V) and their dimers (VI), since the hydrogen iodide formed in the hydrolysis caused the reduction of IV and the dimerization of V (cf. basic hydrolysis, which yielded I) (Scheme I). Deiodination of

SCHEME 1



adduct III by potassium metal or bis(trimethylsilyl)mercury (VIII) (cf. infra) and subsequent hydrolysis did yield principally *cis*-stilbene (70—92% of the stilbenes). These findings support the assignment of the *E*-configuration to the original adduct III.

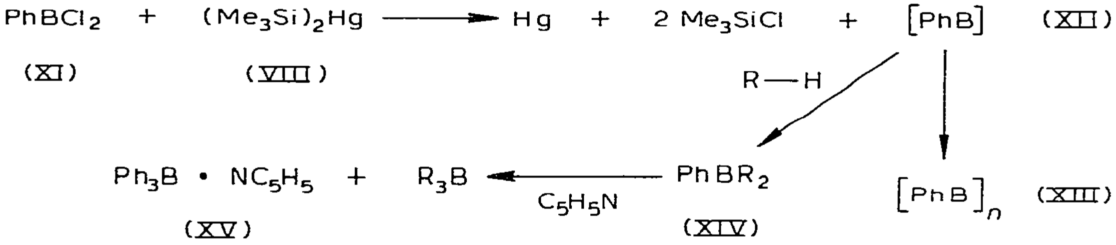
Since III rapidly cleaved THF, even at —40° C, the deiodination of III by potassium sand or VIII was carried out in a hydrocarbon medium. The reduction with $(Me_3Si)_2Hg$ was cleaner and rapid. At least 95% of the expected mercury and iodo(trimethyl)silane were found and the hydrolysis of a reaction aliquot showed that the volatile hydrocarbon fraction contained preponderantly *cis*-stilbene (90%). The possibility that ring closure (IX) or dimerization (X) might have occurred was investigated by direct NMR spectral examination of the boron products. The NMR spectrum of the unhydrolyzed reaction mixture showed two singlets of similar intensity at 0.88 and 0.98 ppm (combined intensity of 2 relative to 10 for phenyl). Although such proton signals could be due to the presence of IX and X, all attempts to isolate such boron heterocycles or their pyridine adducts have thus far been unsuccessful.

Reduction of phenylboron dichloride with bis(trimethylsilyl)mercury (VIII)

Because of the ease with which VIII deiodinated the adduct III and its known capability to dechlorinate R_2SnCl_2 to yield $[R_2Sn]_2$ [20], the reduction of phenylboron dichloride (XI) itself showed promise as a route to phenylborene. The reduction of XI by VIII in cyclohexane was instantaneous at 25° C, leading to 99% of the expected mercury and 92% of Me_3SiCl. The boron-containing product had no B—H bonds in its IR spectrum and it underwent rapid acetolysis to yield benzene and slower acetolysis of apparently alkyl—boron bonds. Oxidation of a reaction aliquot (from which all volatiles had been removed) with alkaline hydrogen peroxide gave only phenol. Treatment of a further aliquot with pyridine led to a 35% yield of triphenylborane pyridine.

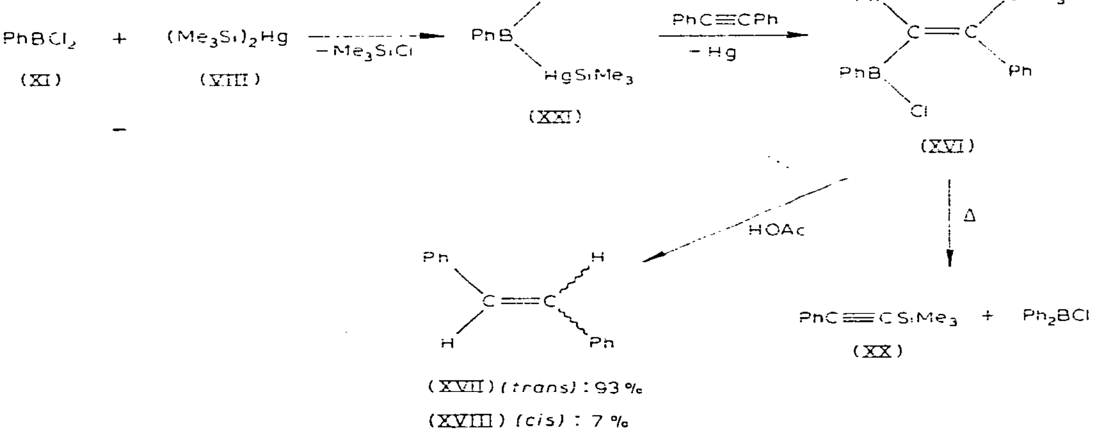
These results are in accord with the dechlorination of XI by VIII to yield phenylborene (XII), which either immediately underwent oligomerization to $[PhB]_n$ (XIII) [16] or reacted with carbon—hydrogen bonds to yield alkyl (phenyl)boranes (XIV). The disproportionation of the latter would account for the formation of Ph_3B (XV) (Scheme 2).

SCHEME 2



In order to trap any intermediate in this reaction, the reduction was conducted in the presence of diphenylacetylene (I). In this reaction only 58% of the expected Me_3SiCl was formed and a boron- and silicon-containing adduct of I was produced (XVI). This adduct underwent acetolysis to yield the stilbenes (XVII and XVIII) in a 93/7 ratio and pyrolysis to yield diphenylboron chloride (XIX) and trimethyl(phenylethynyl)silane (XX) (Scheme 3).

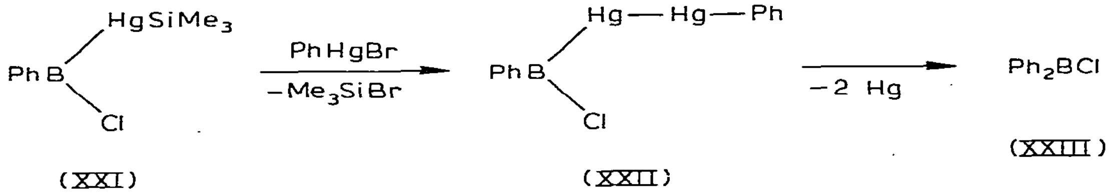
SCHEME 3



These results point to the initial formation of XXI, which adds to I with the loss of mercury. This elimination of mercury may well be a free-radical process; such a mechanism would account for the *trans* addition of the boryl and silyl groups.

When a combination of VIII and phenylmercuric bromide was used to reduce phenylboron dichloride, almost a quantitative yield of Me_3SiBr was obtained. Furthermore, 63% of diphenylboron chloride (XXIII) was isolated. A reasonable interpretation of these findings is that intermediate XXI can react with PhHgBr to yield a new intermediate XXII, which loses mercury to form XXIII (Scheme 4).

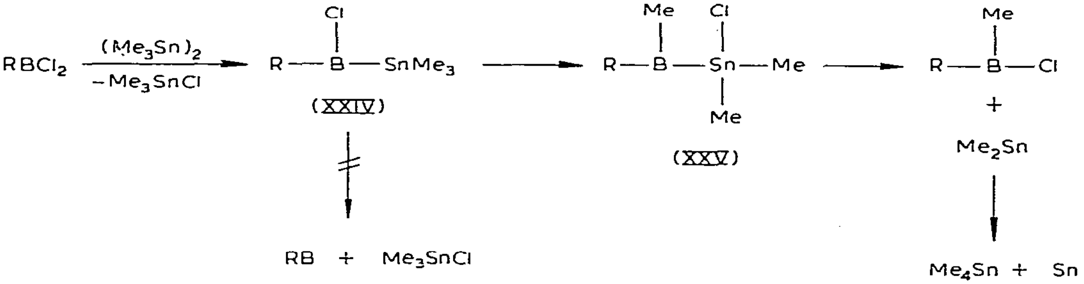
SCHEME 4



Reduction of boron halides by polystannanes

The reaction of diethyltin oligomer with phenylboron dichloride led to the formation of the ethyltin halides and possibly boron—tin bonds. But the reaction of XI or boron chloride with hexamethyldistannane gave a clearer understanding of the behavior of XI toward tin—tin bonds. Exactly one equivalent of Me_3SnCl was formed, as well as tin metal, Me_4Sn and methylboranes, Me_nBCl_{3-n}. These facts support the formation of XXIV, which undergoes rearrangement to XXV, rather than the formation of phenylborene by eliminating another equivalent of Me_3SnCl. Intermediate XXV then loses RBMeCl at higher temperatures to yield Me_2Sn, which disproportionates (Scheme 5).

SCHEME 5

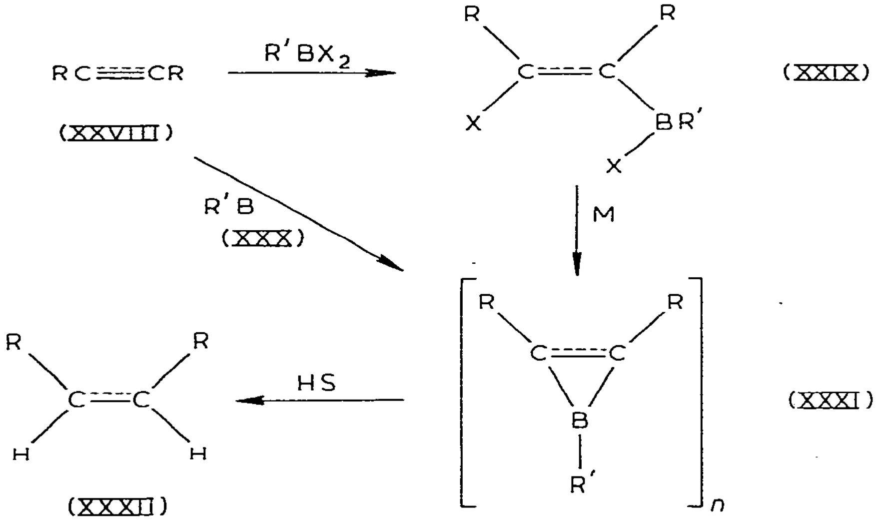


Discussion

Our findings show that the attempted detection of borenes, generated from organoboron dibromides or diiodides and metal reducing agents, by acetylenes cannot give reliable evidence. The ease with which haloboration of the carbon—carbon unsaturated linkage (XXVIII) occurs means that intermediates of the type XXIX will be formed very readily. These intermediates will possess *syn* or *cis* stereochemistry, especially if formed under conditions of kinetic control ([18] and eq. 1 and Scheme 1). Subsequent dechalogenation of such adducts by lithium (eq. 1), potassium or bis(trimethylsilyl)mercury (Scheme 1) and protodemetallation would yield the same *syn* or *cis* reduction (XXXII) products that would be expected from the addition of a borene (Scheme 6). Thus, the detection of either XXXI or XXXII constitutes no definitive proof for the operation of a borene process.

The foregoing considerations apply with equal validity to the use of olefins as trapping agents. The reported isolation of 7-methyl-7-borabicyclo[4.1.0]-heptane from cyclohexene, methylboron dibromide and potassium [8] cannot be taken as proof for the intervention of a methylborene intermediate. Since cyclohexene undergoes rapid bromoboration with BBr_3 [7], a non-borene pathway (XXIX → XXXI) is possible.

SCHEME 6



As to the actual structure of XXXI, no unambiguous physical data are available on the value of *n*. Although a kinetic argument can be made for the initial formation of a three-membered ring ($n = 1$ [18]), the definitive work on the trapping of BF would suggest that XXXI would tend to form a dimer ($n = 2$) or perhaps a linear polymer. This study has shown that the reported synthesis of hexaphenyl-1,4-dibora-2,5-cyclohexadiene from phenylboron dibromide, potassium and diphenylacetylene cannot be reproduced and that, in all likelihood, the supposed heterocycle was actually triphenylborane.

Because phenylboron dichloride does not chloroborate diphenylacetylene (I) at 25° C *, this halide could be reduced by bis(trimethylsilyl)mercury in the presence of I. That the reduction of the boron chloride occurred in discrete steps was shown by intercepting an adduct derived from XXI. In the absence of

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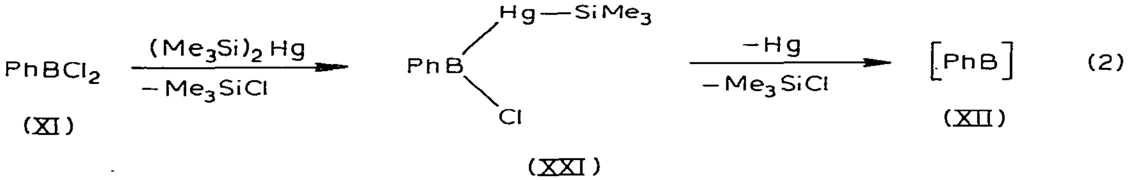
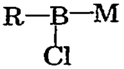
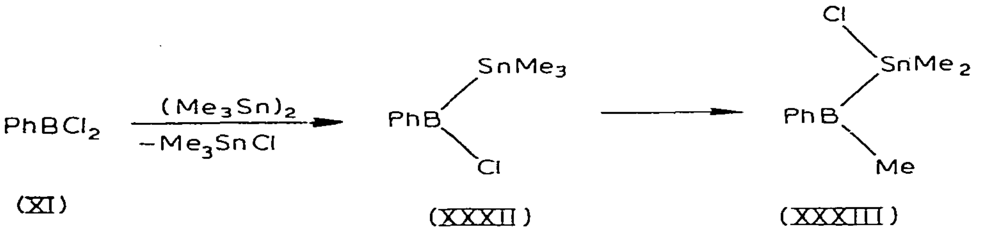
* But phenylboron dichloride does react with this alkyne at elevated temperatures to yield products ascribable to phenylboration: upon acetolysis, triphenylethylene and 1,2,3,4-tetraphenylnaphthalene are detectable [19].

I an alpha-elimination from XXI ensued to give PhB, which led to Ph_3B and the PhB oligomer (Scheme 2). An alternative trapping of XXI was effected with PhHgBr to yield diphenylboron chloride.

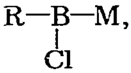


(2)

As a further approach to generating  $R{-}\underset{\displaystyle Cl}{\underset{|}{B}}{-}M$ intermediates suitable for alpha-elimination, distannanes were investigated. Cleavage of the metal—metal bond gave intermediate XXXII, which underwent a transalkylation (XXXIII). This intermediate underwent an alpha-elimination to yield a tin(II) derivative, rather than a boron(I) intermediate (eq. 3).



(3)

From this study it is clear that borenoids of the type,  $R{-}\underset{\displaystyle Cl}{\underset{|}{B}}{-}M$, where M = $HgSiMe_3$ or $SnMe_3$ vary widely in their tendencies to undergo alpha-elimination or rearrangement. Since borenoids, such as XXI, themselves react readily with alkynes, it is clear that selecting agents for the unambiguous trapping of borenes will require much circumspection.

Experimental

General technique

All reactions involving metals or organometallic reagents were conducted under an atmosphere of dry, oxygen-free nitrogen [21].

Starting materials

Methylboron diiodide. Tetramethylstannane (2.04 ml, 12.1 mmol) was added slowly to 18.7 g (48.4 mmol) of BI_3, which was cooled in an ice bath. (The excess BI_3 was used to suppress the formation of $(CH_3)_2BI$, which was difficult to separate.) After 1 h of reflux the CH_3BI_2 was removed at 50°C (0.01 mmHg) and caught in a bath chilled to —50°C; 4.8 g (46%) of slightly red product; NMR (neat) δ 1.72 [22,23]. The moisture- and light-sensitive compound was stored under nitrogen at —10°C.

Bis(trimethylsilyl)mercury (VIII). Sodium amalgam, prepared from 860 g of mercury and 6 g of sodium in toluene, was transferred under nitrogen to a 200 ml, thick-walled bottle having a 19/38 standard-taper, ground glass neck joint. During the transfer the bottle was provided with a two-necked 19/38 adapter, which allowed one neck for a nitrogen inlet and one neck for introducing the amalgam. Then 28.4 g (0.26 mol) of freshly distilled chloro(trimethyl)silane were added, the adapter quickly removed and the bottle sealed with a well-greased stopper, which was secured by rubber bands. The flask was placed on a shaker and agitated for 3 days (all the $(CH_3)_3SiCl$ should then have been consumed and dark yellow globules have formed). The stopper was quickly replaced by the above-mentioned two-way adapter (*Caution*: any product adhering to the stopper usually ignites at this point, so all solvent should be kept away until the adapter is in place). Then the bis(trimethylsilyl)mercury (VIII) was dissolved gradually by the portionwise addition of 300 ml of dry pentane to the bottle. After each addition the pentane extract was pipetted off and allowed to filter, under nitrogen, through a glass frit of fine porosity (a two-necked flask equipped with a nitrogen inlet and with a pressure-equalized glass frit was employed). After filtration the clear yellow solution was evaporated to dryness to remove residual chlorosilane and yellow VIII was obtained, yield 30 g (67%), m.p. 100—102° C. For use, VIII was redissolved in 60 ml of dry and deaerated benzene and the stock solution kept in the refrigerator in a Schlenk vessel or a bottle provided with a septum. For analysis, 1 ml samples were placed in a tared beaker and exposed to air. The precipitated mercury was washed with diethyl ether, dried and weighed.

Diethyltin oligomer. This compound was prepared from diethylstannane and di-t-butylmercury in diethyl ether [19] (*Caution*: product ignites in air). Yellow diethyltin: NMR (neat) δ 1.42 ppm, m. The absorption for $(CH_3CH_2)_2SnH_2$ (Sn—H at 4.40 ppm) and $[(CH_3)_3C]_2Hg$ (0.88 ppm) has disappeared.

Reaction of phenylboron dibromide with potassium metal in the presence of diphenylacetylene *

To a suspension of 1.26 g (32.2 mg-at) of the potassium metal in a solution of 2.86 g (16.1 mmol) of diphenylacetylene dissolved in 50 ml of ligroine (b.p. 80—100° C) were added 4.0 g (16.1 mmol) of phenylboron dibromide. A yellow color developed immediately. After 4 h of stirring under reflux the suspension was filtered under nitrogen. The dark-colored salt was washed with butanol (slight hydrogen evolution from residual potassium), then with absolute ethanol and finally dried. Yield: 4 g (100%) of potassium bromide.

The organic filtrate was evaporated to dryness to give 4.24 g of a dark syrup. Stirring this residue with 50 ml of petroleum ether (b.p. 40—60° C) gave essentially complete dissolution (only hexaphenylbenzene did not dissolve; contrast the report in ref. 7). Cooling to —50° C deposited a yellow oil; the decanted solution was found to contain 420 mg (15%) of the diphenylacetylene (GLC on a UCON-W98 phase at 200° C). The acetolysis of this decanted solution with glacial acetic acid did not yield any stilbenes.

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* Dr. S. Kozima cooperated in our reinvestigation of the published procedure [7] and was the first to show the actual complexity of the reaction (1968, The Catholic University of America).

Acetolysis of the yellow oil obtained at —50° C yielded an oil, whose GLC analysis showed it to contain 150 mg (5%) of *cis*-stilbene, 500 mg (18%) of the starting acetylene and 500 mg of 1,2,3,4-tetraphenylnaphthalene. The last compound was also separated and was identified by IR and mixture melting point comparisons. In addition, 120 mg of hexaphenylbenzene (m.p. 425° C, IR) was isolated.

In a run carried out exactly as described in the literature, the KBr was filtered from the reaction mixture and the ligroine was evaporated from the resulting filtrate. Addition of petroleum ether dissolved all the residue except for the small amount of hexaphenylbenzene (150 mg). The petroleum ether extract was chromatographed on a silica gel column and eluted with hexane. In this manner 65% of the diphenylacetylene was recovered and 5% of *cis*-stilbene and 15% of 1,2,3,4-tetraphenylnaphthalene were obtained. By elution of the column with a ligroine/benzene pair 1.95 g of a semi-solid component was eluted, whose recrystallization from an ethanol/benzene pair gave 1.85 g (55%) of phenylboronic anhydride, m.p. 210—212° C (mixture m.p. and IR comparisons).

This same reaction was attempted at least six times, both with strict adherence to the reported procedure [7] or with changes in the order of admixing the reagents and in the time of reaction. In no instance was any boron-containing compound melting in the reported range of 146—149° C ever found. Only when the reaction was conducted as described above, the KBr filtered off, the solvent removed and the residue distilled under reduced pressure, did we succeed in distilling over a boron-containing product, m.p. 147—148° C from toluene, but this proved to be triphenylborane (mixture m.p., IR, NMR).

Reaction of the adduct of methylboron diiodide with reducing agents

(a) Formation of iodo(E-2-iodo-1,2-diphenylethenyl)methylborane (III). To 1.01 g (3.59 mmol) of methylboron diiodide in 3 ml of dry pentane was added 640 mg (3.59 mmol) of diphenylacetylene. The color turned rapidly from faint red to yellow. After stirring for 30 min at 25° C the solvent was removed at 100° C in vacuo. The residual oil did not solidify, when cooled neat or in hexane, down to —80° C. NMR (CCl_4) δ(ppm): 6.80, s, 10 and 1.60, s, 3; IR (neat): 1509 cm^{-1} (C=C).

When a pentane solution of III stood for 5 days at 25° C, a new phenyl multiplet appeared at 7.57 ppm. This might have signaled the formation of the *Z* isomer.

The adduct turned dark upon exposure to light and hydrolyzed very readily to yield stilbenes and higher-boiling hydrocarbons.

(b) Adduct III and potassium. Tetrahydrofuran could not be used to promote these reactions, for methylboron diiodide rapidly cleaves THF, possibly forming $CH_3B(OCH_2CH_2CH_2CH_2I)_2$ (new peaks appeared at 0.17 (s), 1.85 (m) and 3.25 (m) ppm).

A solution of 3.71 g (8.0 mmol) of III in 10 ml of pentane was added to 630 mg (16.0 mg-at.) of potassium dispersion and the reaction mixture stirred vigorously for 3 days. An aliquot of the supernatant liquid was hydrolyzed and titrated with standard NaOH; this showed that 10% of B—I bonds were still present. The KI solid was filtered off and washed with pentane. The combined filtrate was freed of volatile matter and examined by NMR (CCl_4) δ(ppm) 6.9—7.6, m, 10; 1.35—1.55, m, 0.7; 1.1—1.3, m, 0.6; 0.95—1.1, 0.6; 0.7, s, 1.1. Acetolysis of an aliquot of this residue with glacial acetic acid yielded a 2.8/2/1 mixture of *cis*-stilbene, diphenylacetylene and *trans*-stilbene. Attempts to crystallize the boron-containing residue directly or in the form of a pyridine adduct failed.

(c) Adduct III and bis(trimethylsilyl)mercury (VIII). To 2.15 g (4.65 mmol) of III in 5 ml of cyclohexane was added 1.5 g (4.6 mmol) of VIII in 6 ml of cyclohexane. Immediately 88 mg (95%) of mercury precipitated and an NMR spectrum of the filtered reaction mixture showed 95% of all $(CH_3)_3Si$ groups were present as $(CH_3)_3SiI$. Two closely spaced singlets occurred at 0.88 and 0.92 ppm (relative intensity to phenyl multiplet at 7.05 ppm = 2/10) and a cluster of singlets occurred at 0.1—0.35 ppm (CH_3Si, ?).

The organic residue after removal of the volatiles was analyzed: 465 mg of the residue in 4 ml of cyclohexane was treated with 0.6 ml of glacial acetic acid. A GLC analysis taken immediately thereafter showed the presence of *cis*-stilbene, *trans*-stilbene and diphenylacetylene in a ratio of 35/3/1.

Reactions of diethyltin oligomer with phenylboron dichloride (XI)

After admixture of 750 mg (4.24 mmol) of diethyltin with 670 mg (4.24 mmol) of XI in 5 ml of benzene for 12 h the solvent was removed at 25°C (0.1 mmHg) and all volatiles at 70°C (0.1 mmHg). The latter proved to be a mixture of 20% of triethyltin chloride and 12% of diethyltin dichloride (identified as its bispyridine complex, m.p. 134—135°C). The orange reaction residue displayed NMR ($CDCl_3$) absorptions at 7.85, m, 2; 7.20, m, 3; 1.42, m, 7 and 1.03, m, 2 (ppm). Acetolysis of the NMR sample in C_6H_6 yielded a gas (H_2), benzene and diethyltin diacetate. Upon heating to 150°C tin metal was deposited (m.p., dissolution in HCl).

Reactions of bis(trimethylsilyl)mercury (VIII) with metalloid halides

(a) Phenylboron dichloride (XI). To 1.73 g (5 mmol) of VIII in 9 ml of cyclohexane were added 795 mg (5 mol) of phenylboron dichloride. Metallic mercury deposited instantly (99 mg, 99%). The brown suspension was stirred for 15 min and then all volatile substances were removed at 40°C (0.15 mmHg) and caught in a cold trap. Quantitative GLC showed that 92% of the expected $(CH_3)_3SiCl$ had been formed, as well as ca. 5% of boron-containing compounds, b.p. 150°C, NMR (CCl_4) δ 0.2, s, with smaller singlets at 0.1 and 0.5 ppm.

An infrared spectrum of the brown residue resulting from the removal of volatiles showed no B—H absorptions in the 2000—2500 cm^{-1} region. It was redissolved in hexane and cooled to —70°C to precipitate 200 mg of a yellow oil; NMR (C_6H_6) δ 7.7, m, 2; 7.3, m, 3; 0.0—1.5, br. m, 5. Upon treating this oil with glacial acetic acid the aromatic multiplet immediately collapsed to a benzene singlet (separated and identified), while the aliphatic slowly yielded sharper absorptions upon heating the acetolysis mixture.

The hexane-soluble fraction was treated with ether and dry pyridine to precipitate 185 mg (35% of all phenyl groups) of triphenylborane, m.p. 216—218°C (mixture m.p., IR and NMR).

Oxidation of the total non-volatile residue from a similar run with sodium hydroxide and 30% hydrogen peroxide gave only phenol; no sign of dihydroxybenzenes was obtained.

(b) Phenylboron dichloride (XI) in the presence of diphenylacetylene. To 786 mg (4.95 mmol) of XI and 88 mg (4.95 mmol) of diphenylacetylene in 5 ml of cyclohexane was added 1.71 g (4.95 mmol) of VIII in 8 ml of cyclohexane. In an exothermic reaction 87 mg (90%) of the mercury precipitated and NMR analysis showed the formation of 58% of $(CH_3)_3SiCl$. After filtration all components volatile up to 80°C (0.2 mmHg) were removed and the NMR spectrum of the residue measured (C_6H_{12}) (ppm): 8.73, m, 2; 7.40, m, 3; 6.90, m, 10; —0.05, s, 9. These data are in accord with structure XVI. Acetolysis of a sample yielded *trans*- and *cis*-stilbenes in a ratio of 93/7. Attempted distillation of this residue at 200°C and 0.2 mmHg gave a distillate composed of diphenylboron chloride (hydrolysis to diphenylborinic acid), trimethyl(phenylethynyl)silane (GLC, IR), tolane and compounds yielding *cis*- and *trans*-stilbenes upon acetolysis (ratio of 7/93).

(c) Phenylmercuric bromide and phenylboron dichloride (XI). To 955 mg (6 mmol) of XI and 2.14 g (6 mmol) of phenylmercuric bromide in 5 ml of benzene were added 2.07 g (6 mmol) of VIII in 10 ml of benzene. In an exothermic reaction 73% of the expected mercury precipitated; the filtrate was then evaporated and 50% of $(CH_3)_3SiCl$ and ca. 100% $(CH_3)_3SiBr$ were estimated in the volatiles by GLC. The residue was distilled to yield 63% of diphenylboron chloride, b.p. 108—110°C (1 mmHg), which was hydrolyzed and the resulting diphenylborinic acid identified by MS. The distillation residue was insoluble in hot benzene; strong heating did generate mercury metal.

Reactions of hexamethyldistannane

(a) Boron trichloride *. To a suspension of 3.27 g (10 mmol) of the distannane in 10 ml of dry toluene was added at —78°C 1.17 g (10 mmol) of boron trichloride. The cooling bath was removed and the stirred mixture allowed to attain 20—25°C, whereupon it set to a white paste. After 90 min at 25°C the volatile components were drawn off into a cold trap over 12 h at 0.1 mmHg. The residue was resuspended in 15 ml of toluene and the volatiles again removed at 75°C and 0.1 mmHg. The resulting residue was filtered and washed with ether and acetone to yield 413 mg (70%) of tin metal (m.p., solubility in HCl). Analysis of the toluene solution from the cold trap by GLC (bromobenzene as standard) showed the presence of 2.00 g (100%) of chloro(trimethyl)stannane. Distillation of this toluene solution under nitrogen gave a pyrophoric forerun (methylboron chlorides; NMR [24]) and a main fraction, boiling up to 105°C, which by NMR analysis was shown to contain 16% of tetramethylstannane.

(b) Phenylboron dichloride *. A solution of 530 mg (3.3 mmol) of phenylboron dichloride in 2.0 ml of benzene was treated with 1.10 g (3.4 mmol) of the distannane in 2.0 ml of benzene. An NMR spectrum of the reaction mixture, with a cyclohexane standard, showed the presence of one equiv. of

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* These experimental results were obtained by Dr. James E. Galle of this Laboratory, who was helped by the orientating investigations of Dr. H.R.H. Patil.

$(CH_3)_3SnCl$, $(CH_3)_4Sn$, a broad singlet at δ +0.82 and two sharp singlets at +0.60 and +0.28 ppm. Tin metal formed upon heating the reaction mixture.

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