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BORA-AROMATIC SYSTEMS
I[*]. COMPETITION BETWEEN HALOBORATION AND PHENYLBORATION IN THE ATTEMPTED SYNTHESIS OF TRIPHENYLBORACYCLOPROPENE[**]

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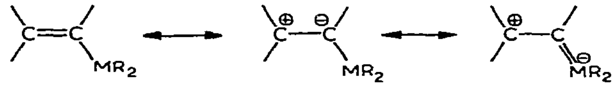
INTRODUCTION

The ability of Group IIIA metals to form π-bonds to carbon (1) remains one of the classic and fundamental questions of organometallic chemistry. Because of the well-documented ability of Group IIIA metal alkyls to accept electron pairs from extramolecular donors (R_3N, R_2O, X^-, or R^-)[2], it seems reasonable to postulate an intramolecular π-electron donation as depicted in (1). Further considerations suggest that observation of such a so-called p_π–p_π overlap would be more probable in organoboranes than in other Group IIIA metal alkyls. In the first place, trivalent boron is a pronouncedly Lewis acidic center and, in the absence of steric effects, apparently a stronger Lewis acid than compounds of gallium, indium and thallium[2,3]. Secondly, organoboranes are monomeric whereas organoaluminum compounds are associated[4]. Thus, observation of the postulated p_π–p_π effect (1) in the monomer would be more difficult with aluminum. Thirdly, the covalent radius of boron is almost the same (0.80 Å) as that of carbon (0.77 Å), thus permitting some overlap of the adjacent $2p_z$ orbitals. And, finally, the polarity of the carbon–boron bond is the lowest among Group IIIA metal bonds to carbon, as judged by Allred–Rochow electronegativities ($B = 2.01$, $C = 2.51$)[5]. This reduced polarity should be more compatible with a π-electron density increase on the α-carbon atom (1).



(1)

The interpretation of chemical and spectroscopic data on vinyl- and arylboranes has invoked this postulated p_π–p_π effect[6], but existing evidence is open to other reasonable explanations. Consequently, previous researchers have attempted to incorporate boron into cyclic conjugated systems, in order to learn whether the resulting boracarbocycles would furnish more compelling evidence for or against carbon–boron π-conjugation. Recently pentaphenylborole[7] and 5-phenyldibenzoborole[8] have been prepared and characterized. But of especial interest have been

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[*] Paper VIII of the series, "Organometallic Compounds of Group III"; for previous paper see ref. 1.

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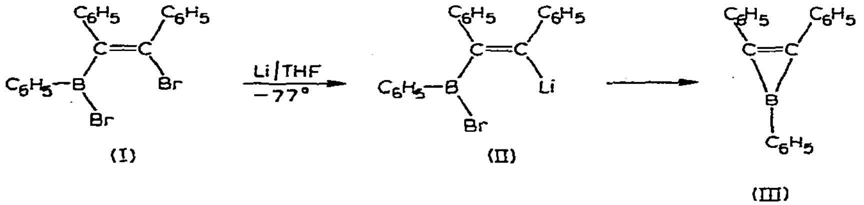
efforts to prepare bora-aromatic systems such as borepin (boracycloheptatriene) and borirene (boracyclopropene), where the total number of π-electrons would conform to Hückel's criterion for aromaticity (*cf.* ref. 9).

As part of a continuing interest in Group IIIA heterocycles the synthesis of the borirene nucleus recently has engaged our attention. Indeed, the theoretical importance of this system as a boron counterpart of the cyclopropenyl cation or cyclopropenone ring[10] has been appreciated previously[11,12]. The present work describes a possible tactical approach to the synthesis of triphenylborirene and reports on the interesting competitive bromoboration and phenylboration of tolane encountered in this projected synthesis. In addition, preliminary chemical evidence consistent with the initial formation of the borirene ring in solution is presented and evaluated.

RESULTS

Since organoboranes may be prepared readily by the action of organolithium reagents on boron halides[13], a logical starting material for the synthesis of the borirene nucleus is a *cis*-β-halovinylboron halide (I). For the subsequent generation of a carbon–lithium bond (II) could lead to the borirene nucleus (III) by an intramolecular nucleophilic displacement:



The initial problem, therefore, was to obtain the desired intermediate (II). Fortunately, recent studies of the haloboration of alkynes provide excellent guidance on the synthesis of β-halovinylboranes[14]. Thus diphenylacetylene(tolane) and boron tribromide were found to react readily to yield (2-bromo-1,2-diphenylvinyl)dibromoborane in 75% yield. Consequently, in this research the addition of phenyl boron dibromide to tolane appeared to be the most promising route to the requisite (*cis*-2-bromo-1,2-diphenylvinyl)phenylboron bromide (I). Although reaction occurred promptly upon the neat admixture of these reagents, the course of the reaction showed an amazing sensitivity to kinetic and thermodynamic factors. Spectra examination of the initial adduct displayed new bands at 850, 1050 and 1250 cm^{-1} in the infrared and at 7.09, 7.54, 8.13 and 8.25 ppm in the NMR spectrum (δ-scale). Subsequent treatment of the adduct with glacial acetic acid (reagent for cleaving carbon–boron bonds[14]) gave up to a 60% yield of *cis*-α-bromostilbene. These observations are in accord with a successful bromoboration leading to the desired intermediate (I) (eqn. 1)*.

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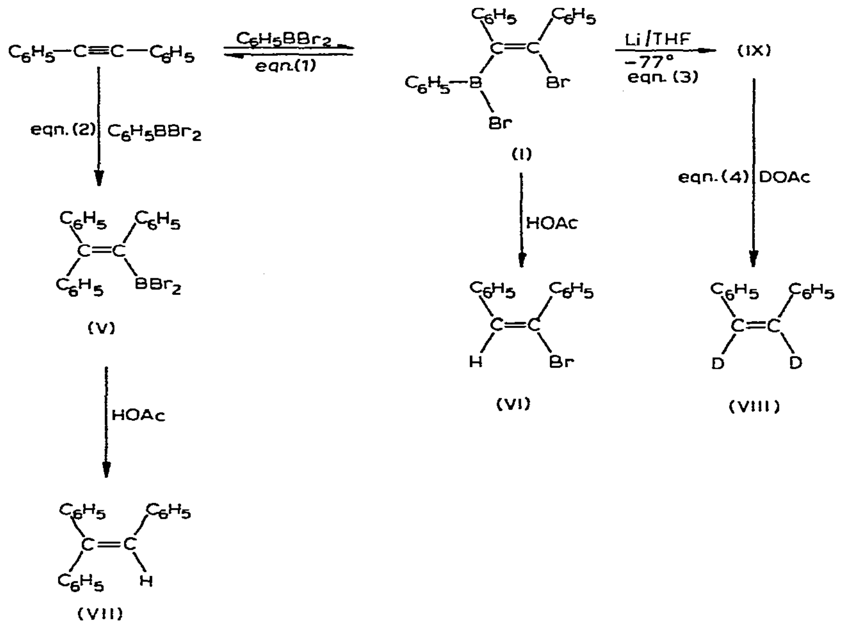
* Possible addition of hydrogen bromide, formed by the acetolysis of phenylboron dibromide, to diphenylacetylene would be expected to yield *trans*-α-bromostilbene[15].



Scheme 1. Reactions of phenylboron dibromide with diphenylacetylene.

However, attempts to purify (I) revealed its lability. Prolonged storage at ambient temperature or attempted crystallization from hydrocarbon solvents led to a high yield of triphenylethylene upon acetolysis. This result suggests that bromoboration occurred in a kinetically controlled, easily reversible manner, and that phenylboration could ensue as a slower, but essentially irreversible, competiting process (eqn. 2).

The reversibility of the haloboration shown in eqn. (1) was demonstrated by two additional experiments. In the first study, donor substances were added to the neat mixture of diphenylacetylene and phenylboron dibromide before acetolysis. Thus, addition of either anhydrous ethyl ether or of water and subsequent treatment with acetic acid caused almost complete regeneration of diphenylacetylene. In the second study, a pentane solution of the adduct was allowed to interact with lithium metal at 25°. The slow reaction eventually led to the deposition of lithium bromide. The subsequent acetolysis permitted a 93% recovery of diphenylacetylene and phenylboronic acid. Because of the absence of the $B(C_6H_5)_4$ anion in the hydrolysis products, these preliminary results point to the formation of a phenylboron polymer or possibly $C_6H_5BLi_2$*. In any event, it is certain that the phenylboron dibromide is dehalogenated by the alkali metal, causing adduct (I) to revert to its components. Both these experiments are consistent with a mobile equilibrium between adduct (I) and its components. In sum, then, chemical diversion of the phenylboron dibromide by phenylboration (eqn. 2), by etherate formation, by hydrolysis to the boronic acid, or by dehalogenation, causes disruption of the adduct.

Since the foregoing findings indicated that admixture of tolane and phenylboron dibromide gave only about 50–60% conversion to the unstable (I), the closure

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* This reaction is under investigation in this laboratory.

of (I) with lithium metal to form triphenylborirene (III) was attempted directly with the crude adduct. Therefore, the kinetically controlled adduct (I) was cooled to −77° to "freeze in" the equilibrium of eqn. (1). In order to foster the formation of the *cis*-*β*-(bromophenylboryl)stilbenyllithium reagent (II) from (I), tetrahydrofuran (THF) was chosen as the reaction medium[16]. Separate control experiments gave assurance that the THF at −77° did not cause dissociation of (I) as ethyl ether did at 25°. Acetolysis of low temperature samples of (I) in THF gave yields of *cis*-*α*-bromostilbene ranging up to 70%.

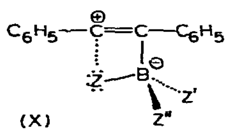
The interaction of adduct (I) in THF with lithium metal at −77° caused the development of a deep yellow and eventually a dark brown solution (eqn. 3). Acetolytic work-up revealed the presence of *cis*-stilbene (VIII) and traces of triphenylethylene (eqn. 2). By the acetolysis of aliquots the reaction was monitored until the yield of *cis*-stilbene was optimal (65–75%) and that of *cis*-*α*-bromostilbene was negligible. Previous control experiments had demonstrated that the *cis*-stilbene could not have arisen from the interaction of lithium metal with diphenylacetylene directly, even in the presence of phenylboron dibromide.

Evidence on the nature of the organometallic precursor (IX) of the *cis*-stilbene (VIII) was obtained by the following reactions. First, a solution aliquot of the reaction mixture was treated with CH_3COOD (eqn. 4). The *cis*-1,2-dideuteriostilbene isolated was shown by NMR spectroscopy and mass spectrometry to have a deuterium content in fair agreement with the purity of the deuterated acetic acid employed. Secondly, treatment of large aliquots of (IX) separately with benzyl chloride, with methyl iodide, and with carbon dioxide gave no alkylated or carboxylic acid derivatives of *cis*-stilbene. Taken together, these results support the presence of an organometallic precursor of *cis*-stilbene having *cis*-vicinal carbon–metal bonds. The failure of this precursor to react with reactive alkyl halides or with carbon dioxide rules out the presence of carbon–lithium bonds. Therefore, it is concluded that the precursor (IX) must have vicinal *cis* carbon–boron bonds.

Thus far, attempts to isolate the organoborane precursor (IX) of *cis*-stilbene have not been successful. Distillation of the reaction mixture has led to a distillate consisting principally of triphenylborane, admixed with a compound yielding *cis*-stilbene upon protolysis. In continuing research non-distillative purification will be employed, in order to minimize decomposition of the desired organoborane precursor (IX).

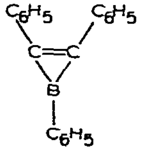
DISCUSSION

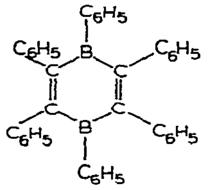
Two important aspects in the proposed synthesis of triphenylborirene deserving comment at this time are: (*a*) the competition between bromoboration and phenylboration of diphenylacetylene; and (*b*) the nature of the organoborane precursor (IX) of *cis*-stilbene, formed from (I) by the action of lithium metal. In the first case, the observation of kinetic control in the *cis*-bromoboration of diphenylacetylene adds perspective to our knowledge of haloboration. Although previous workers[14] have been inclined to view haloborations as thermodynamically controlled processes, these results stress that kinetic factors cannot be neglected. Since *cis*-adduct (I) is formed faster than the more stable adduct (V), it is appealing to propose a four-center transition state (X) involving electrophilic attack by boron and bridging by the migrating group Z. The more readily group Z can furnish electron density to the electron-deficient carbon, the more readily Z can bridge and thus migrate. The

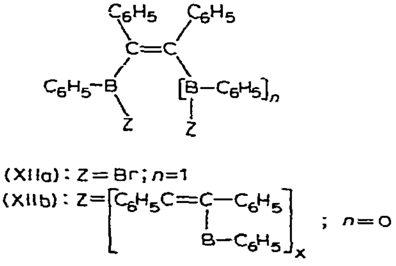

(X)

expected kinetic migratory aptitude of Z in BZZ'Z" on this basis would be Br > Cl > R. Although existing data generally are in accord with this view, further studies on such additions are in order. Similar interpretations have proved fruitful in understanding the additions of Al–H and Al–C bonds to unsaturated hydrocarbons[17–19].

As to the behavior of adduct (I) toward lithium metal, the chemical evidence adduced above strongly supports the conclusion that (IX) is a stilbene derivative having vicinal *cis*-carbon–boron bonds at the vinyl carbons. Therefore, the possible structures for (IX) which merit consideration are: (*a*) triphenylborirene (III); (*b*) hexaphenyl-1,4-diboracyclohexadiene (XI); and (*c*) some open-chain boron monomer or polymer of type (XII)*. Structure (XI) has been assigned recently[12] to a compound melting at 149°, but neither molecular weight data nor organic degradation products have been reported. Structure (XIIa) might be formed from the interaction of (I) and (II); however, in this case the maximum yield of *cis*-stilbene could be only 50%. A choice among (III), (XI) and (XIIb) as being the organoborane precursor (IX) must await the examination of a pure sample. Nevertheless, a cogent stereochemical argument favoring the *initial* formation of triphenylborirene, rather than hexaphenyl-1,4-diboracyclohexadiene or a polymer can be put forward at this time. Examination of a Stuart–Briegleb model of adduct (I) shows that the plane containing the trigonal bonds from boron to bromine, phenyl and the vinyl carbon is constrained to be essentially perpendicular to the plane of the C=C and C–Br bonds. As a consequence, $2p_z$ orbital of boron is projected toward and in the plane of the carbon–bromine bond. Therefore, the subsequent generation of the carbon–lithium bond (II) should


(III)


(XI)


(XIIa): Z = Br; *n* = 1
(XIIb): Z = [...]ₓ ; *n* = 0

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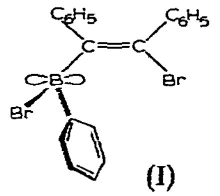
* Another group of possible structures for the $C_4B_2R_6$ system would be some type of organocarborane, involving multicenter bonding of the type encountered in boron hydrides. Recent preliminary reports suggest either an octahedral array ($R = C_6H_5$) or a pentagonal pyramidal array (R = alkyl) for this class of carboranes[20,21].


(I)

strongly favor intramolecular nucleophilic attack at boron leading to triphenylborirene (III). Such an intramolecular reaction should proceed at a rate higher than that of the intermolecular displacement because of a smaller decrease in entropy in the transition state. Furthermore, the rate of cyclization would be expected to be independent of concentration, in contrast to the cyclic dimerization to (XI).

EXPERIMENTAL

General technique

Starting materials and products. The diphenylacetylene was prepared from benzyl dihydrazone according to a published procedure[22] and was shown to be free *trans*-stilbene. *cis*-α-Bromostilbene was synthesized from DL-dibromobibenzyl by base-promoted dehydrohalogenation[23] and triphenylethylene was obtained from dehydration of 1,1,2-triphenylethanol[24]. *cis*-Stilbene, *trans*-stilbene, phenylboron dichloride and boron tribromide were obtained commercially from Aldrich–Alpha Chemical Company and were found by chromatographic and spectroscopic examination to be sufficiently pure.

The phenylboron dibromide was prepared from mercuric bromide in the following modified two-step procedure[25]. Phenylmercuric bromide was prepared from phenylmagnesium bromide in ethyl ether and anhydrous mercuric bromide[26] (the finely ground mercuric salt was warmed in an evacuated flask and repeatedly flushed with dry nitrogen). The crude phenylmercuric bromide subsequently obtained was dried very thoroughly but was not recrystallized. The fine powder reacted more promptly with the boron tribromide in the following heterogeneous reaction than did the recrystallized phenylmercuric bromide. Thus, from the reaction of 200 g (0.8 mole) of boron tribromide with 286 g (0.8 mole) of phenylmercuric bromide in refluxing benzene and subsequent removal of solvent, one obtained 153 g (78%) of colorless phenylboron dibromide, b.p. 65–66°/1.0 mm, m.p. 29–30°.

All hydrocarbon and ether solvents were of reagent grade and were distilled from lithium aluminum hydride immediately before use.

Instrumentation. Melting points were determined in glass capillaries and are corrected. Infrared spectra were measured in carbon disulfide solution on a Perkin–Elmer Infrared Spectrophotometer, Model 137. Gas chromatograms were obtained with an F & M Gas Chromatograph, Model 720, by use of a programmed heating rate of 10°/min and electronic integration of the peaks. A 10% silicone oil-on-firebrick column was satisfactory for all the reported analyses. Response factors were determined with authentic samples. NMR spectra were recorded with a Varian A-60 NMR spectrometer and chemical shift values are reported on the δ-scale, relative to tetramethylsilane as an internal standard.

Manipulation. Because of the oxygen- and moisture-sensitivity of organoboron, organolithium and haloboron compounds, all transfers and reactions were conducted under an atmosphere of pure, dry nitrogen. Even protolyses of organoboranes with acetic acid were performed under nitrogen, since the cleavage of the carbon–boron bond by oxygen could compete with the slow protolytic cleavage.

Control experiments

The following experiments demonstrated the individual behavior of the diphenylacetylene and the phenylboron dibromide toward alkali metals.

a. Diphenylacetylene and lithium in tetrahydrofuran. A flask containing a solution of 1.00 g (5.6 mmole) of diphenylacetylene in 60 ml of absolute tetrahydrofuran (THF) was cooled to −77° in a bath of solid carbon dioxide in methanol contained in a Dewar flask. Thereupon 200 mg (29 mg-atom) of finely divided, freshly cut lithium metal was added and the suspension then stirred vigorously by a motor-driven glass blade stirrer. After 48 h, the clear colorless solution was decanted and then treated with 30 ml of a 1 : 4 by volume solution of acetic acid in petroleum ether (b.p. 30–60°). Solvent removal led to a 98% recovery of diphenylacetylene. Examination of this solid by thin-layer chromatography on alumina (Woelm neutral) with development by either cyclohexane or carbon tetrachloride revealed no trace of *cis*-stilbene. *Cis*-stilbene would have separated cleanly from tolane under these TLC conditions.

b. Diphenylacetylene and lithium in pentane/ether. A solution of 1.00 g (5.6 mmole) of tolane in 25 ml of absolute pentane was stirred vigorously with 400 mg (58 mg-atom) of lithium cuttings at 25° for 5 h. Since there was no sign of reaction, 3 ml of absolute ethyl ether were added. After a further 13 h of stirring, only a slight straw color had developed. Within the next 8 h an additional 8 ml of ether was added. Finally, after a total of 26 h a red solution and a brown precipitate formed. The suspension was stirred for an additional h. Protolysis in the aforementioned manner yielded principally *cis,cis*-1,2,3,4-tetraphenylbutadiene. A TLC analysis revealed no *cis*-stilbene and no remaining tolane.

c. Phenylboron dibromide, diphenylacetylene and lithium in tetrahydrofuran. A solution of 810 mg (3.21 mmole) of phenylboron dibromide in 40 ml of absolute THF was stirred with 800 mg (116 mg atom) of lithium cuttings at −77°. After 120 h the lithium was unattacked and the colorless organic solution gave a negative flame test for lithium.

Then 565 mg (3.2 mmole) of diphenylacetylene were added and the suspension was stirred for a further 48 h at −77°. Samples were withdrawn after each 24 h and protolyzed by refluxing with 30 ml of acetic acid in petroleum ether. The protolyzed samples were diluted with water and extracted with ether. The ether extract was treated with dilute sodium hydroxide to remove boric acids. Removal of solvent from the dried ether solution yielded only tolane, as revealed by infrared analysis and thin-layer chromatography.

The remaining reaction mixture was stirred at room temperature for another 24 h and then divided into two parts. One portion was protolyzed with acetic acid, as above; the other was treated with water. Usual work-up yielded only tolane. In fact, 98–100% of the original tolane was recovered from all the combined samples. The absence of *cis*-stilbene (monomolecular reduction of tolane), *cis,cis*-1,2,3,4-tetraphenylbutadiene (bimolecular reduction of tolane) and *cis*-α-bromostilbene (adduction of tolane and phenylboron dibromide) was significant.

d. Phenylboron dibromide, diphenylacetylene and lithium in pentane/ether. A solution of 660 mg (2.64 mmole) of phenylboron dibromide in 50 ml of absolute pentane was stirred at 25° with 400 mg (58 mg-atom) of fine lithium cuttings. Since stirring for 5 h caused no precipitate (LiBr) 8 ml of absolute ethyl ether were added over 5 h. At the end of this time a white precipitate began to form; within the next 12 h a copious precipitate had formed.

Then 469 mg (2.6 mmole) of tolane were introduced. During the next 6 h no red coloration signaling the tolane–lithium metal reaction appeared. Therefore, 20 ml of absolute ethyl ether were added and the system stirred for an additional 18 h. Over this period the solution was the characteristic dark red of the tetraphenylbutadienylenedilithium. Protolysis with acetic acid and usual work-up showed the presence of the tetraphenylbutadiene, but also demonstrated the absence of tolane, *cis*-stilbene and *cis*-α-bromostilbene.

e. Phenylboron dibromide and sodium in pentane. A solution of 1.45 g (5.81 mmole) of phenylboron dibromide in 50 ml of absolute pentane was stirred vigorously with 1.00 g (43.4 mg-atom) of freshly cut sodium pieces at 25°. After 4 h a small amount of gray precipitate had formed in the colorless solution. After an additional 12 h a copious light gray precipitate had formed in the yellow solution. At this point 10 ml of absolute ether was added. Finally, after 20 h (total of 36 h) the dark brown suspension was treated in two portions with: (*a*) solid carbon dioxide; and (*b*) with glacial acetic acid. Usual work-up yielded phenylboronic acid as the only detectable product in both cases.

Reactions of phenylboron dibromide with diphenylacetylene

The following experiments demonstate the reversible addition of the boron–bromine bond to the C≡C bond of tolane and the irreversible addition of the boron–phenyl bond to the C≡C bond of tolane.

a. Hydrolysis. Admixture of 656 mg (2.66 mmole) of phenylboron dibromide and 465 mg (2.60 mmole) of tolane at 25° led to a viscous, straw-colored liquid without any exotherm. After one h the mixture was warmed with water under nitrogen. Titration of the generated hydrogen bromide accounted for 80% of the theoretical. The organic layer now was heated with glacial acetic acid at 50° and then diluted with water. Ether extraction of the mixture, removal of boron compounds from the ether layer with dilute sodium hydroxide and the removal of solvent from the dried ether extract gave principally tolane and a small amount of *cis*-α-bromostilbene.

b. Acetolysis in pentane. A mixture of 700 mg (2.81 mmole) of phenylboron dibromide and 500 mg (2.79 mmole) of tolane was allowed to interact for 30 min at 25°. Protolysis with acetic acid in pentane and the usual work-up provided *ca.* a 1 : 1 mixture of tolane and *cis*-bromostilbene. The latter component was identified by comparing its infrared, VPC and TLC behavior with that of an authentic sample. On a subsequent occasion the *cis*-α-bromostilbene actually was isolated by column chromatography.

c. Reversibility of boron–bromine bond addition by solvation. A mixture of 3.21 g (12.9 mmole) of phenylboron dibromide and 2.30 g (12.8 mmole) of tolane was permitted to interact for 20 min at 25°. A 1.9 g sample was withdrawn and treated with 5 ml of absolute ethyl ether (sample 1). After standing for an hour at 25° the ether was removed at reduced pressure. The sample residue was protolyzed with acetic acid in pentane and worked up in the usual manner. Only tolane was found in the recovered organic layer.

A 2.13 g sample of the original reaction mixture was treated directly with acetic acid in pentane (sample 2). Usual work-up revealed tolane (*ca.* 65%), *cis-α*-bromostilbene (30%) and triphenylethylene (5%), as verified by spectroscopic and chromatographic comparison with authentic samples.

d. Reversal of boron–bromine bond addition during reaction. A mixture of 1.01 g (4.05 mmole) of phenylboron dibromide and 730 mg (4.05 mmole) of tolane was allowed to interact for 20 min at 25°. Thereupon, 400 mg (58 mmole) of finely divided, freshly cut lithium pieces was added to the syrupy yellow adduct, but no reaction was observed after 10 min. Fifty ml of pentane (freshly distilled from $LiAlH_4$) was introduced and the mixture was stirred vigorously. After 40 min a fine, white precipitate began to appear and the solution began to turn yellow. Finally, after 24 h a considerable amount of precipitate was present in the ocher-colored system. The solid was filtered off and freed from the unreacted lithium. The solid (lithium bromide) dissolved readily in water and gave no precipitate with potassium chloride, thus showing the absence of the $(C_6H_5)_4B$ anion.

The pentane solution gave upon protolysis only tolane. By column chromatography 680 mg (93%) of the starting tolane was recovered, m.p. 57–58°. From the acidification of the base extracts from the protolytic work-up, phenylboronic acid anhydride was isolated, m.p. 210–216°.

e. Irreversible boron–phenyl bond addition. A mixture of 3.71 g (15.0 mmole) of phenylboron dibromide and 2.68 g (15.0 mmole) of tolane formed a honey-like liquid at room temperature. Upon heating at 80° for 1 h the reaction liquid assumed a dark red color. The reaction mixture was then protolyzed by heating under reflux with glacial acetic acid. Usual work-up provided an organic product whose thin-layer chromatogram (*cf. supra*) revealed triphenylethylene as the predominant product; only very minor amounts of diphenylacetylene were detected, in addition to several minor unknown components. The reaction product was chromatographed on an alumina column with cyclohexane as the eluent. The triphenylethylene fractions were recrystallized from ethanol to yield 3.25 g (85%) of pure triphenylethylene, m.p. 67–68°. Its identity was verified by mixture melting point and infrared spectral comparisons.

Reaction of (cis-2-bromo-1,2-diphenylvinyl)phenylboron bromide with lithium in tetrahydrofuran

Experiment one. The following typical procedure represents a set of conditions chosen: (*a*) to maximize the formation and persistence of the phenylboron dibromide–tolane adduct; (*b*) to promote prompt reaction of the adduct with lithium metal; (*c*) to foster intramolecular cyclization of the resulting vinyllithium compound; and (*d*) to prevent decomposition of the anticipated boracyclopropene ring.

Admixture of 11.1 g (44.8 mmole) of phenylboron dibromide and 7.95 g tolane (44.8 mmole) and stirring at 25° for 30 min formed the honey-like adduct. A five-fold excess of finely divided lithium pieces (3.1 g, 450 mmole) was added and the suspension cooled down to −77°. A stiff glass in which most of the lithium pieces were firmly embedded resulted. Thereupon 200 ml of absolute tetrahydrofuran, previously cooled to −77°, was introduced. The glassy adduct dissolved only slowly in the solvent as the mixture was stirred vigorously at −77°. The course of the reaction was monitored by withdrawing aliquots periodically and treating them with glacial acetic acid. Usual work-up gave *cis*-stilbene, tolane and *cis*-α-bromostilbene. Minor amounts of *trans*-stilbene and *trans*-α-bromostilbene were thought to arise thermally during vapor phase chromatographic analysis. If the phenylboron dibromide–tolane adduct was allowed to stand over 1 h at 25°, some triphenylethylene was obtained upon protolysis.

In the various reaction runs the first protolysis performed after 2–3 h of stirring at −77° revealed the presence of 30–40% of the adduct (amount of α-bromostilbenes), 2–10% of *cis*-stilbene and 50–60% of tolane. The molar percentages of the α-bromostilbenes were the least reliable, as the phenylboron dibromide adduct with tolane apparently dissociates partially while being protolyzed in acetic acid. In this particular run the reaction mixture was stirred for a total of 17 h at −77° and aliquots withdrawn every 2 h. The last VPC analysis showed the presence of 74% *cis*-stilbene, 23% tolane and 3% α-bromostilbene. Noteworthy is the observation of a definite gas evolution when the reaction mixture aliquots were injected into glacial acetic acid (*vide infra*).

All organic products in this and each succeeding experiment were examined by thin-layer chromatography. The absence of tetraphenylbutadiene could be established in each case.

Experiment two. An adduct was formed between phenylboron dibromide (26.6 g, 107 mmole) and tolane 19.0 g, 107 mmole) in the usual manner. Treatment with 3.5 g of lithium pieces and 400 ml of absolute tetrahydrofuran at −77° for 13 h gave upon acetolysis of an aliquot a yield of 65% *cis*-stilbene, 30% tolane and 5% triphenylethylene. The yellow-brown solution was poured into 1500 ml of petroleum ether (E_1). The dark semi-solid phase was separated and extracted with benzene (E_2). Removal of the solvent from E_1 and distillation gave a wide main fraction, b.p. 130–180°/0.08 mm. Acetolysis revealed the presence of approximately equal amounts of *cis*- and *trans*-stilbene, together with some tolane. Removal of the benzene from E_2 and distillation of the residue yielded tolane and a crude distillate, b.p. 150–180°/0.09 mm. (Protolysis yielded a small amount of *cis*-stilbene and tolane. A mass spectral analysis confirmed the presence of tolane and triphenylborane.) Repeated distillation of the latter fraction gave a colorless distillate, b.p. 170–175°/0.09 mm. By VPC this fraction was shown to be pure. Infrared and NMR spectral comparison with an authentic sample showed this product to be triphenylborane. The acetolysis of the distillation residue of the benzene extract yielded *cis*-stilbene and some tolane.

Experiment three. In the usual manner 27.5 g (111 mmole) of phenylboron dibromide was admixed with 19.7 g (111 mmole) of tolane. After 45 min a 1.25 g sample was removed and treated with acetic acid. Customary work-up, column chromatographic separation of the products and their VPC analysis gave, in 92% overall recovery, a mixture of 47% tolane, 46% α-bromostilbene and 7% triphenylethylene.

A five-fold excess of lithium metal was added and the system stirred in 360 ml of tetrahydrofuran at −77° for 9 h. Treatment of a 20 ml aliquot with CH_3COOD and usual chromatographic work-up yielded pure deuterated *cis*-stilbene. Mass spectral analysis at 11 e.v. showed a content of 77% dideuterio-*cis*-stilbene and 16% monodeuterio-*cis*-stilbene and 7% undeuterated *cis*-stilbene. An NMR analysis of the same sample revealed a phenyl hydrogen : vinyl-hydrogen ratio of 10 : 0.40, in good agreement with the mass spectral analysis and with the conclusion that the vinyl hydrogens had been deuterated. The deuterioacetic acid used in the protolysis was shown to be at least 85% pure by treating a sample with lithium and analyzing the hydrogen gas by a mass spectrometer. As a control experiment, an authentic sample of *cis*-stilbene was subjected to an identical treatment with glacial CH_3COOD. Spectral examination of the recovered *cis*-stilbene showed that no deuterium incorporation had ensued.

After 10 h of stirring at −77° a 40 ml aliquot was withdrawn and poured onto solid carbon dioxide. There was no decoloration of the reaction solution. During 10 h it warmed up to room temperature. After acetolysis and usual chromatographic work-up 468 mg of a mixture of *cis*-stilbene, tolane, triphenylethylene and a small amount of *trans*-stilbene were obtained. No α-phenylcinnamic acid could be detected in the aqueous layer from the acetolysis work-up.

A sample of the low temperature reaction mixture was filtered through a fine glass frit and the filtrate treated with *o*-deuterioacetic acid. The evolved gas was collected and by mass spectrometric analysis was found to contain 85% deuterium and 15% hydrogen.

Finally, two 20 ml aliquots of the reaction mixture were treated individually with benzyl chloride or with methyl iodide. In each case the dark brown solution slowly became light yellow in color. Usual acetolysis and work-up yielded only *cis*-stilbene, tolane and triphenylethylene. Careful thin-layer chromatography on alumina with carbon tetrachloride revealed no new hydrocarbon derivatives.

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SUMMARY

A possible tactical approach to the synthesis of triphenylboracyclopropene (triphenylborirene) is described as involving: (*a*) the addition of phenylboron dibromide to the triple bond of diphenylacetylene; and (*b*) the interaction of the resulting (*cis*-2-bromo-1,2-diphenylvinyl)phenylboron bromide with lithium metal in tetrahydrofuran at −77°. Factors determining the competition between B–Br bond addition in step "a" and the slower B–C_6H_5 bond addition to the triple bond are analyzed. By treatment of aliquots of the reaction product of steps "a" and "b" with alkyl halides, with carbon dioxide and with O-deuterioacetic acid, it is concluded that a stilbene derivative with vicinal *cis*-carbon–boron bonds has been formed. The nature of the organoborane precursor of *cis*-stilbene is discussed in terms of structural alternatives, such as triphenylborirene, hexaphenyl-1,4-diboracyclohexadiene or a polymer.

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