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ORGANOBORANES

XVIII *. REACTION OF LITHIUM ALKYNES WITH METHYL DIALKYLBORINATES: THE SYNTHESIS OF *B*-1-ALKYNYLDIALKYLBORANES

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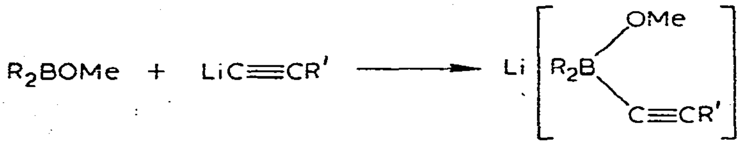
Summary

The reaction of alkynyllithium reagents with methyl dialkylborinates in tetrahydrofuran proceeds readily to form lithium methyl alkynyldialkylborinates.



Reaction of this "ate" complex with 1.3 equivalents of boron trifluoride diethyl etherate gives the alkynyldialkylboranes in essentially quantitative yield.

Introduction

Alkynyldialkylboranes ($R_2BC{\equiv}CR'$) reveal promise of being valuable synthetic reagents [1]. A number of such alkynyldialkylboranes have been reported [2—7]. The most general procedure utilizes the reaction between chlorodialkylborane—amine complexes and alkynyllithium reagents with subsequent removal of the amine by treatment with boron trifluoride diethyl etherate (eqn. 1) [7].

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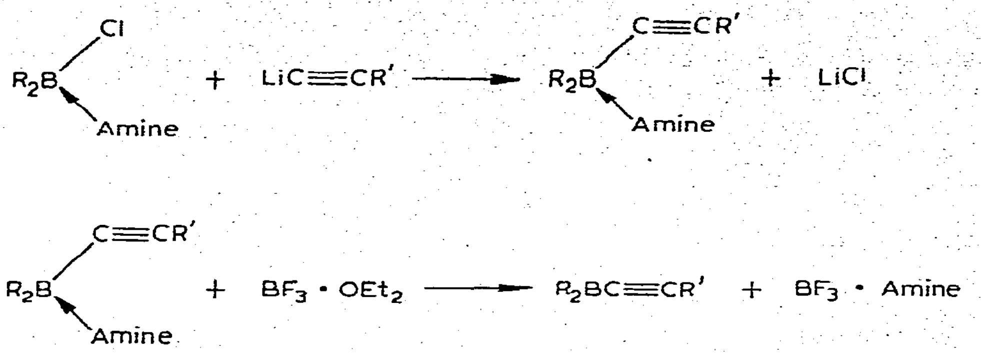
[*] For part XVII see ref. 11.



(1)

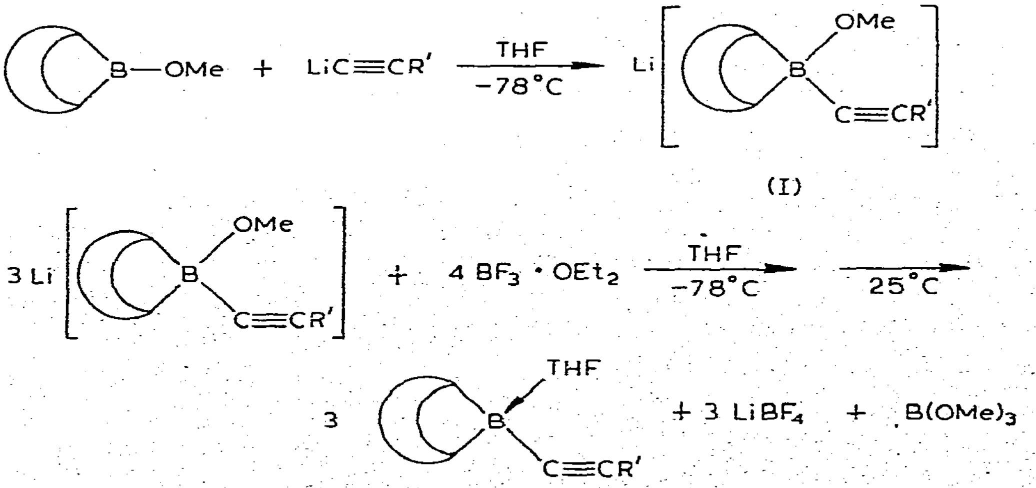
Attempts to apply this reaction to the 9-borabicyclo[3.3.1]nonane (9-BBN) system yielded unsatisfactory results. Accordingly, we undertook a systematic study of the preparation of *B*-alkynyl-9-BBN derivatives, as well as other alkynyldialkylboranes. This study has provided a convenient, easily applied route to many such alkynyldialkylboranes.

Results and discussion

Alkynyldialkylboranes have previously been prepared in variable yields by the reaction of alkynylmetallics with dialkylborinic esters, halides, or halide—amine complexes [2—7]. We chose the 9-borabicyclo[3.3.1]nonyl system as our model because of its commercial availability, ease of preparation, remarkable stability, and the selective utility of its *B*-alkyl derivatives [8—10]. Alkynyllithium reagents were utilized because of their ease of preparation.

Reaction of B-methoxy-9-BBN with alkynyllithium reagents

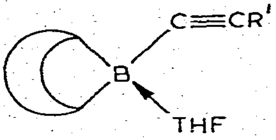
Treatment of *B*-methoxy-9-BBN in tetrahydrofuran with an alkynyllithium reagent at —78°C results in the formation of the simple adduct I. This adduct is stable and may be isolated as a complex with THF. Treatment of this "ate" complex with 1.3 equivalents of boron trifluoride diethyl etherate at —78°C, followed by warming, results in the formation of trimethyl borate, lithium tetrafluoroborate and the desired *B*-1-alkynyl-9-BBN (analysis by ^{11}B NMR) (eqn. 2).



(2)

TABLE 1

PREPARATION OF *B*-1-ALKYNYL-9-BBN TETRAHYDROFURANATE DERIVATIVES

	Yield (%) isolated [a]	^{11}B NMR (ppm)
R' = H	— [b]	− 9
R' = ethyl	88	−10
R' = n-butyl	86	−11
R' = t-butyl	94	−10
R' = n-hexyl	100 [c]	−10
R' = phenyl	90	−10
R' = 3-chloro-n-propyl	95	−17

[a] Isolated by crystallization from pentane. [b] Product decomposed on warming from −78°C. [c] Isolated by solvent evaporation.

The *B*-1-alkynyl-9-BBN derivatives can be isolated as 1 : 1 THF complexes in excellent yields (Table 1). They are easily isolated by evaporation of the tetrahydrofuran solvent, extraction with pentane, and crystallization. The *B*-1-alkynyl-9-BBN—THF complexes are stable crystalline solids which have been stored at room temperature for up to one year with no apparent decomposition.

Preparation of other alkynyldialkylboranes

Methyl dialkylborinates are readily prepared via hydroboration with chloroborane diethyl etherate [12]. This reaction allows the direct preparation of *B*-chlorodialkylboranes from which the corresponding methyl dialkylborinates can be formed by methanolysis (eqns. 3, 4).

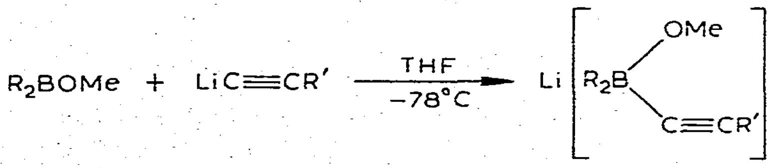
$$H_2BCl : OEt_2 + 2\,RCH{=}CH_2 \xrightarrow{Et_2O} (RCH_2CH_2)_2BCl \qquad (3)$$

$$(RCH_2CH_2)_2BCl + MeOH \rightarrow (RCH_2CH_2)_2BOMe + HCl \qquad (4)$$

Alternatively, methyl dialkylborinates may be prepared by the methanolysis of the readily available trialkylboranes using pivalic acid as a catalyst [13] (eqn. 5).

$$R_3B + MeOH \xrightarrow{(CH_3)_3CCOOH} R_3BOMe + RH \qquad (5)$$

Representative methyl dialkylborinates react in a manner analogous to that of *B*-methoxy-9-BBN. Treatment of a typical methyl dialkylborinate with a lithium alkyne at −78°C forms the adduct II (eqn. 6).



(6)

(II)

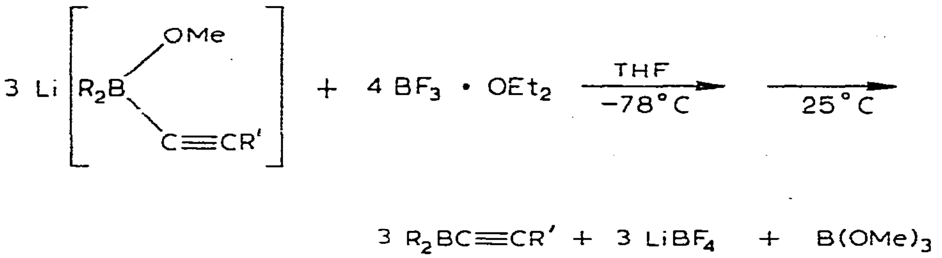
TABLE 2

PREPARATION OF 1-ALKYNYLDIALKYLBORANES

$R_2BC{\equiv}CR'$		Yield (%) isolated	Physical properties		
R	R′		B.p. (°C/mmHg)	^{11}B NMR δ (ppm)	IR ν(C≡C) (cm^{-1})
n-Butyl	Ethyl	90	74—77/5	—72	2185
sec-Butyl	Ethyl	85	62—65/5	—72	2185
Isobutyl	Ethyl	89	53—55/5	—72	2185
Siamyl	Ethyl	85	64—67/1.2	—72	2185
Cyclohexyl	Ethyl	89	84—90/0.01	—72	2185
Cyclohexyl	n-Butyl	100 [a]		—72	2185
Siamyl	n-Butyl	100 [a]		—73	2185

[a] Product not distilled. ^{1}H NMR showed no change on distillation.

Treatment of the "ate" complex with 1.3 equivalents of boron trifluoride diethyl etherate at —78°C, followed by warming, results in the formation of trimethyl borate, lithium tetrafluoroborate, and the desired 1-alkynyldialkylborane (analysis by ^{11}B NMR) (eqn. 7).



(7)

The generality of the preparation of alkynyldialkylboranes from methyl dialkylborinates is revealed by the data summarized in Table 2.

Experimental

General comments

All glassware was dried at 140°C for at least 4 h, assembled hot, and cooled under a stream of prepurified nitrogen. All reactions and distillations were carried out under a static pressure of nitrogen. All additions of liquids, organoboranes, solvents, or organometallics, were carried out with oven-dried, nitrogen-purged, hypodermic syringes fitted with stainless steel needles. Gases were introduced via a gas syringe [15]. All reactions were stirred magnetically using oven-dried, Teflon-coated stirring bars. The reaction flasks were fitted with sidearms capped with rubber septums.

Materials

THF was distilled from lithium aluminum hydride prior to use. Technical grade pentane was stirred over portions of concentrated sulfuric acid for 2 days, treated with solid potassium carbonate, distilled from lithium aluminum hydride, and stored under nitrogen in crown-capped bottles. Benzene (Baker Spectrophotometric) was dried over 5Å Molecular Sieves and flushed with nitrogen. Solvent transfers were done via hypodermic syringe or by the double-ended needle technique [16,18].

The n-butyllithium (Alfa) was standardized via the Watson—Eastham method [17]. Total base was determined by hydrolysis of an aliquot followed by titration with standard acid.

B-Methoxy-9-BBN was prepared as described previously [11,18]. Methyl di-n-butylborinate, methyl di-sec-butylborinate, and methyl diisobutylborinate were prepared according to reported procedures [12,13].

Methanol (Mallinckrodt SpectrAR) was dried over 3Å Molecular Sieves. Alkynes and olefins were used directly as obtained (Farchan, Chemical Samples Co.) and were greater than 99% pure in most cases. Diethyl ether (Mallinckrodt Anhydrous) was used directly from a fresh can after flushing with nitrogen. Boron trifluoride diethyl etherate was purified via published procedures [18].

Analyses

^{1}H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer, and all ^{1}H chemical shifts are relative to tetramethylsilane (δ 0 ppm). ^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz), and all ^{11}B chemical shifts are relative to boron trifluoride diethyl etherate (δ 0 ppm). Infrared spectra were taken on a Perkin—Elmer Model 137 instrument and calibrated with polystyrene film.

Preparation of methyl dicyclohexylborinate and methyl disiamylborinate

To a 300-ml flask fitted with a pressure equalizing dropping funnel and cooled with an ice-water bath, there was added 16.4 g (200 mmol) of cyclohexene, followed by 75 ml of anhydrous ethyl ether. Next, 7.7 g (100 mmol) of borane—methyl sulfide complex was added over a period of 0.5 h and the dropping funnel rinsed with 25 ml of ether to ensure quantitative borane addition. The reaction mixture was stirred for 3 h at 0°C. Under a rapid purge of nitrogen, the dropping funnel was replaced with a gas inlet tube vented through a mercury bubbler to the fume hood. Fifteen ml of dry methanol was added slowly and the mixture allowed to warm to room temperature. After about 2 h, gas evolution had ceased, and the solvent and excess methanol were removed under aspirator vacuum. The product was distilled (b.p., 75—80°C/0.005 mmHg) to yield material greater than 95% pure by ^{1}H NMR. ^{1}H NMR (CCl_4): 0.9—1.8 ppm (multiplet, ~22 H, rings) and 3.65 ppm (s, 3 H, OCH_3).

A similar procedure, using 14.1 g (200 mmol) of 2-methyl-2-butene in place of cyclohexene, was used to prepare methyl disiamylborinate. This product, which was about 96% pure by ^{1}H NMR, was used without distillation. ^{1}H NMR (CCl_4): 0.7—1.0 ppm (multiplet, ~18 H), 1.6 ppm (multiplet, ~4 H) and 3.70 ppm (s, 3 H, OCH_3).

General procedure for the preparation of 1-alkynyldialkylboranes (50 mmol scale)

To a 250-ml flask cooled with a Dry Ice—acetone bath there was added 75 ml of tetrahydrofuran and 50 mmol of the appropriate alkyne. The n-butyllithium (50 mmol) was added dropwise and the reaction mixture stirred 15 min. Fifty mmol of the appropriate methyl dialkylborinate was then added and the solution stirred 1.5 h. Next, 65 mmol of boron trifluoride diethyl etherate was added and the reaction mixture was stirred at —78° C for an additional 15 min.

Workup conditions for the 1-alkynyldialkylboranes (50 mmol scale)

(i) *B*-1-Alkynyl-9-BBN. Following the addition of the boron trifluoride etherate, the reaction mixture was stirred for 15 min at —78° C, then removed from the Dry Ice—acetone bath, connected to an aspirator, and the volatiles evaporated to yield a white solid. To the solid was added 50 ml of pentane. The suspension was stirred for a few minutes, allowed to settle, and the supernatant liquid was carefully decanted via a double-ended needle to a 100-ml flask. The remaining solid was washed with pentane (2 X 10 ml) and the extracts combined *. The pentane solution was then cooled to —78° C to crystallize the product. The mother liquor was removed and the crystals dried in vacuo.

(ii) 1-Alkynyldialkylboranes. Following the addition of the boron trifluoride etherate and stirring 15 min at —78° C, the reaction flask was removed from the Dry Ice—acetone bath, connected to an aspirator where the volatiles were evaporated to give a two-phase system. Fifty ml of pentane was added to the mixture. The mixture was stirred for a few minutes, allowed to separate, and the pentane solution carefully decanted via double-ended needle to a distillation apparatus with a 6" Vigreux column and 100-ml pot. The remaining viscous liquid was washed with pentane (2 X 10 ml) and the extracts combined. The solvent was removed, and the 1-alkynyldialkylborane was vacuum distilled.

Preparation and isolation of B-1-butynyl-9-BBN tetrahydrofuranate

To a 250-ml flask cooled with a Dry Ice—acetone bath, there was added 75 ml of tetrahydrofuran and 1250 ml (50 mmol) of gaseous 1-butyne. Next, 21.1 ml of 2.37 *M* (50 mmol) n-butyllithium in hexane was added, and the solution stirred at —78° C for 15 min. *B*-Methoxy-9-BBN, 7.6 g (50 mmol), was added, and the cold reaction was stirred an additional 1.5 h. Boron trifluoride etherate, 9.4 g (66 mmol), was introduced via syringe and the reaction mixture stirred at —78° C for about 30 min. The reaction flask was removed from the cold bath and allowed to warm to room temperature while the solvent was removed under aspirator vacuum. Fifty ml of pentane was added to the white solid and the mixture stirred a few minutes. After allowing the remaining white solid to settle, the supernatant liquid was decanted into a 100-ml flask. The solid was washed with pentane (2 X 10 ml) and the extracts combined. The pentane solution was slowly cooled to —78° C to crystallize the product. The mother liquor was decanted and the solid dried in vacuo to give 10.8 g (88%) of *B*-1-butynyl-9-BBN tetrahydrofuranate which was pure by ^{1}H NMR. ^{1}H NMR (CCl_4): 1.09 ppm (t, *J* 7 Hz, 3 H), 1.70 and 2.05 ppm (multiplet, 18 H), 2.25 ppm (q, *J* 7 Hz, 2 H), and 4.0 ppm (multiplet, 4 H). IR: 2190 cm^{-1} (C≡C). ^{11}B NMR (THF): —10 ppm.

Isolation of B-1-butynyl-9-BBN

The decanted pentane solution of *B*-1-butynyl-9-BBN tetrahydrofuranate

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* The *B*-1-phenylethynyl-9-BBN derivative was only slightly soluble in pentane or hexane, but readily soluble in benzene. The borane—benzene solution was filtered through a Kramer filter [18,19] to remove the lithium tetrafluoroborate. The bulk of the benzene was then removed by aspirator vacuum and the product washed with pentane. Vacuum-drying yielded a white, free-flowing powder.

from the above procedure was placed in a distillation apparatus equipped with a 6″ Vigreux column. The pentane solution was evaporated and the organoborane slowly distilled to yield two fractions. The first fraction, 0.55 g (10%) b.p., 50—65°C/0.5 mmHg, crystallized in the receiver and was shown to be *B*-1-butynyl-9-BBN tetrahydrofuranate by ^{1}H NMR. The second fraction, 2.32 g (55%), b.p., 65—67°C/0.5 mmHg, was *B*-1-butynyl-9-BBN. ^{1}H NMR (CCl_4): 1.10 ppm (t, *J* 7 Hz, 3 H), 1.90 ppm (multiplet, 14 H), and 2.50 ppm (q, *J* 7 Hz, 2 H). IR: 2190 cm^{-1} ($C\equiv C$)

Preparation and isolation of 1-butynyldisiamylborane

To a 250-ml flask, cooled with a Dry Ice—acetone bath, there was added 75 ml of tetrahydrofuran and 1250 ml (50 mmol) of gaseous 1-butyne. Next, 21.1 ml of 2.37 *M* (50 mmol) n-butyllithium in hexane was added, and the solution stirred at —78°C for 15 min. Methyl disiamylborinate, 9.1 g (50 mmol), was added. The cold mixture was stirred an additional 1.5 h and 9.4 g (66 mmol) of boron trifluoride etherate added. The reaction mixture was stirred at —78°C for about 30 min, and then allowed to warm to room temperature while the solvent was removed under aspirator vacuum. Fifty ml of pentane was added and the mixture stirred for a few minutes. The viscous lower layer was allowed to separate and the supernatant liquid decanted into a distillation apparatus fitted with a 6″ Vigreux column. The residue was washed with pentane (2 × 10 ml) and the pentane solutions were combined. The pentane was removed under vacuum. The residual oil was distilled (b.p., 64—67°C/1.2 mmHg) giving 8.7 g (85%) of 1-butynyldisiamylborane which was greater than 99% pure by ^{1}H NMR. ^{1}H NMR (CCl_4): 0.9 ppm (multiplet, 18 H), 1.15 ppm (t, *J* 7 Hz, 3 H), 1.90 ppm (multiplet, 4 H), and 2.45 ppm (q, *J* 7 Hz, 2 H). ^{11}B NMR (THF): —72.5 ppm. IR: 2190 cm^{-1} ($C\equiv C$).

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