Organoboranes. 50. Preparation and Characterization of Organyl-1-alkynylborinic Esters

Herbert C. Brown* and Morris Srebnik[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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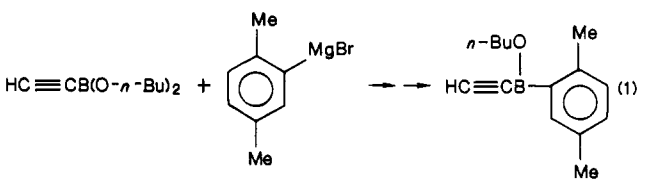
Contrary to earlier attempts, organyl-1-alkynylalkoxyboranes, RB(OR″)C≡CR′, are obtained in high purity and yield from the addition of a lithioacetylide to a borinic ester, followed by treatment with either hydrogen chloride in ethyl ether (EE) or acetyl chloride. The addition step is shown to be reversible, low temperatures favoring the "ate" complex. No dependence of the alkoxy moiety on product selectivity is observed, consistent with a reversible formation of the "ate" complex. The new compounds have been fully characterized: the proposed structures are in agreement with the spectral and combustion data.

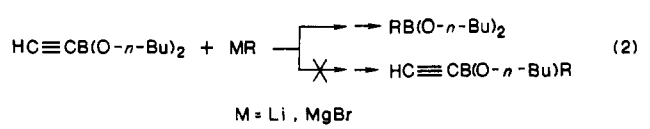
In connection with our recent studies on the synthesis of borinic esters,[2] we were interested in preparing organyl-1-alkynylalkoxyboranes (**1**).

$$\underset{\mathbf{1}}{RB(OR'')C{\equiv}CR'}$$

Surprisingly, a survey of the literature revealed these compounds to be practically unknown. Matteson[3] has reported that *p*-xylylmagnesium bromide reacts with ethynyldi-1-butoxyborane to give, after workup, sterically hindered ethynyl(2,5-dimethylphenyl)-1-butoxyborane (eq 1).



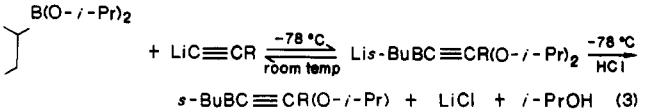
However, treatment of ethynyldi-1-butoxyborane with ethyl or vinyl Grignards resulted in the preferential expulsion of the ethynyl group to yield the corresponding boronic acids and esters after workup (eq 2). Zavgordnii



and Petrov[4] observed similar results in the reaction of but-1-en-3-ynyldi-1-butoxyborane with ethyllithium, which yielded ethyldi-1-butoxyborane. Since organyl-1-alkynylalkoxyboranes are potentially useful organoborane intermediates,[5] a general method for their preparation would be highly desirable. In this study we report the results of our endeavors to achieve a successful synthesis.

Results and Discussion

When *sec*-butyldiisopropoxyborane was treated with a lithioacetylide at −78 °C in ethyl ether (EE) or THF and the reaction mixture immediately analyzed by ^{11}B NMR, one peak was observed (δ 3.0), attributable to the formation of the lithium "ate" complex.[6] As the reaction mixture warmed to room temperature, the "ate" peak gradually disappeared and a new peak (δ 30.1) formed, presumably the starting boronic ester. When the reaction mixture was recooled to −78 °C, the "ate" species again formed at the expense of the starting material. However, quenching the reaction at −78 °C with HCl/EE cleanly liberated the alkynylborinate (δ 42.0), whereas quenching at 25 °C gave mixtures of starting material and product. No higher alkylated boranes could be detected. These results may be interpreted by assuming a reversible addition of the alkynyllithium reagent to the borinate (eq 3).



Low temperatures favor the addition complex, which can be cleanly decomposed at −78 °C with hydrogen chloride in ethyl ether to liberate the alkynylborinate.

We have shown that the alkoxy moiety profoundly influences the product distribution in the irreversible addition of an alkyl- or aryllithium reagent to a boronic ester,[2] followed by preferential expulsion of lithium alkoxide (eq 4).

$$RB(OR'')_2 + R'Li \rightarrow \underset{\mathbf{2}}{LiRR'_xB(OR'')_{3-x}} \xrightarrow{HCl} RR'BOR'' + RR'_2B + LiCl + ROH \quad (4)$$

$$x = 1, 2, \text{ or } 3$$

Thus, the factors affecting the stability of **2** affect the selectivity of this reaction, i.e. temperature and choice of alkoxy moiety. We therefore also investigated the possible influence of the alkoxy group in the addition of a lithioacetylide to a boronic ester. Whereas ring size of the alkoxy moiety is crucial to success in the reaction of a boronic ester with an alkyllithium or aryllithium reagent,[2] no such dependence is observed in the reaction of an alkynyllithium reagent and a boronic ester. Both five-membered ring esters, i.e. dioxaborolanes or benzodioxaboroles, and six-membered rings, i.e. dioxaborinanes, give equally satisfactory results. In addition, the steric requirements of the alkoxy moiety are of less importance here. Thus both diisopropoxy and diethoxy esters give

(1) We thank the Borane Research Fund for financial support of this project.

(2) Brown, H. C.; Cole, T. E.; Srebnik, M. *Organometallics* **1985**, *4*, 1788.

(3) Matteson, D. S.; Peacock, K. *J. Organomet. Chem.* **1964**, *2*, 192.

(4) Zavgorodnii, V. S.; Petrov, A. A. *Zh. Obshch. Khim.* **1961**, *31*, 2433; *J. Gen. Chem. USSR (Engl. Transl.)* **1961**, *31*, 2268.

(5) For instance, in the conversion to 1-alkynyl ketones.

(6) Nöth, H.; Wrackmeyer, G. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Flock, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978.

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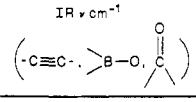
Table I. Alkylation of Organyldialkoxyboranes with Alkynyllithium Reagents

borane	alkynyllithium	selectivity,[a] %
methyldiisopropoxyborane	1-hexynyllithium	>99
methyldi-*tert*-butoxyborane	(5-chloro-1-pentynyl)lithium	80
2-methyl-1,3,2-dioxaborinane	1-hexynyllithium	>99
2-methyl-1,3,2-benzodioxaborole	(5-chloro-1-pentynyl)lithium	>99
2-*n*-hexyl-1,3,2-dioxaborolane	(5-chloro-1-pentynyl)lithium	>99
2-(2,3-dimethyl-2-butyl)-1,3,2-dioxatetramethylborolane	(5-chloro-1-pentynyl)lithium	>99
(3-methyltetrahydrofuryl)diethoxyborane	ethynyllithium	>99
exo-2-norbornyldiisopropoxyborane	ethynyllithium	>99

[a] Borinate ester: determined by peak heights of ^{11}B NMR spectra. See Experimental Section.

Table II. Yields and Properties of Isolated Organyl-1-alkynylalkoxyboranes

	IR, cm^{-1} 	$n^{20}D$	^{11}B δ	bp, °C (*p*, mmHg)	isolated yield, %
methyl(phenylethynyl)isopropoxyborane	2178, 1326	1.5290	40.2		91[a]
1-hexyl(3,3-dimethyl-1-butynyl)isopropoxyborane	2186, 1327	1.4265	40.6	80–82 (0.1)	79
sec-butyl(5-chloro-1-pentynyl)isopropoxyborane	2185, 1325	1.4496	41.3	72–74 (0.1)	85
sec-butyl-1-octynylisopropoxyborane	2183, 1324	1.4366	41.6	68–70 (0.1)	74
(2,3-dimethyl-2-butyl)(3,3-dimethyl-1-butynyl)(2-acetoxy-1-ethoxy)borane	2189, 1318, 1745	1.4436	43.5	96–98 (0.1)	79
cyclopentyl-1-octynylisopropoxyborane	2186, 1334	1.4557	41.2	100–102 (0.1)	76
phenyl-1-hexynylisopropoxyborane	2195, 1324	1.5008	36.5	102–105 (0.4)	86

[a] Crude yield; product decomposes upon attempted distillation.

consistently high selectivity. Only in the case of the di-*tert*-butoxy ester is a somewhat lowered product selectivity observed. The results summarized in Table I are consistent with the reversible addition mechanism proposed.

Isolation and Stability. The boronic esters were added to a slight excess of preformed lithioacetylide in THF or ethyl ether cooled to −78 °C. The reaction was stirred for 1 h and then quenched with hydrogen chloride in ethyl ether or with neat acetyl chloride[7] for cyclic esters. Filtration, followed by solvent removal at reduced pressure, and distillation furnished the organyl-1-alkynylalkoxyboranes (Table II). The methodology presented here is applicable to a large variety of boronic esters and is not restricted by more highly hindered systems, i.e. (2,3-dimethyl-2-butyl)boronic esters. Analogously, no steric restraint has been observed in the lithioacetylide moiety. In general, organyl-1-alkynylalkoxyboranes are stable, colorless, distillable liquids that show no decomposition (^{11}B NMR) on storage in the cold under nitrogen, but alkyl(phenylalkynyl)alkoxyboranes are thermally unstable and polymerize on attempted vacuum distillation. These thermally labile compounds can be obtained in reasonably pure form by removing volatiles under reduced pressure.

^{11}B NMR. The ^{11}B NMR resonances of organyl-1-alkynylborinates (δ 36.5–41.6) absorb at a much higher field than the corresponding dialkylborinates (δ 51–53). While sp-hybridized carbon attached to boron can lead to pπ-interaction between boron and carbon and shift the ^{11}B NMR resonance to a higher field relative to the corresponding alkylboranes, the increased shift relative to alkenylboranes is most likely not due to increased π-bonding between boron and carbon but to the diamagnetic anistropy of the carbon–carbon triple bond.[8]

IR. The infrared absorption of the CC triple bond in organyl-1-alkynylalkoxyboranes (2170–2195 cm^{-1}) is somewhat lower than in alkynyl hydrocarbons (2210 cm^{-1}). This is similar in trend to alkynylboronates.[9] The lowering of the stretching frequency of the organyl-1-alkynylborinates, in spite of the fact that the mass of boron is less than carbon, may be due to the interaction of the π-electrons of the carbon–carbon triple bond with vacant p orbitals of boron.

The B–O band is very intense and occurs in the narrow range of 1335–1315 cm^{-1}. The high frequency and intensity of this absorption are probably associated with some double-bond character for the B–O bond.[10,11]

Conclusion

We have demonstrated that lithioacetylides add reversibly to boronic esters, low temperatures favoring the addition complex. Treatment of these complexes with hydrogen chloride in ethyl ether or with neat acetyl chloride cleanly liberates the organyl-1-alkynylborinates. These organoboranes are now available to the organic chemist for further transformations.

Experimental Section

All glassware was dried at 140 °C for at least 3 h, assembled hot, and cooled under a stream of nitrogen. Anhydrous ethyl ether (EE; Mallinckrodt) was stored over 4-Å molecular sieves under nitrogen and used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under nitrogen prior to use. Techniques for handling air-sensitive compounds have been previously described.[12] The alkenes were obtained from commercial sources (Aldrich or Wiley Organics) and were distilled from lithium aluminum hydride and stored over 4-Å molecular sieves. The boronic esters were prepared according to standard procedures.[7,13,14] Anhydrous hydrogen chloride in ether (ca. 3 M) was prepared with use of a Brown□ apparatus from hydrochloric acid and sulfuric acid.[15] The solutions were standardized by hydrolyzing an aliquot in water and titrating with a standard solution of sodium hydroxide. Acetyl chloride was distilled from calcium hydride and stored under nitrogen.

The ^1H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer relative to tetramethylsilane. ^{11}B NMR were obtained on a Varian FT-80A spectrometer (25.517 MHz) relative

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(12) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.
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to trifluoroborane etherate. Infrared spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrometer. Mass spectra were obtained on a Finnigan Model 4000 gas chromatographic mass spectrometer. Microanalysis was performed in house.

General Procedure for Determining the Selectivity of Alkynyllithium Alkylation with Various Boronic Esters. To a 50-mL centrifuge tube fitted with a magnetic stirring bar and rubber septum was added via syringe ca. 5.5 mmol of alkyne and about 5.5 mL of tetrahydrofuran or ethyl ether. The solution was cooled to −78 °C, and *n*-butyllithium (5.5 mmol) was added. After being stirred for 15 min, a solution of boronic ester (5.0 mmol) in ether/THF or ethyl ether was slowly added via a syringe and the reaction stirred at −78 °C for 1 h. Hydrogen chloride in ethyl ether (5.5 mmol) was added and the cooling bath removed. The mixture was allowed to warm to room temperature. A sample was removed for analysis by ^{11}B NMR for the various alkylated boranes. The percentage of trialkylboranes, starting material, and product borinic ester were estimated by using peak height. This procedure appears to give good mass balances, ±5%, for compounds with similar peak widths at half-height.

General Procedure for the Isolation of Alkylborinic Esters. The preparation of *sec*-butyl(5-chloro-1-pentynyl)isopropoxyborane is typical. To a THF solution of (5-chloro-1-pentenyl)lithium prepared from 5-chloro-1-pentyne (5.43 g, 53 mmol) and *n*-butyllithium (20.4 mL, 53 mmol) cooled to −78 °C was added *sec*-butyldiisopropoxyborane (8.74 g, 48 mmol) in 48 mL of THF. The reaction mixture was stirred at −78 °C for 1 h and then quenched with hydrogen chloride in ethyl ether (15.5 mL, 53 mmol). The cooling bath was removed and the reaction mixture allowed to warm to room temperature. The lithium chloride was allowed to settle, and the clear supernatant was decanted via double-ended needle into a distillation flask. The remaining solid lithium chloride was washed with THF, 2 × 15 mL, and added to the distillation flask. Volatiles were removed with reduced pressure, followed by high vacuum distillation: yield 9.5 g (92%); bp 72–74 °C (0.1 mmHg); n^{20}_D 1.4496; ^{1}H NMR ($CDCl_3$) δ 4.63 (septet, J = 18 Hz, 1 H), 3.60 (t, J = 18 Hz, 2 H), 2.47 (t, J = 18 Hz, 2 H), 1.17 (d, J = 18 Hz, 6 H), 0.87 (m, 6 H); ^{11}B NMR (EE) +41.3 ppm (s); mass spectrum (chemical ionization, isobutane), m/e (relative intensity) 213 (M + H, 8); IR (thin film) 2185, 1325 cm^{-1}. Anal. Calcd for $C_{12}H_{28}BClO$: C, 63.06; H, 9.70; B, 4.73. Found: C, 63.14; H, 9.60; B, 4.48.

Preparation of Phenyl-1-hexynylisopropoxyborane. The reaction was run as described above with 1-hexynyllithium (64 mmol) prepared from 1-hexyne and *n*-butyllithium in EE (64 mL) and phenyldiisopropoxyborane (11.95 g, 58 mmol) dissolved in ethyl ether (60 mL) and quenched with hydrogen chloride in EE (18.7 mL, 64 mmol): yield 11.2 g (86%); bp 102–105 °C (0.4 mmHg); n^{20}_D 1.5008; ^{1}H NMR ($CDCl_3$) δ 7.90 (m, 2 H), 7.31 (m, 3 H), 4.87 (septet, J = 18 Hz, 1 H), 2.33 (t, J = 18 Hz, 2 H), 1.23 (d, J = 18 Hz, 6 H), 0.90 (t, 3 H); ^{11}B NMR ($CDCl_3$) +36.5 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 229 (M + H, 10); IR (thin film) 2195, 1324 cm^{-1}. Anal. Calcd for $C_{15}H_{21}BO$: C, 78.97; H, 9.28. Found: C, 78.18; H, 9.27.

Preparation of *n*-Hexyl(3,3-dimethyl-1-butynyl)isopropoxyborane. *n*-Hexyldiisopropoxyborane (8.35 g, 39 mmol) in ethyl ether (18 mL) was added to an ethyl ether solution of (3,3-dimethyl-1-butynyl)lithium (44 mmol in 44 mL of ethyl ether), as described above, and quenched with HCl in EE (12.87 mL, 44 mmol): yield 7.2 g (79%); bp 80–82 °C (0.1 mmHg); n^{20}_D 1.4265, ^{11}B NMR (ethyl ether) +40.6 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 237 (M + H, 7); IR (thin film) 2186, 1327 cm^{-1}. Anal. Calcd for $C_{15}H_{29}BO$: C, 76.23; H, 12.38; B, 4.58. Found: C, 76.35; H, 12.02; B, 4.61.

Preparation of (2,3-Dimethyl-2-butyl)(3,3-dimethyl-1-butynyl)(2-acetoxy-1-ethoxy)borane. The dioxaborolane ester (4.52 g, 29 mmol) in ethyl ether (20 mL) was added to an ethyl ether solution of (3,3-dimethyl-1-butynyl)lithium (32 mmol in 33 mL of ethyl ether), but the reaction was quenched with acetyl chloride (2.5 g, 32 mmol), as described above: yield 6.5 g (79%); bp 96–98 °C (0.1 mmHg); n^{20}_D 1.4436; ^{1}H NMR ($CDCl_3$) δ 4.13 (s, 4 H), 1.93 (s, 3 H), 1.20 (s, 9 H), 0.77 (m, 2 H); ^{11}B NMR ($CDCl_3$) +43.5 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 281 (M + H, <1), 105 ($HO(CH_2)_2OAc$ + H, 100); IR (thin film) 2189, 1745, 1318 cm^{-1}. Anal. Calcd for $C_{16}H_{29}BO_3$: C, 68.58; H, 10.43; B, 3.86. Found: C, 69.03; H, 10.07; B, 3.97.

Preparation of *sec*-Butyl-1-octynylisopropoxyborane. The reaction was conducted as described above with *sec*-butyldiisopropoxyborane (10.79 g, 58 mmol) in ethyl ether (58 mL) and added to a solution of 1-octynyllithium (64 mmol in 64 mL of THF) and quenched with HCl in EE (18.82 mL, 64 mmol): yield 10.1 g (74%); bp 68–70 °C (0.1 mmHg); n^{20}_D 1.4366; ^{1}H NMR ($CDCl_3$) δ 4.60 (septet, J = 18 Hz, 1 H), 2.23 (t, 2 H), 1.17 (d, J = 18 Hz, 6 H), 0.87 (m, 9 H); ^{11}B NMR ($CDCl_3$) +41.6 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 237 (M + H, 15); IR (thin film) 2183, 1324 cm^{-1}. Anal. Calcd for $C_{15}H_{29}BO$: C, 76.77; H, 12.38; B, 4.58. Found: C, 76.30; H, 12.39; B, 4.63.

Preparation of Cyclopentyl-1-octynylisopropoxyborane. Cyclopentyldiisopropoxyborane (2.33 g, 37 mmol) in ethyl ether (37 mL) was added to an ethereal solution of 1-octynyllithium (41 mmol in 41 mL of ethyl ether) and then quenched with HCl in EE (12.0 mL, 41 mmol). Workup as described above yielded 6.95 g (76%): bp 100–102 °C (0.1 mmHg); n^{20}_D 1.4557; ^{1}H NMR ($CDCl_3$) δ 4.63 (septet, J = 18 Hz, 1 H), 2.23 (t, 1 H), 1.17 (d, J = 18 Hz, 6 H), 0.83 (t, 3 H); ^{11}B NMR (EE) +41.2 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 249 (M + H, 40); IR (thin film) 2186, 1334 cm^{-1}. Anal. Calcd for $C_{16}H_{29}BO$: C, 77.42; H, 11.78. Found: C, 77.02; H, 11.92.

Preparation of Methyl(phenylethynyl)isopropoxyborane. The reaction was run as described above with methyldiisopropoxyborane (6.34 g, 44 mmol) in ethyl ether (44 mL) and (phenylethynyl)lithium (4.9 mmol) in ethyl ether (50 mL) and then quenched with hydrogen chloride (14.33 mL, 49 mmol). This compound could not be distilled, even at very low pressures. Thus, attempted distillation at 0.1 mm caused polymerization. Volatiles were removed under reduced pressure at ambient temperature to yield 7.45 g (91%): n^{20}_D 1.5290; ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 5 H), 4.73 (septet, J = 18 Hz, 1 H), 1.23 (d, J = 18 Hz, 6 H), 0.53 (b s, 3 H); ^{11}B NMR (EE) +40.2 ppm (s); mass spectrum (chemical ionization, isobutene), m/e (relative intensity) 187 (M + H, 6); IR (thin film) 2178, 1326 cm^{-1}. Anal. Calcd for $C_{12}H_{15}BO$: C, 77.46; H, 8.13. Found: C, 76.00; H, 7.69.