stirred ethoxyethynylmagnesium bromide solution, which was cooled in an ice bath. Ethylene was evolved during the addition. The mixture was then refluxed 2 h, after which no further ethylene evolution was detected. Cooling to −70° froze out magnesium bromide etherate and some tar, which were removed from the filtrate with a water aspirator and the residue was distilled in a falling-film molecular still (Nester and Faust, Newark, Del.), yield 6.2 g (44 %). The product decomposed if ordinary distillation was attempted without prior molecular distillation. Pure dipropyl ethoxyacetyleneboronate was obtained by fractionation with a short column, b.p. 50° (0.1 mm), $n_D^{20.3}$ 1.4273, infrared C≡C band at 4.52 μ. The compound blackened on storage at 0° under nitrogen. (Found: C, 60.37; H, 9.93; B, 5.68. $C_{10}H_{19}BO_3$ calcd.: C, 60.63; H, 9.67; B, 5.46 %.)

Dibutyl acetyleneboronate. A solution of 10.6 g of dibutyl 2-bromoethaneboronate[1] in 10 ml of tetrahydrofuran was added over a period of 30 min to 0.04 mole of ethynylmagnesium bromide[8] in 60 ml of tetrahydrofuran stirred at room temperature under nitrogen. After 1 h, the mixture was cooled in an ice bath, filtered, concentrated on the water pump, treated with 50 ml of pentane, filtered, and distilled to yield 4.8 g (65 %) of dibutyl acetyleneboronate, b.p. 33–37° (0.1 mm), confirmed by infrared comparison with an authentic sample[3].

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Reactions of dibutyl acetyleneboronate with Grignard reagents*

From the lability of acetyleneboronic esters[2] together with the relative instability of dialkylalkoxyboranes (borinic esters), it might be expected that loss of the ethynyl group would occur on treatment of an acetyleneboronic ester with a Grignard reagent.

$$HC{\equiv}C{-}B(OBu)_2 + RMgBr \longrightarrow R{-}B(OBu)_2 + HC{\equiv}C{-}MgBr$$

A closely analogous result has been observed in the reaction of dibutyl vinylacetyleneboronate with ethyllithium, which yielded dibutyl ethaneboronate[2]. We have ob-

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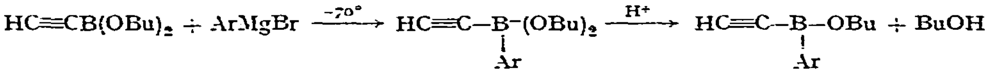
tained similar results from treatment of dibutyl acetyleneboronate with ethylmagnesium bromide, vinylmagnesium bromide, or ethynylmagnesium bromide.

In contrast, we have found that aryl Grignard reagents react with dibutyl acetyleneboronate to yield *B*-aryl-*B*-ethynyl-*B*-butoxyboranes*.

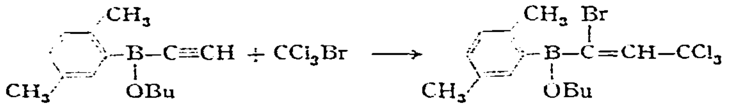


$$HC{\equiv}CB(OBu)_2 + ArMgBr \xrightarrow{-70^\circ} HC{\equiv}C{-}\underset{\displaystyle Ar}{B^-}(OBu)_2 \xrightarrow{H^+} HC{\equiv}C{-}\underset{\displaystyle Ar}{B}{-}OBu + BuOH$$

We did not find any significant variations in yield in our limited exploration of solvents and conditions. Phenylmagnesium bromide in either ether or tetrahydrofuran added to dibutyl acetyleneboronate at —70°, initially neat or diluted with solvent, led to high yields of *B*-phenyl-*B*-ethynyl-*B*-butoxyborane. Allowing the mixture to warm to 0° before cooling back to —70° and acidifying did not affect the result.

The success with aryl and failure with alkyl Grignard reagents may be due to several factors. The tetracovalent boron anion, precipitated as the magnesium salt, may in the aryl case survive until acidification of the reaction mixture, when protonation should occur rapidly at butoxy oxygen and not cause ethynyl cleavage. In the alkyl and vinyl cases loss of the ethynyl group may result from greater solubility of the magnesium salt or the weaker Lewis acid strength of alkaneboronic esters. It is also possible that *B*-alkyl- and *B*-vinyl-*B*-ethynyl-*B*-butoxyboranes decompose rapidly under the conditions of workup.

B-Phenyl-*B*-ethynyl-*B*-butoxyborane was unstable to simple distillation and we were unable to remove all the impurities (which appeared on infrared examination to be largely dibutyl benzeneboronate) by molecular distillation. In the light of past experience with *B*-aryl-*B*-vinyl-*B*-alkoxyboranes[3] we prepared an analogous compound with some steric hindrance, *B*-(2,5-dimethylphenyl)-*B*-ethynyl-*B*-butoxyborane, and succeeded in obtaining a suitable analytical sample. This compound was sufficiently stable to permit the radical-catalyzed addition of bromotrichloromethane to the triple bond, yielding *B*-(2,5-dimethylphenyl)-*B*-(3,3,3-trichloro-1-bromo-1-propenyl)-*B*-butoxyborane.



*Experimental***

Dibutyl acetyleneboronate and alkyl Grignard reagents. Dropwise addition of 0.05 mole of vinylmagnesium bromide in 25 ml of tetrahydrofuran to 9.10 g of dibutyl acetyleneboronate[1] stirred under nitrogen at —70° followed by addition of aqueous hydrochloric acid saturated with sodium chloride to the cold mixture and then appropriate extraction with ether and distillation yielded 4.3 g (47 %) of dibutyl ethyleneboronate, confirmed by infrared, and a residue of 1.8 g of butyl borate.

Similar treatment of dibutyl acetyleneboronate in ether with ethynylmagnesium bromide in tetrahydrofuran yielded a mixture of unchanged dibutyl acetylene-

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* Traditionally these would be named butyl arylethynylborinates. We favor the borane nomenclature because it seems more general and is probably clearer to those who are not specialists in organoboron chemistry.

** Microanalyses by Galbraith Laboratories, Knoxville, Tenn. (U.S.A.).

boronate and some butyl borate. Ethylmagnesium bromide (0.05 mole) in ether with 9.1 g dibutyl acetyleneboronate under similar conditions, except that the reaction mixture was warmed to 0° and cooled back to −70° before acidification, led to approx. 1.6 g of unchanged dibutyl acetyleneboronate and 3.4 g of dibutyl ethaneboronate, identified by infrared comparison with authentic samples.

B-Phenyl-B-ethynyl-B-butoxyborane. Addition of 0.05 mole of phenylmagnesium bromide in 25 ml of ether to 9.1 g of dibutyl acetyleneboronate stirred under nitrogen at −70° was followed by warming to 0°, cooling again to −70°, and acidification. (In another run the mixture was kept at −70° until it was acidified.) The product was extracted with ether. Attempts to distill the substance led to decomposition, but passage through a falling-film molecular still yielded 7.3 g (79%) of fairly pure material, n_D^{24} 1.5005. The infrared acetylenic C–H peak appeared at 3.05 μ, the aromatic C–H at 3.28 μ, the C≡C peak at 4.82 μ, and an aromatic C=C peak at 6.23 μ. The compound decomposed on storage. (Found: C, 75.1; H, 8.2; B, 6.1. $C_{12}H_{15}BO$ calcd.: C, 77.5; H, 8.1; B, 5.8%).

B-(2,5-Dimethylphenyl)-B-ethynyl-B-butoxyborane. A solution of 0.05 mole of *p*-xylylmagnesium bromide in 25 ml of tetrahydrofuran was added in 0.5 h under nitrogen to a stirred solution of 9.1 g of dibutyl acetyleneboronate in 50 ml of ether at −70°, then acidified below −60° with aqueous hydrochloric acid (2–3 *M*) saturated with sodium chloride. The phases were separated, the aqueous layer was extracted with three 20-ml portions of ether, the organic phase was washed with aqueous sodium chloride until a pH of 5–6 was reached (bicarbonate must not be used[1]), and the product was distilled, b.p. 70–76° (0.1 mm), yield 7.6 g (71%). The analytical sample was fractionated in a short column, b.p. 75° (0.1 mm), $n_D^{24.5}$ 1.5095, infrared acetylenic C–H at 3.07 μ, C≡C at 4.83 μ, and aromatic C=C at 6.20 and 6.35 μ. The compound blackened on storage at 5° under nitrogen. (Found: C, 78.66; H, 9.03; B, 5.20. $C_{14}H_{19}BO$ calcd.: C, 78.53; H, 8.95; B, 5.05%.)

B-(2,5-Dimethylphenyl)-B-(3,3,3-trichloro-1-bromo-1-propenyl)-B-butoxyborane. A mixture of 7.6 g of *B*-(2,5-dimethylphenyl)-*B*-ethynyl-*B*-butoxyborane and 21 ml of bromotrichloromethane kept at 80–85° for 5 h was treated with 0.1-g portions of azobisisobutyronitrile after 0, 1.5 and 3 h. Attempted simple distillation of the product led to decomposition. The material was purified by heating to 90° for 0.5 h at 0.1 mm to remove tetramethylsuccinonitrile followed by molecular distillation in a falling-film still, yield 10.5 g, $n_D^{24.7}$ 1.5419. The infrared spectrum showed complete disappearance of the acetylenic C–H and C≡C peaks and appearance of a C=C band at 6.12 μ. (Found: C, 43.85; H, 4.92; B, 2.89; halogen as Br, 77.62. $C_{15}H_{29}BBrCl_3O$ calcd.: C, 43.68; H, 4.64; B, 2.62; halogen as Br, 77.32%.)

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