tion of the filtrate with concentrated hydrochloric acid yielded a yellow-brown solid. This was recrystallized from benzene and ligroin (b.p. 30–60°) to yield 0.40 g (38 %) of 2-(phenylamino)-1-naphthoic acid, m.p. 146°.

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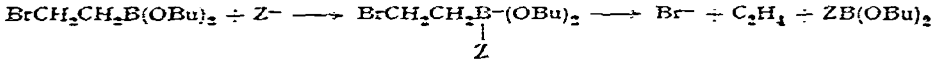
Use of the bromoethyl leaving group for the synthesis of an ethoxyacetyleneboronic ester*

The elimination of ethylene from dibutyl 2-bromoethaneboronate has been found to occur with extreme ease in the presence of mild bases[1]. It was postulated that the base, Z^-, initially attacked the boron atom.



$$BrCH_2CH_2B(OBu)_2 + Z^- \longrightarrow BrCH_2CH_2\underset{\underset{Z}{|}}{B^-}(OBu)_2 \longrightarrow Br^- + C_2H_4 + ZB(OBu)_2$$

With the bases used in our original study, the product $ZB(OBu)_2$ was unstable toward disproportionation. However, reaction of *B*-tris(β-bromoethyl)-*N*-triphenylborazine with phenyl- or ethylmagnesium bromide has been reported to replace the bromoethyl group with phenyl or ethyl, respectively[2]. It occurred to us that replacement of the bromoethyl group in the boronic ester series might be a particularly useful route to moderately labile carbon–boron bonds that resist synthesis by other methods.

To test the feasibility of this method, we began with the preparation of dibutyl acetyleneboronate from dibutyl 2-bromoethaneboronate and ethynylmagnesium bromide.

$$BrCH_2CH_2B(OBu)_2 + HC{\equiv}CMgBr \longrightarrow HC{\equiv}CB(OBu)_2 + MgBr_2 + C_2H_4$$

As anticipated, ethylene was evolved, magnesium bromide (as the tetrahydrofuran or ether complex) crystallized, and a good yield of dibutyl acetyleneboronate was obtained on distillation of the solution.

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Dibutyl acetyleneboronate is available directly from ethynylmagnesium bromide and methyl borate[3]. However, it seems unlikely that this route would be satisfactory for the preparation of an ethoxyacetyleneboronic ester because ethynylboron compounds are extremely sensitive to cleavage by bases[3] and ethynyl ethers are similarly sensitive to acids, the half-life of ethoxyacetylene in aqueous ethanol at 25° being[4], only a few minutes at pH 5. Exposure to too much acid or base would be difficult to avoid in the conventional synthesis from the Grignard reagent and methyl borate or a boron halide. Thus, the use of the bromoethyl leaving group is particularly suited to this problem*.

It turned out that butyl borate boiled too close to dibutyl ethoxyacetyleneboronate to permit separation by distillation, but use of the propyl ester circumvented

$$\mathrm{EtOC{\equiv}CMgBr + BrCH_2CH_2B(OPr)_2 \longrightarrow EtOC{\equiv}CB(OPr)_2 + C_2H_4 + MgBr_2}$$

this difficulty and the preparation proceeded smoothly. Some disproportionation of the product may have occurred, since substantial amounts of propyl borate were formed in spite of efforts to exclude air.

We explored the chemistry of dipropyl ethoxyacetyleneboronate briefly. The results were not encouraging. The compound decomposed on storage or on heating. Tar and propyl borate were obtained on heating with cyclopentadiene, tar and unchanged tetracyanoethylene with tetracyanoethylene. Treatment with hydrogen chloride at 0° for two hours led to propyl borate. Free radical addition of butanethiol (80°, benzene solvent, azobisisobutyronitrile initiator) did occur without extensive deboronation, but the elemental analysis and infrared spectrum suggested a mixture of 1:1 and 1:2 adducts contaminated with propyl borate. Since molecular distillation was the only mode of purification this mixture would survive, the matter was not explored further.

We tried to use the bromoethyl leaving group for the synthesis of tetrabutyl acetylenediboronate from acetylenebismagnesium bromide, but only obtained butyl borate and a low yield of dibutyl acetyleneboronate.

*Experimental***

Dipropyl 2-bromoethaneboronate. Dipropyl ethyleneboronate, b.p. 57–61° (20 mm), was prepared by substituting propyl alcohol for butyl alcohol in the previously described preparation of the corresponding butyl ester[6]. Comparison of the infrared spectrum with that of the butyl ester showed close similarity. Passing anhydrous hydrogen bromide through the propyl ester under irradiation as previously described for the butyl ester[1] yielded 90 % of dipropyl 2-bromoethaneboronate, b.p. 46° (0.1 mm), fractionated for analysis, n_D^{26} 1.4386. (Found: C, 40.42; H, 7.75; B, 4.69; Br, 33.94. $C_8H_{18}BBrO_2$ calcd.: C, 40.55; H, 7.66; B, 4.57; Br, 33.72 %.)

Dipropyl ethoxyacetyleneboronate. Ethoxyethynylmagnesium bromide was prepared by the procedure of Heilbron, Jones, and Sondheimer[7] from 4.95 g (0.0708 mole) of freshly distilled ethoxyacetylene (Pfister Chemical Co.) and an equivalent amount of ethylmagnesium bromide in 30 ml of ether. Dipropyl 2-bromoethaneboronate, 16.8 g (0.0708 mole) was added dropwise under nitrogen in about 30 min to the vigorously

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* A failure of an attempted synthesis of ethoxyacetyleneboronic acid has been reported[5].

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

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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