dimensional hyperspace"[16] might favorably compete with collisional deactivation to the strained ground-state allene. If this suggested reaction pathway is accurate, we would expect the singlet excited allene also to give the cyclopropylidene, but we have not yet been able to verify this expectation.

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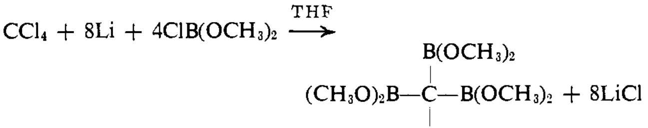
A Methanetetraboronic Ester

Sir:

We wish to report the synthesis of compounds having three and four boronic ester groups attached to one carbon atom. Although *gem*-diboronic acids and esters[1-3] and *gem*-diborylalkanes[4] are well known, attempts to prepare 1,1,1-triboryl compounds by hydroboration of an ethynylboron compound have failed.[5] Our successful method is based on the tetrasilylmethane synthesis by Merker and Scott[6] and includes some modifications similar to those used by Gilman and Smith[7] for tetrasilylsilanes. Much trial and error was required to adapt this synthesis to boron.



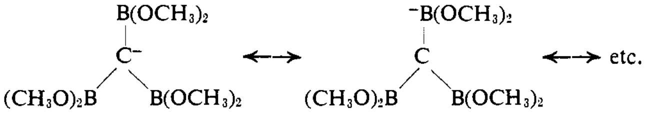
$$\mathrm{CCl_4 + 8Li + 4ClB(OCH_3)_2 \xrightarrow{THF} (CH_3O)_2B{-}\overset{\displaystyle B(OCH_3)_2}{\underset{\displaystyle B(OCH_3)_2}{\overset{|}{\underset{|}{C}}}}{-}B(OCH_3)_2 + 8LiCl}$$

1

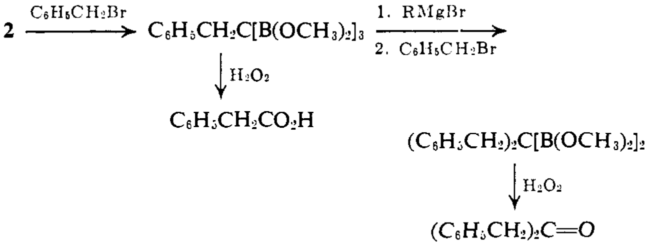
Dimethoxyboron chloride (3.4 mol) was freshly prepared by adding 236.5 g of trimethyl borate dropwise to 133.5 g of boron trichloride stirred at ~−70°. This was mixed with 125 g (0.8 mol) of carbon tetrachloride and 300 ml of trimethyl borate, and the mixture was added dropwise under argon to a vigorously stirred suspension of 90 g (~6.4 g-atoms) of 50% lithium dispersion in hexane (Foote Mineral Co.) in 1.2 l. of tetrahydrofuran and 300 ml of trimethyl borate kept at −50° (±5°) by means of a Dry Ice–acetone bath. The reaction is highly exothermic and the addition required about 2 hr. The mixture was allowed to warm slowly to −20°, then heated to reflux for 30 min. (*Caution!* If unreacted lithium remains, sudden exothermic reaction beyond the capacity of a reflux condenser may occur on warming. We encountered this problem when smaller amounts of tetrahydrofuran were used. Immediate application of a cooling bath always controlled the reaction, but an unattended reaction once opened itself to the air and caught fire spontaneously.) The mixture was cooled to 0° and filtered to remove the lithium chloride, which was rinsed with ether. The filtrate was concentrated and distilled rapidly under vacuum, and the crude octamethyl methanetetraboronate (**1**) was redistilled: bp 70–90° (0.1 mm); mp ~70–75°; no impurities evident in the infrared; 125 g (50%). An analytical sample was recrystallized from methanol and sublimed, mp 76–78°; *Anal.* Calcd for $C_9H_{24}B_4O_8$: C, 35.61; H, 7.97; B, 14.25. Found: C, 35.55; H, 8.11; B, 14.01.

We have used variations of this method to prepare hexamethyl methanetriboronate, $HC[B(OCH_3)_2]_3$, mp ~45°, hexamethyl phenylmethanetriboronate, $C_6H_5C[B(OCH_3)_2]_3$, mp ~35°, tetramethyl methanediboronate, $CH_2[B(OCH_3)_2]_2$, bp 24–27° (0.1 mm), and tetramethyl phenylmethanediboronate, $C_5H_5CH[B(OCH_3)_2]_2$, bp 50–54° (0.1 mm), to be reported in detail later.

Octamethyl methanetetraboronate (**1**) appears stable indefinitely in neutral methanol. With 0.1–0.2 equiv of sodium methoxide, little change occurs in 0.5 hr but most of the compound is degraded to methanediboronic ester in a day, according to nmr observations. One equivalent of methylmagnesium bromide in tetrahydrofuran converts the tetraboronic ester **1** to tris(dimethoxyboryl)methide ion (**2**). Refluxing the solution of **2** with benzyl bromide for 12 hr followed by oxidation of the high-boiling residue with hydrogen peroxide yielded a small amount of phenylacetic acid and 20% of dibenzyl ketone as the 2,4-dinitrophenylhydrazone, both verified by infrared comparison with authentic samples. Parallel behavior of 1,1-diborylalkanes has been reported.[4] We did not verify the presence of another probable degradation product, phenylacetaldehyde. We are working on the development of this alkylation into a synthesis of new types of carbon-functional boronic esters.



2



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(8) (a) Alfred P. Sloan Foundation Fellow. (b) We thank the National Science Foundation, Grant GP 6069, and the National Cancer Institute, U. S. Public Health Service Grant CA-05513-07, for financial support.

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A Valence Tautomer of a *cis*-15,16-Dihydropyrene

Sir:

The *trans*-15,16-dihydropyrenes, which have recently been reported,[1-4] are a unique addition to non-