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Preliminary communication

Alkene-1,1-diboronic esters from methanetetraboronic ester[*]

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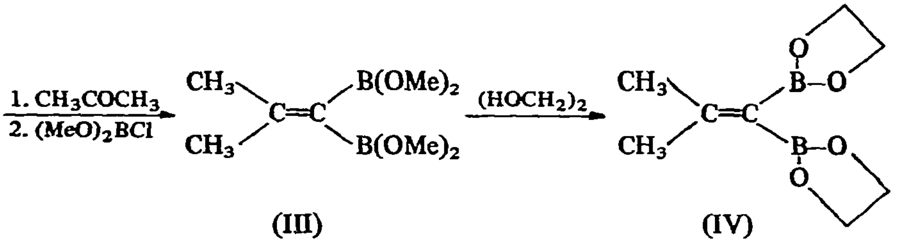
Octamethyl methanetetraboronate[1,***] (I) and methyllithium in tetrahydrofuran serve as a source of tris(dimethoxyboryl)methide ion (II), not necessarily as a free species but at least as a readily transferable nucleophilic unit. Ketones or aldehydes react with "II" to form alkene-1,1-diboronic esters, a new class of reactive and potentially useful organoboron compounds. For example, acetone yields tetramethyl 2-methylpropene-1,1-diboronate (III).

$$\underset{\text{(I)}}{[(MeO)_2B]_4C} + MeLi \rightarrow [MeB(OMe)_2 + \underset{\text{(II)}}{[(MeO)_2B]C^-}]$$



(III) (IV)

Twenty ml of 1.6 *M* methyllithium in ether was added dropwise in 15 min to a stirred solution of 6 g of octamethyl methanetetraboronate (I) in 30 ml of tetrahydrofuran at 0° under argon. Addition of 1.1 g of acetone to the yellow solution resulted in exothermic reaction and decolorization. The mixture was refluxed 0.5 h, cooled to 0°, treated with 2.2 g of dimethoxyboron chloride (to neutralize lithium borates), again refluxed 0.5 h, chilled, and filtered to remove LiCl. Addition of ethylene glycol precipitated the ester IV, which was recrystallized from chloroform, 52%, m.p. 101°; NMR (CCl_4): τ 5.85 (s, 8, CH_2O), 8.04 (s, 6, CCH_3); IR ($CHCl_3$): 1598 cm^{-1} (C=C). (Found: C, 48.87; H, 6.93; B, 11.33. $C_8H_{14}B_2O_4$ calcd.: C, 48.97; H, 7.14; B, 11.22%). Alternatively, the methyl ester III was

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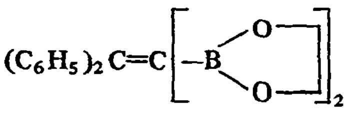
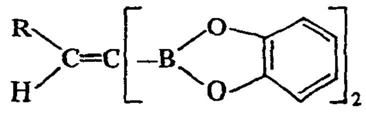
[***] In the most recently proposed systematic nomenclature, this is tetrakis(dimethoxyboryl)methane.

obtained by distillation through a spinning-band column, 28%, b.p. 30° (5 mm); NMR (CCl_4): τ 6.48 (s, 12, OCH_3), 8.29 (s, 6, CCH_3). (Found: C, 48.2; H, 9.0; B, 11.1. $C_8H_{18}B_2O_4$ calcd.: C, 48.2; H, 9.0; B, 10.6%). Hydrolysis of one boron–carbon bond occurs readily, $Me_2C{=}C[B(OH)_2]_2$ (from III) degrading to $Me_2C{=}CHB(OH)_2$ on attempted recrystallization from hot water.

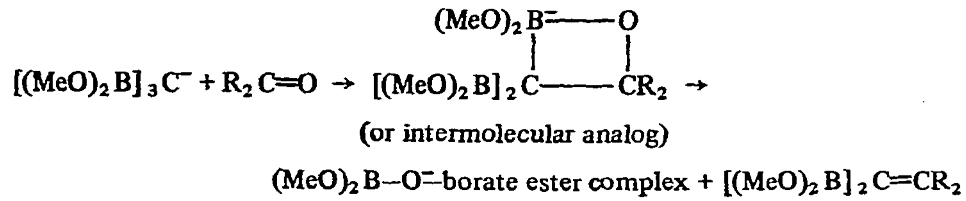
Benzophenone did not evolve heat with a solution of II, and the mixture was therefore refluxed 6 h. The product was isolated in 48% yield by the procedure described in the preceding paragraph as the ethylene glycol ester V, m.p. 162°; NMR (DMSO-d_6) τ 2.63–3.13 (m, 10, C_6H_5) and 6.15 (s, 8, OCH_2). (Found: C, 67.79; H, 5.74; B, 6.52. $C_{18}H_{18}B_2O_4$ calcd.: C, 67.56; H, 5.66; B, 6.76%.)


(V)


(VIa, R = C_6H_5; VIb, R = CH_3)

Aldehydes also react readily with the anion II, though the products have proved difficult to purify and yields are only fair. Benzaldehyde led to styrene-β,β-diboronic acid, recrystallized from water but not obtained analytically pure, m.p. 110° (dec.); yields phenylacetic acid on deboronation with alkaline hydrogen peroxide; NMR (DMSO-d_6) τ 2.33–3.25 (m, C_6H_5 + C=C–H); 6.17–6.83 (broad OH). This boronic acid was treated with catechol in benzene to form the catechol ester VIa, m.p. 149°; NMR ($CDCl_3$) τ 2.68–3.22 (m, ArH). (Found: C, 69.5; H, 4.2; B, 6.3. $C_{20}H_{14}B_2O_4$ calcd.: C, 70.6; H, 4.1; B, 6.5%). The vinyl proton peak is missing from the NMR spectra of these compounds, evidently because it is shifted so far downfield that it is hidden unter the aromatic peak. The acetaldehyde derivative of II, tetramethyl propene-1,1-diboronate, $[(MeO)_2B]_2C{=}CHCH_3$, has the vinyl CH quartet (J = 6 Hz) at τ 2.60; other peaks, τ 7.9 (d, 3, J = 6, CCH_3), 6.38 (s, 12, OCH_3). Distillation failed to purify this compound, and the catechol ester VIb was therefore prepared, m.p. 138°; NMR ($CDCl_3$) τ 2.58–3.08 (m, 9, C_6H_4 + C=C–H), 7.65 (d, J = 6 Hz, 3, C–CH_3). (Found: C, 64.0; H, 4.7; B, 8.0. $C_{15}H_{12}B_2O_4$ calcd.: C, 64.7; H, 4.3; B, 7.9%).

Precedent for our boronic ester condensations is provided by analogous reactions of 1,1-bis(dialkylboryl)alkanes (from dihydroboration of acetylenes) and butyllithium with aldehydes or ketones to yield olefins[2]. The mechanism of our reaction is probably similar.



$$[(MeO)_2B]_3C^- + R_2C{=}O \rightarrow \begin{array}{ll} (MeO)_2\overset{-}{B} & \!\!—O \\ \quad\ | & \ \ | \\ [(MeO)_2B]_2C & \!\!—CR_2 \end{array} \rightarrow$$

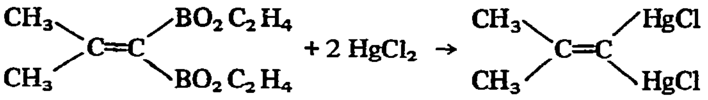
(or intermolecular analog)

$$(MeO)_2B{-}O^{-}\text{-borate ester complex} + [(MeO)_2B]_2C{=}CR_2$$

The twinned vinylic boronic ester groups of IV are easily displaced by a variety of other electrophiles. For example, reaction of $Me_2C{=}C(BO_2C_2H_4)_2$ (IV) with one equivalent of bromine in carbon tetrachloride at -20° results in cleavage to $BrBO_2C_2H_4$

and ethylene glycyl 1-bromo-2-methylpropene-1-boronate, $Me_2C{=}CBrBO_2C_2H_4$, b.p. 55–56° (0.5 mm), 62% isolated; NMR (CCl_4) τ 5.75 (s, 4, OCH_2), 7.94 (s, 3, C–CH_3), 8.00 (s, 3, C–CH_3). (Found: C, 34.3; H, 4.7; B, 5.2; Br, 38.1. $C_6H_{10}BBrO_2$; calcd.: C, 35.1; H. 4.8; B, 5.3; Br, 39.0%). We postulate an addition–elimination mechanism. Normally, β-bromoalkaneboronic esters do not undergo spontaneous elimination at moderate temperatures[3], but the postulated intermediate, $(CH_3)_2CBrCBr[B(OMe)_2]_2$, would be more reactive than $BrCH_2CH_2B(OR)_2$.

Rapid electrophilic displacement of the boronic ester group occurs in the reaction of IV with two moles of mercuric chloride and sodium acetate in methanol, which precipitates 88% of 2-methylpropene-1,1-dimercuric chloride (VII), m.p. 250°; NMR (DMSO-d_6): τ 7.98 (s, CH_3 with ^{199}Hg satellites, $J = 36$ Hz). (Found: C, 8.92; H, 1.11; Cl, 13.02; Hg, 76.51. $C_4H_6Cl_2Hg_2$ calcd.: C, 9.14; H, 1.14; Cl, 13.3; Hg, 76.38%).



(IV) (VII)

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