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The Use of Alkenylboronate Esters in [2+2] Enone-Olefin Photocycloadditions

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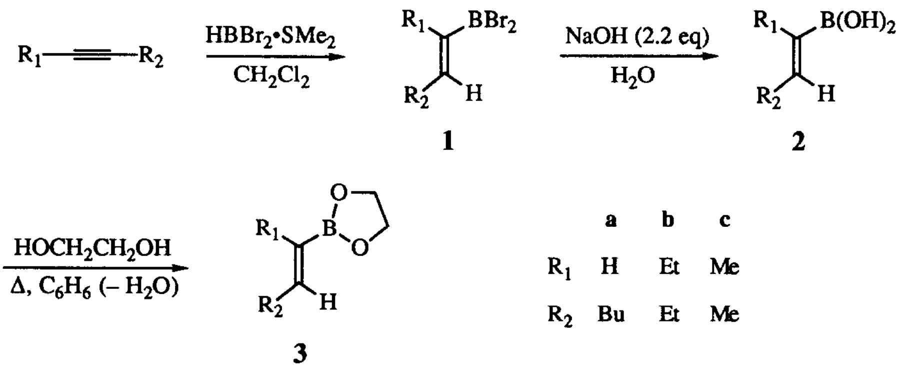
Abstract: The participation of alkenylboronate esters in intermolecular [2+2] enone-olefin photocycloadditions has been demonstrated using the E-1-hexenyl, Z-3-hexenyl, and Z-2-butenyl derivatives. The major photoadducts are those which result from head-to-head addition. Oxidative fragmentation of the boron-substituted cyclobutanes could be accomplished under relatively mild conditions.

The [2+2] enone-olefin photocycloaddition, in both its inter- and intramolecular modes, has been used quite successfully to address a number of synthetic problems over the past thirty years, and the literature in this area has been extensively reviewed [1]. Among the advantages claimed by this reaction include the formation of two carbon-carbon bonds, a high regioselectivity in most cases, and access to a variety of ring systems through fragmentation or expansion of the cyclobutane-containing photoadducts. Likewise, the versatility of the boronate ester moiety as a functionality which can be readily transformed has been documented [2]. These studies chart the course of reaction of boron-substituted olefins with photochemically excited enones.

The boronate esters **3a-c** [3] were prepared by the method outlined below. Treatment of the appropriate alkyne with dibromoborane-methyl sulfide complex [4, 5] (CH_2Cl_2, 3 h) efficiently generated the desired dibromoboranes **1a-c** which were hydrolyzed *in situ* to the corresponding boronic acids **2a-c**.



1

2

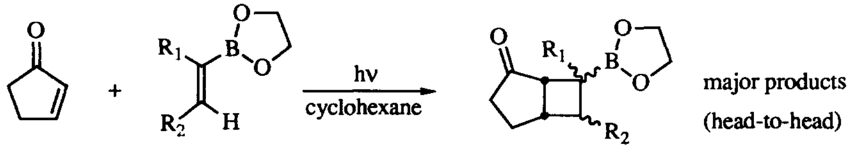
3

	a	b	c
R_1	H	Et	Me
R_2	Bu	Et	Me

A reaction temperature of 0 °C during the hydroboration yielded constitutionally homogenous product in the case of the terminal alkyne. When internal alkynes were subjected to similar conditions, a complex mixture of hydroboration products resulted. Smooth conversion was possible however when these reactions were carried out at -20 °C. The boronic acids were isolated as white semisolids from the crude organic extract and were esterified without further purification. These boronic acids were always contaminated with varying amounts of the trimeric boronic acid anhydride, visible in both the ^{1}H and ^{13}C NMR. The dioxaborolane esters were prepared from the acids and ethylene glycol via azeotropic removal of water from a benzene mixture and were purified by Kugel Rohr distillation (colorless oils, 75-90% overall yield from alkyne).

The photocycloadditions of these substrates with 2-cyclopentenone and 2-cyclohexenone were carried out in cyclohexane solution (1.0 M in enone) using a Pyrex reaction vessel and a 450W medium-pressure mercury lamp. The enone:boronate ester ratio was optimized at 1:12 to assure efficient conversion to the desired cycloadducts with minimal formation of enone dimer. At 23 °C, irradiation for a period of 8-10 hours allowed complete consumption of enone as monitored by GC/MS. Excess boronate ester was recovered via Kugel Rohr distillation from the crude product mixture. The recovered esters exhibited spectral and chromatographic evidence consistent with some olefinic isomerization during irradiation.

Literature precedent [1] indicates that head-to-head regioselection is favored in cases where the olefin is substituted with an electron-withdrawing group. Since the boronate ester is such a group, the major products in these photoreactions were expected and eventually shown to be head-to-head as in **4**. These cycloadditions are not concerted processes but proceed through diradical intermediates in which the configurational intergity of the reacting substrates is lost. The photoadduct mixtures were less complex when the enone component used was 2-cyclopentenone as only the cis ring fusion is generated in the resulting five-four systems. Both the cis- and trans-fused bicycles are produced when 2-cyclohexenone is used.



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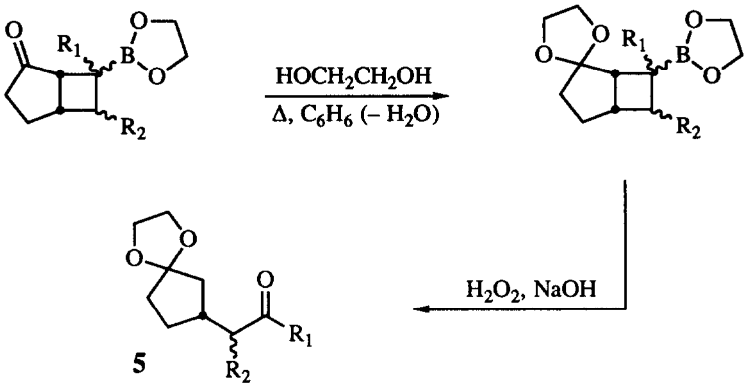
The GC trace of the photoadduct mixture produced in the case of ester **3a** indicated four compounds comprising >95% of the mixture in a ratio of 6:2.4:1:1. Each compound gave a mass spectrum consistent with the expected structures. The presence of boron in each was confirmed by the intensities of the M^+ and M^+-1 peaks. ^{1}H and ^{13}C NMR spectra of the mixture provided little definitive information due to the number of distinct compounds present. However, none of the signals were inconsistent with the those expected. Oxetane structures like those arising from a Paterno-Buchi reaction were ruled out since carbonyls were found in each product as indicated by ^{13}C and IR data.

Purification of the product mixtures proved problematic. Flash chromatography on silica gel was ineffective due to reaction between the gel and the boronate ester group, and reverse phase liquid chromatography failed as well. The compounds were stable to preparative gas chromatographic conditions, but isolation of each photoadduct in pure form was not achieved.

The mixture of cycloadducts could be protected as ketals in the standard fashion, and subsequently subjected to oxidation using alkaline hydrogen peroxide at 0 °C. Such oxidation produced two diastereomeric aldehydes [6] in the case of **5a** and two diastereomeric ketones [6] for **5b** and **5c** via cyclobutane opening from the intermediate alcohols. In addition to these compounds, in each case a minor amount of uncleaved alcohol was observed by GC/MS. Such alcohol is assumed to arise from oxidation of the small amount of head-to-tail regioisomers generated in the photocycloaddition.



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Participation of B-alkenyldioxaborolanes in [2+2] enone-olefin photocycloadditions has been demonstrated. Such reactions proceed with the anticipated favoring of the head-to-head regioisomer. Future efforts will be directed to examining how asymmetry in the boron-containing substituent affects the stereochemical course of the photoaddition and if alkenylboranes can be used in a manner similar to the boronate esters used in these studies. Finally, this reaction should prove particularly beneficial as a synthetic tool. The boronate ester moiety allows straightforward homologation of the alkyl group to which it is bound and can be converted simply to a wide array of other functional groups [2] (amine, alcohol, aldehyde, carboxylic acid, borohydride, etc.).

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3. For **3a, (E)-B-(1-Hexenyl)-1,3-dioxaborolane**: ^{1}H NMR ($CDCl_3$) δ 6.66 (dt, 1H, J = 6.6, 17.7 Hz), 5.40 (d, 1H, J = 17.7 Hz), 4.19 (s, 4H), 2.15 (m, 2H), 1.34 (m, 4H), 0.89 (t, 3H, J = 6.6 Hz) ; ^{13}C NMR ($CDCl_3$) δ 155.55, 117.70 (br), 65.53, 35.63, 30.50, 22.28, 13.92; MS m/z 154 (M^+), 139, 125, 112 (base), 97, 81, 68, 55.
   For **3b, (Z)-B-(3-Hexenyl)-1,3-dioxaborolane**: ^{1}H NMR ($CDCl_3$) δ 6.32 (t, 1H, J = 7.0 Hz), 4.21 (s, 4H), 2.19 (m, 4H), 1.00 (t, 3H, J = 7.6 Hz), 0.95 (t, 3H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 147.95, 132.00 (br), 65.46, 21.57, 21.41, 14.63, 13.63; MS m/z 154 (M+), 139, 125, 112 (base), 97, 81, 67, 55.
   For **3c, (Z)-B-(2-Butenyl)-1,3-dioxaborolane**: ^{1}H NMR ($CDCl_3$) δ 6.46 (br q, 1H, J = 6.7 Hz), 4.20 (s, 4H), 1.70 (d, 3H, J = 6.7 Hz), 1.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 141.32, 126.28 (br), 65.53, 14.17, 13.25; MS m/z 126 (M^+), 83, 67 (base), 54 .

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6. The compounds produced ^{1}H and ^{13}C NMR, MS, and IR spectral data consistent with the structures proposed.

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