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1,3,2-BENZODIOXABOROLE IN ORGANIC SYNTHESIS: PREPARATION OF VINYL IODIDES

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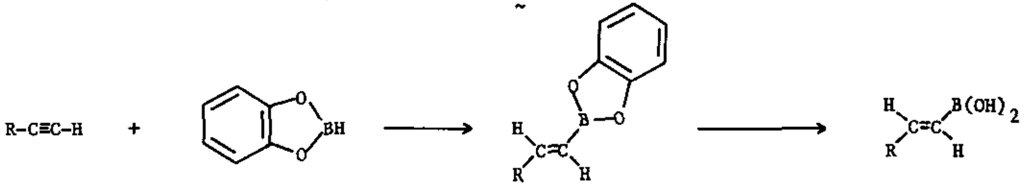
Abstract - 1,3,2-Benzodioxaborole readily hydroborates alkynes to form vinylboronic esters. The esters can be hydrolyzed to the corresponding vinylboronic acids which react with sodium iodide and chloramine-T to form isomerically pure (E)-iodoalkenes.

INTRODUCTION

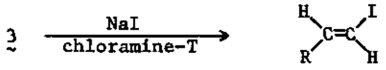
1,3,2-Benzodioxaborole (1) has proven to be a versatile hydroborating[1,2] and reducing reagent.[3] The reaction of 1 with alkynes produces the corresponding vinylboronic esters (2) which are readily hydrolyzed to the vinylboronic acids (3).



1 2 3

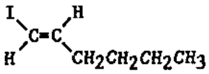
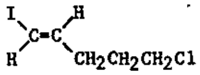
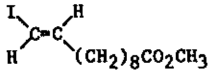
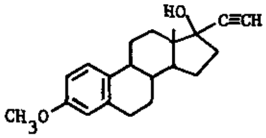
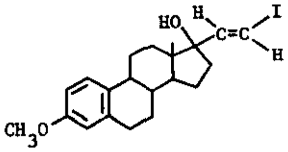
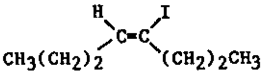
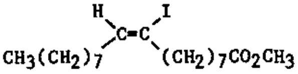
The boron in 2, or 3, is readily replaced by halogens,[4,5] metals,[6] and deuterium.[7] The reactions are generally stereospecific, producing the pure E-alkenyl derivatives.

We wish to report that vinylboronic acids 3 can be readily transformed into the isomerically pure E-alkenyl iodides via the reaction of 3 with sodium iodide and chloramine-T.[8] The reaction conditions are mild and tolerate a number of functional groups. The reaction should prove useful in syntheses involving radioiodine labeling.[9]



We have synthesized a variety of functionally substituted vinyl iodides and our results are summarized in Table I.

Table I

Alkyne[a]	Product[b]	Isolated[c] Yield, %
$HC\equiv CCH_2CH_2CH_2CH_3$		83
$HC\equiv CCH_2CH_2CH_2Cl$		85
$HC\equiv C(CH_2)_8CO_2CH_3$		81
		83
$CH_3(CH_2)_2C\equiv C(CH_2)_2CH_3$		38
$CH_3(CH_2)_7C\equiv C(CH_2)_7CO_2CH_3$		82[d]

[a] The alkynes were hydroborated with 1,3,2-benzodioxaborole (catecholborane) and then hydrolyzed to the corresponding vinylboronic acids. [b] The vinylboronic acids were reacted with sodium iodide and chloramine-T to yield the product. [c] Yields based on boronic acids. [d] Product is a mixture of the 9- and 10-iodo isomers.

EXPERIMENTAL

General Procedures

(a) Boronic acids were prepared via the hydroboration of the appropriate alkyne with 1,3,2-benzodioxaborole at 70°C for 6 hours[1] followed by an overnight hydrolysis with a large excess of water.[5] The solid boronic acids were filtered, dissolved in tetrahydrofuran and dried over anhydrous magnesium sulfate. The THF solution was filtered and the product precipitated by the addition of dry petroleum ether.

(b) Vinyl iodides were prepared by dissolving the boronic acids in sufficient aqueous tetrahydrofuran (50:50); the solution was shielded from light, cooled to 0°C, and one equivalent of aqueous sodium iodide (1M) was added followed by two equivalents of chloramine-T (0.5 M, 50:50 H_2O/THF solvent). After 15 minutes, petroleum ether (100 mL) was added; the solids were removed and the organic layer was separated, dried, and the solvent removed. In general, the products were 98% pure. Further purification was performed via chromatography (silica gel, pentane-ethyl acetate, 90:10).

Products

(E)-1-Iodohexene. 1-Hexyne (4.1g, 50mmol) was hydroborated with catecholborane (5.46 ml, 50mmol).[5] The hexenylboronic acid (256 mg, 2 mmol) was reacted sequentially with aqueous sodium iodide (2 mmol) and chloramine-T (0.908g, 4mmol). The yield of (E)-1-iodohexene was 346 mg (83%). The product exhibited spectral characteristics in accord with an authentic sample.[5]

(E)-1-Iodo-5-chloro-1-pentene. 5-Chloro-1-pentyne (5.12g, 50 mmol) was hydroborated with one equivalent of catecholborane.[5] The boronic acid (296 mg, 2 mmol) was reacted sequentially with sodium iodiode and chloroamine-T. The yield of (E)-1-iodo-5-chloro-1-pentene was 390 mg (85%). The colorless liquid exhibited spectral characteristics in accord with an authentic sample.[5]

Methyl (E)-11-Iodo-10-undecenoate. Methyl 10-undecynoate[5] was hydroborated with catecholborane. The vinylboronic acid (484 mg, 2 mmol) was reacted sequentially with sodium iodide and chloromine-T to yield 525 mg (81%) of the methyl (E)-11-iodo-10-undecenoate. The product exhibited spectral characteristics in accord with an authentic sample.[5]

17α-(E-2-iodovinyl)-$\Delta^{1,3,5}$-estratrien-3,17β-diol-3-Methyl Ether. Mestranol (3.1g, 10 mmol) was hydroborated with catecholborane (3.27 ml, 30 mmol). The vinylboronic acid was purified by precipitation from THF using petroleum ether; nmr ($CDCl_3$) δ 0.9 (s, 3H, $-CH_3$), 1.1-2.9 (broad envelope, 15H, steroid nucleus), 3.6 (s, 3H, $-OCH_3$), 5.4 (d, 1H, $-CH{=}C\underline{H}B(OH)_2$, J = 17.5 Hz), 6.5-7.2 (complex m, 4 H, ArH and $-C\underline{H}{=}CHB-$).[10]

The vinylboronic acid (357 mg, 1 mmol) was reacted sequentially with sodium iodide and chloramine-T. The product was extracted into ether, dried over anhydrous magnesium sulfate, and isolated by preparative TLC (silica gel GF, 2000 microns) using petroleum ether-methanol-ethyl acetate (200:35:35) [R_f = 0.5]; the yield was 364 mg (83%); nmr (CCl_4) δ 0.9 (s, 3H, $-CH_3$), 1.1-2.8 (broad envelope, 15 H, steroid nucleus), 3.6 (s, 3H, $-OCH_3$), 6.2 (d, 1H, $-CH{=}C\underline{H}I$), 6.4-7.2 (complex m, 4H, ArH and $-C\underline{H}{=}CHI$).[10]

(E)-4-Iodooctene. 4-Octyne (3.67 ml, 25 mmol) was hydroborated with catecholborane (2.73 ml, 25 mmol). The reaction was stirred for 8 h at 80°C. The catecholborane ester was isolated by chromatography on silica gel using petroleum ether as eluent.[11] The yield was 4.65 g (81%). Ethanol (40 ml) and water (30 mL) were added to the ester and the mixture stirred under nitrogen for 20 min. The product was extracted into petroleum ether and washed with copious amounts of water to remove the catechol. The yield was 2.3g (60%); nmr ($CDCl_3$) δ 0.9 (broad s, 6H, $-CH_3$), 1.5 (broad envelope, 4H, $-C\underline{H_2}CH_3$), 2.4 (broad multiplet, 4H, $=CHC\underline{H_2}-$), 6.7 (t, 1H, $-C{=}CHCH_2-$). The vinylboronic acid (312 mg, 2 mmol) was dissolved in THF (7.5 ml) and reacted sequentially with sodium iodide (2 mmol) and chloramine-T (4 mmol) to yield 180 mg (38%)[12] of the product which was isolated via column chromatography (alumina) using petroleum ether as eluent; mass spectrum, m/e 238.6 (calcd. 238); nmr ($CDCl_3$) δ 0.9 (t, 6H, $-CH_3$), 1.5 (broad m, 4H, $-C\underline{H}_2-CH_3$), 1.9 (m, 2H, $-C\underline{H}_2CH{=}C$), 2.4 (t, 2H, $C{=}CIC\underline{H}_2-$), 6.2 (t, 1H, $-CH{=}CI-$).

Mixture of (E)-9 and (E)-10-Iodooctadecen-9-oate. Methyl 9-octadecynoate[13] (11.8g, 40 mmol) was hydroborated with catecholborane for 8 h at 80°C. The product was distilled (bp 200°/2mm) to yield 13.0g (78%).[12] The catecholborane ester (415 mg, 1 mmol) was hydrolyzed in ethanol (10 ml) and water (2 ml) for 15 minutes under a nitrogen atmosphere. The product was extracted into petroleum ether and the extract washed with water (3 x 50 ml) to remove the catechol. The yield of the vinylboronic acid was 305 mg (89%); nmr ($CDCl_3$) δ 0.9 (broad s, 3H, CH_3),m 1.3 (broad s, 24 H, $-CH_2-$), 2.2 (broad envelope, 4H, $C{=}CHC\underline{H}_2-$), 3.6 (s, 3H, $-OCH_3$) 6.6 (t, 1H, $-C{=}CH-$). The vinylboronic acid (340 mg, 1 mmol) was dissolved in THF (10 ml) and reacted sequentially with sodium iodide (1 mmol) and chloramine-T (2 mmol) to yield 345 mg (82%) of the product; mass spectrum, 423 (M+1, calcd. m/e 422); nmr ($CDCl_3$) δ 0.9 (broad s, 3H, $-CH_3$), 1.2 (broad s, 24H, $-CH_2-$), 2.2 (broad m, 4 H, $-C\underline{H}_2CH{=}CIC\underline{H}_2-$), 3.6 (s, 3H, $-OCH_3$), 6.2 (t, 1 H, $-CH{=}CI-$).

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11. Higher yields of the boronic acids were obtained when the boronic ester was isolated.

12. The conversion of internal vinylboronic acids to the corresponding vinyl iodides is complicated by a rapid addition-elimination sequence which produces iodoketones.
13. Prepared via the bromination-dehydrohalogenation of methyl oleate (b.p. 140° at 2 torr.).

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