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A STEREOSPECIFIC SYNTHESIS OF CONJUGATED (E,Z)-AND (E,E)-ALKADIENES BY THE PALLADIUM-CATALYZED REACTION OF (E)-1-ALKENYLBORONIC ACIDS AND 1-ALKENYL IODIDES

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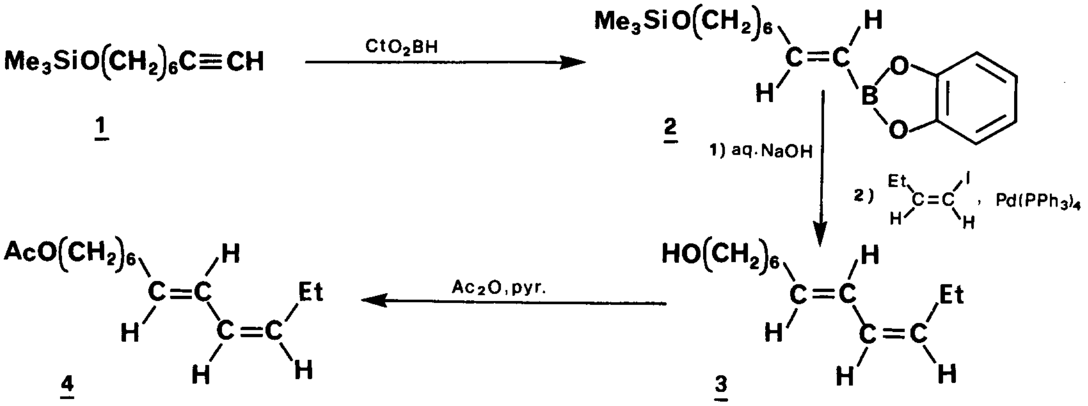
Abstract - The reaction of (E)-1-alkenylboronic acids with (Z)-or(E)-1-alkenyl iodides in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium and sodium hydroxide gave the corresponding conjugated (E,Z)-or (E,E)--alkadienes with high stereospecificity.

Cross-coupling reactions between 1-alkenylboranes and 1-alkenyl halides in the presence of palladium catalyst provide convenient syntheses of stereodefined 1,3-alkadienes.[1] Since the conjugated (Z,E)- or (E,E)-diene grouping is an essential feature of a number of important insect sex-pheromones,[2] we extended this reaction to functionally substituted 1-alkenylboranes to prepare the sex-pheromone of the European grapevine moth, Lobesia botrana, (7E, 9Z)-7,9-dodecadien-1-yl acetate (Scheme 1).

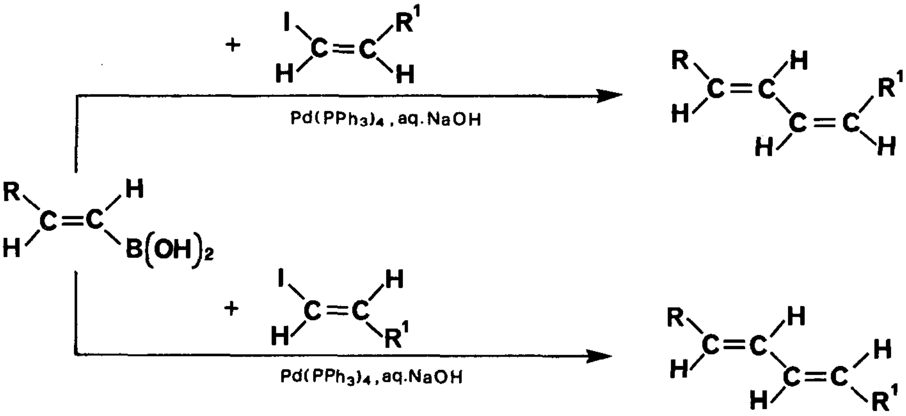
Scheme 1



7-Octyn-1-ol (10 mmol) was converted to the trimethylsilyl ether 1 (Me_3SiCl-$-Et_3N$ in CH_2Cl_2) and hydroborated with catecholborane (11 mmol) in THF (20 ml) under nitrogen at 65° for 2 h. After cooling to room temperature, the THF solution of the vinylboron intermediate 2 was treated with 20 ml of aqueous 1N-NaOH and then with (Z)-1-iodo-1-butene[3] (10 mmol) and tetrakis(triphenylphosphine)-palladium (0.2 mmol). The mixture was stirred at 65° for 2 h, poured into ice water, extracted with hexane and filtered through a silica gel column. Evaporation of the hexane in vacuo, followed by acetylation[4] of the crude alcohol 3 gave the sex pheromone 4. The yield of pure 4 was 62% (74% by g.l.c.) and the isomeric purity of the isolated 4 as well as the crude alcohol 3 was 98.5% by g.l.c.[5]

Although it is known[6] that alkenylcatecholboranes undergo rapid hydrolysis upon stirring with water at 25°C, the use of aqueous NaOH in the cross-coupling reaction was satisfactory. However, the suspect of at least a partial formation of an alkenylboronic acid during the base addition prompted us to explore the reaction of (E)-1-alkenylboronic acids with 1-alkenyl halides in the presence of palladium catalyst (Scheme 2). We have found that the reaction proceeds smoothly and with high stereospecificity.

Scheme 2



The following procedure for the preparation of (5Z,7E)-5,7-hexadecadiene is representative. (E)-1-Decenylboronic acid (1.1 mmol) was dissolved in 7.0 ml of water containing 2.2 mmol of sodium hydroxide, by stirring at room temperature for 15 min under nitrogen atmosphere. The solution was treated with $Pd(PPh_3)_4$ (0.022 mmol) and then with (Z)-1-iodo-1-hexene (1 mmol) in hexane (6 ml). After refluxing for 3 h, the mixture was cooled, extracted with hexane, washed with a saturated NaCl solution, dried with anhydrous sodium sulfate and filtered through a short silica gel column. Analysis of the extract by g.l.c.[5] indicated that 0.74 mmol of (5Z,7E)-5,7-hexadecadiene (isomeric purity 99%) had been formed. The product was recovered by column chromatography and gave the expected ^1H n.m.r. and mass spectra.[7]

Table 1. Palladium-catalyzed cross-coupling reaction of (E)-1-decenylboronic acid and 1-iodo-1-hexene[a]

Stereoisomery of 1-iodo-1-hexene	Solvent	Temp. °C	Time h	Isomeric composition of 5,7-hexadecadiene (%)	Yield[b] %
(E)	Toluene	20	14	5E,7E (99)	74
(Z)	Toluene	65	3	5Z,7E(93); 5E,7Z(1.5); 5E,7E(5.5)	71
(Z)	Tetrahydrofurane	65	2	5Z,7E(99); 5E,7E(1)	74
(Z)	Hexane	65	3	5Z,7E(99); 5E,7E(1)	74
(Z)	Hexane/Toluene	20	48	5Z,7E(99); 5E,7E(1)	50

[a] The reactions were carried out by using 1,1 mmol of (E)-1-decenyl-boronic acid, 1 mmol of 1-iodo-1-hexene in 6 ml of solvent, 2 mole % of $Pd(PPh_3)_4$ and 2,2 mmol of NaOH in 7.0 ml of water under nitrogen atmosphere.

[b] Based on 1-iodo-1-hexene and determined by g.l.c. in comparison with authentic samples.

The results of changing some reaction conditions are summarized in Table 1 which shows that the cross-coupling reaction proceeds with retention of configuration with respect to both the alkenylboronic acid and the halide. Our preliminary observations suggest that allyl, benzyl or aryl halides are possible substrates. Although the detailed mechanistic pathway is not clear yet, the reaction may be rationalized by assuming a transmetallation step from alkenylboronic acids to alkenyl palladium, as proposed for 1-alkenylboranes.[1] Recently similar reaction has been reported using phenylboronic acid and haloarenes.[8] (E)-1-Alkenylboronic acids are often crystalline solids, quite stable to air, inert to various functional groups and readily obtainable from 1-alkynes *via* hydroboration.[6] Thus, the synthetic applicability of the present cross-coupling reaction seems promising.

References and notes

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4. J.N.Labovitz, C.A.Henrick, and V.L.Corbin, Tetrahedron Lett.,1975,4209.
5. Gas-liquid chromatography was performed on a Carlo Erba 4160 gas chromatograph equipped with an automatic splitless injector system and a flame ionization detector. A glass open tubular capillary column (50m x 0.23 mm I.D.) was used, filled with Carbowax 20 M (He carrier at 34 cm/sec; 80-160°C at 15°C/min and then isothermal).
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7. The ^1H n.m.r. spectra were recorded at 90 MHz using a Bruker HX 90 spectrometere. The mass data were obtained using a Varian-MAT 112 S instrument. ^1H n.m.r. ($CDCl_3$/TMS)δ: 6.32(m,1H,$J_{7,8}$ =14.8 Hz, $J_{6,7}$ =10.6 Hz, $J_{7,9}$ =1.3 Hz, H-7); 5.94(ddt, 1H, $J_{6,7}$ =10.6 Hz, $J_{5,6}$ =10.5 Hz, $J_{4,6}$=1.3 Hz,H-6); 5.64(dt, 1H, $J_{7,8}$ =14.8 Hz, $J_{8,9}$ =7 Hz,H-8); 5.29(dt,$J_{5,6}$ =10.5 Hz, $J_{4,5}$ =7.3 Hz,H-5); 2.13(m,4H,H-4,H-9); 1.28(m,16H,other protons); 0.90(m,6H,H-1,H-16). M.S.:m/e=222(M^+,5%), 96(26%), 95(29%), 68(36%), 55(37%), 54(41%), 41(46%), 82(47%), 81(68%), 67(100%).
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