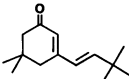
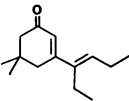
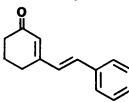
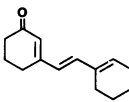
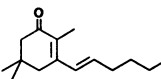
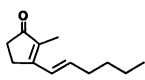
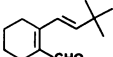
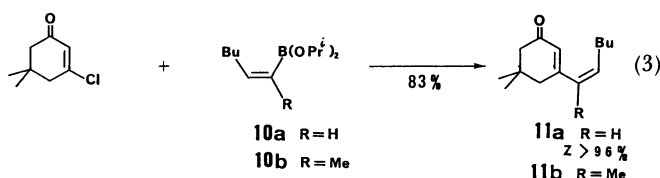


Table 2. Synthesis of Dienones and Trienones 5

Run	1-Alkenylboronate		Haloenone				Product	No.	Yield/% ^{a)}
	R ¹ =	R ² =	R ³ =	R ⁴ =	R ⁵ =	X=			
1	<i>t</i> -Bu	H	H	-CH ₂ CMe ₂ CH ₂ -		Cl		5a	— (87)
2	Et	Et	H	-CH ₂ CMe ₂ CH ₂ -		Cl		5b	96
3		H	H	-CH ₂ CH ₂ CH ₂ -		Cl		5c	98
4		H	H	-CH ₂ CH ₂ CH ₂ -		Cl		5d	84
5	<i>n</i> -Bu	H	Me	-CH ₂ CMe ₂ CH ₂ -		Br		5e	98
6	<i>n</i> -Bu	H	Me	-CH ₂ CH ₂ -		Br		5f	97
7	<i>t</i> -Bu	H						5g	— (85)

a) GLC yields based on haloenones and the isolated yields are shown in parenthesis.

one was reported elsewhere.³⁾



Conjugated dienones and polyenones are promising versatile intermediates for the synthesis of naturally occurring compounds. Most recently, we reported a stereoselective synthesis of a fungal prohormone ($\pm$)trisporel B⁶⁾ by means of such a crosscoupling reaction of 1-alkenylboronates. The present reaction affords an alternative and general procedure of obtaining stereodefined conjugated dienones and trienones.

Experimental

All reactions were carried out under nitrogen atmosphere. 1-Hexyne, 3,3-dimethyl-1-butyne, phenylethyne, and 3-hexyne are commercial products and purified by distillation before use. 1-Cyclohexenylethyne was prepared according to the method reported by Brandsma.⁷⁾ 3-Halo-2-cycloalkene-1-ones^{8,9)} were prepared from the corresponding 1,3-cycloalkadienones.

The IR spectra were recorded on a Hitachi-Perkin Elmer Model 125 spectrometer. The ¹H NMR spectra were taken on a Hitachi R-22 spectrometer (90 MHz, TMS as the internal reference). The measurement of mass spectra was carried out on a JEOL JMS-D 300 spectrometer (70 eV).

Palladium Complexes. Palladium(II) acetate was com-

mercial. Dichlorobis(triphenylphosphine)palladium(II)¹⁰⁾ and tetrakis(triphenylphosphine)palladium(0)¹¹⁾ were prepared according to the reported procedures.

1-Alkenylboronate 3. 1-Alkenyl-1,3,2-benzodioxaboroles were prepared by the Brown's method^{1,12)} from 1,3,2-benzodioxaborole (catecholborane) and 1-alkynes, and they were purified by distillation before use; **3a** (R¹=*n*-Bu, R²=H): Bp 86–87 °C/ 0.3 mmHg (1 mmHg=133.322 Pa) (lit,¹²⁾ 82 °C/0.25 mmHg); **3b** (R¹=*t*-Bu, R²=H): Bp 128 °C/ 12 mmHg; **3c** (R¹=Et, R²=Et): Bp 63 °C/0.1 mmHg (lit,¹²⁾ 81 °C/0.2 mmHg); **3d** (R¹=phenyl, R²=H): Mp 78 °C (lit,¹²⁾ 78–78.5 °C); **3e** (R¹=cyclohexenyl, R²=H): Bp 135–149 °C/0.1 mmHg, Mp 76–79 °C. 1-Alkenylboronates except **3e** are stable toward air and can be handled by the usual method.

Reaction Conditions (Table 1). The best conditions for the formation of conjugated dienone **6** were determined by the following general procedure. The palladium complex (0.03 mmol), an appropriate solvent (3.5 ml of MeOH, DMF, or THF), base (1.5 mmol of NaOAc or Et₃N), and 3-bromo-5,5-dimethyl-2-cyclohexen-1-one (1.0 mmol) were placed in a 25 ml-flask, and flushed with nitrogen. (*E*)-1-Hexenyl-1,3,2-benzodioxaborole (1.1 mmol) was then added by means of a hypodermic syringe through the septum inlet, and the resultant mixture was heated under reflux for 3 h. In the case of DMF, the reaction temperature was controlled at 80 °C for 3 h. After the completion of reaction, the mixture was cooled to room temperature and the residual organoborane was oxidized with an aqueous solution (3 M (1 M=1 mol dm⁻³), 0.2 ml) of NaOH-H₂O₂ (30% solution, 0.2 ml) for 1 h. The product was extracted with benzene, washed with brine, dried over MgSO₄, and analyzed directly by GLC (15% SE-30 on Uniport B, 2 m). The product was isolated by column chromatography over silica gel with hexane/ether. **6**: Bp 90–93 °C/0.1 mmHg; *n*_D²⁵=1.5149; IR

(film) 3040, 1670, 1635, 1595, and 975 cm^{-1} ; ^1H NMR (CCl_4) $\delta=0.93$ (t, 3H, $J=6.5$ Hz), 1.08 (s, 6H), 1.2–1.7 (m, 4H), 2.0–2.3 (m, 6H), 5.78 (broad s, 1H), 6.0 (dt, 1H, $J=6.5$ and 16 Hz) and 6.26 (d, 1H, $J=16$ Hz); Found: C 81.27; H, 10.55%. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50; H, 10.75%.

Standard Procedure for the Synthesis of Dienone 5c (Table 2). In a dry 100 ml-flask equipped with a septum inlet and a magnetic stirring bar were placed $\text{PdCl}_2(\text{PPh}_3)_2$ (0.21 g, 0.3 mmol) and NaOAc (1.23 g, 15 mmol). The flask was flushed with nitrogen and charged with 15 ml anhydrous methanol, 3-halo-2-alken-1-one (10 mmol), and 1-alkenyl-1,3,2-benzodioxaborole (11 mmol). The reaction mixture was then refluxed for 3 h. After completion of the reaction, aqueous NaOH (0.5 ml of a 3 M solution) and 30%- H_2O_2 (0.5 ml) were added at room temperature in order to oxidize the unreacted borane. The product was extracted with benzene, washed with brine and dried over MgSO_4 . The extracts thus obtained were analyzed by GLC (15% SE-30 on Uniport B, 2 m, or fused silica capillary column, 20 m). Analytically pure samples were obtained by chromatography over silica gel with hexane–ether or distillation under reduced pressure.

The dienones prepared by the above procedure are as follows.

5a: Mp 54 °C; IR (film) 3040, 1670, 1635, 1595, and 975 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.07$ (s, 6H), 1.09 (s, 9H), 2.26 (s, 2H), 2.32 (broad s, 2H), 5.91 (t, 1H, $J=1.3$ Hz), 6.24 (d, 1H, $J=16$ Hz), and 6.26 (d, 1H, $J=16$ Hz); MS m/z (rel intensity) 107 (100), 191 (83) and 206 (47); Found: m/z 206.16711. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: M, 206.16711.

5b: Bp 68–69 °C/0.05 mmHg; $n_D^{21}=1.5217$; IR (film) 3040, 1660, 1615, and 1580 cm^{-1} ; ^1H NMR (CCl_4) $\delta=0.9$ –1.2 (m, 6H), 1.07 (s, 6H), 2.12 (s, 2H), 2.3 (s, 2H), 2.0–2.5 (m, 4H), 5.85 (t, 1H, $J=7$ Hz), and 5.96 (s, 1H); Found: C, 81.30; H, 10.55%. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50; H, 10.75%.

5c: Bp 139–140 °C/0.15 mmHg; Mp 49 °C; IR (film) 3030, 1665, 1615, and 1580 cm^{-1} ; ^1H NMR (CCl_4) $\delta=2.0$ –2.25 (m, 2H), 2.25–2.50 (m, 2H), 2.60 (t, 2H, $J=6$ Hz), 5.99 (s, 1H), 6.90 (s, 2H), and 7.2–7.6 (m, 5H); Found: C, 84.97; H, 7.07%. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.81; H, 7.12%.

5d: Bp 123–125 °C/1.5 mmHg; Mp 55 °C; IR (film) 3040, 1725, 1670, 1605, 965, and 865 cm^{-1} ; ^1H NMR (CCl_4) $\delta=1.5$ –1.8 (m, 4H), 1.9–2.6 (m, 10H), 5.87 (s, 1H), 5.96 (broad s, 1H), 6.18 (d, 1H, $J=16$ Hz), and 6.58 (d, 1H, $J=16$ Hz); Found: C, 82.90; H, 9.12%. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97%.

5e: Bp 93–94 °C/0.3 mmHg; $n_D^{21}=1.5192$; IR (film) 3040, 1660, 1630, 1585, and 965 cm^{-1} ; ^1H NMR (CCl_4) $\delta=0.905$ (t, 3H, $J=6.5$ Hz), 1.02 (s, 6H), 1.2–1.6 (m, 4H), 1.34 (s, 3H), 2.19 (s, 2H), 2.29 (s, 2H), 2.0–2.4 (m, 4H), 6.06 (dt, 1H, $J=6$ and 16 Hz), and 6.60 (d, 1H, $J=16$ Hz); Found: C, 81.52; H, 10.73%. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}$: C, 81.76; H, 10.98%.

5f: Bp 84–86 °C/0.3 mmHg; $n_D^{20}=1.5350$; IR (film) 3025, 1690, 1640, 1600, and 965 cm^{-1} ; ^1H NMR (CCl_4) $\delta=0.90$ (t, 3H, $J=6.5$ Hz), 1.1–1.6 (m, 4H), 1.67 (s, 3H), 2.1–2.4 (m, 2H), 2.4–2.7 (m, 2H), 6.14 (dt, 1H, $J=6$ and 16 Hz), and 6.57 (d, 1H, $J=16$ Hz); Found: C, 80.60; H, 10.13%. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18%.

5g: $n_D^{20}=1.5272$; IR (film) 1700, 1670, 1630, 1595, 1145,

and 963 cm^{-1} ; ^1H NMR (CCl_4) $\delta=1.09$ (s, 9H), 1.45–1.90 (m, 4H), 2.15–2.6 (m, 4H), 6.0 (d, 1H, $J=16$ Hz), 6.83 (d, 1H, $J=16$ Hz), and 10.27 (s, 1H); MS m/z (rel intensity) 135 (100), 136 (14), 149 (4), 177 (0.6), and 192 (0.2); Found: m/z 192.15097; Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: M, 192.15093.

Synthesis of (Z)-1-Hexenylboronate 10a and Its Reaction with Halo Enone (Eq. 3). To a solution of diisopropyl (Z)-(1-bromo-1-hexenyl)boronate^{12,13} (1.1 mmol) in ether (2 ml) was added a solution of potassium hydrotriisopropoxyborate in THF (1 M solution, 1.2 mmol) at 0 °C. The mixture was stirred for 15 min at 0 °C. The cooling bath was removed, and stirring was continued for 30 min at room temperature. The solvent was evaporated under reduced pressure (0.01 mmHg) and then diisopropyl (Z)-1-hexenylboronate **10a** thus obtained was dissolved in methanol (4 ml). Sodium acetate (1.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.03 mmol), and 3-chloro-5,5-dimethyl-2-cyclohexen-1-one (1.0 mmol) were added, and the mixture was refluxed for 5 h. The reaction mixture was diluted with benzene–hexane (1/1) (30 ml), washed with water, and dried over MgSO_4 . Chromatography over silica gel with hexane–ether gave **11a** (0.17 g, 83%). Analysis by GLC (fused silica capillary column, OV-101, 20 m) indicated that E/Z is 4/96. **11a:** IR (film) 3020, 1670, and 1630 cm^{-1} ; ^1H NMR (CCl_4) $\delta=0.90$ (t, 3H, $J=6.5$ Hz), 1.07 (s, 6H), 1.2–1.5 (m, 4H), 2.1–2.4 (m, 6H), 5.7 (dt, 1H, $J=6.5$ and 12 Hz), 5.9 (d, 1H, $J=12$ Hz), and 5.93 (broad s, 1H); MS m/z (rel intensity) 206 (76), 191 (10), 177 (15), 163 (15), 149 (30), 121 (39), and 108 (100); Found: C, 81.27; H, 10.55%. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50; H, 10.75%.

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