^{1}H NMR (CCl_4) δ 9.62 (s, 1 H), 3.46-2.50 (m, 1 H), 2.28-1.70 (m, 2 H), 1.04 (t, 3 H, J = 7 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 67.2 (t, 2 F, J = 12.5 Hz), 113.7 (m, 2 F), 120.2 (m, 2 F), 120.8 (m, 6 F); MS, m/z 409, 407 (100), 405, 387. Anal. Calcd for $C_{10}H_7ClF_{12}O$: C, 29.56; H, 1.72; Cl, 9.74; F, 56.16. Found: C, 29.66; H, 1.91; Cl, 9.65; F, 55.57.

***N*-Methyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 92-94 °C (2 mmHg); IR 1580 (O=C-C=C), 1100-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.43 (s, 1 H), 3.17 (t, 2 H, J = 5.7 Hz), 3.10 (s, 3 H), 2.27 (t, 2 H, J = 5.6 Hz), 2.07-1.60 (m, 2 H); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.4 (t, 2 F, J = 11.4 Hz), 108.3 (t, 2 F, J = 11.5 Hz), 118.1 (s, 2 F); MS, m/z 311, 310, 309, 290, 274, 125, 124 (100). Anal. Calcd for $C_{10}H_{10}ClF_6NO$: C, 38.83; H, 3.24; Cl, 11.49; F, 36.89; N, 4.53. Found: C, 38.46; H, 3.39; Cl, 11.01; F, 36.80; N, 4.50.

***N*-Ethyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 76-78 °C (0.2 mmHg); IR 1580 (O=C-C=C), 1060-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.50 (s, 1 H), 3.33 (q, 2 H, J = 6.5 Hz), 3.27 (t, 2 H, J = 6 Hz), 2.28 (t, 2 H, J = 5.5 Hz), 2.10-1.60 (m, 2 H), 1.24 (t, 3 H, J = 6.5 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.5 (t, 2 F, J = 11.2 Hz), 108.5 (m, 2 F), 118.4 (m, 2 F); MS, m/z 325, 324, 323, 288, 139, 138 (100). Anal. Calcd for $C_{11}H_{12}ClF_6NO$: C, 40.87; H, 3.72; Cl, 10.99; F, 35.29; N, 4.33. Found: C, 40.70; H, 3.74; Cl, 10.93; F, 34.82; N, 4.22.

***N*-*n*-Butyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 75-78 °C (0.1 mmHg); IR 1575 (O=C-C=C), 1060-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.46 (s, 1 H), 3.52-2.97 (m, 4 He, 2.30 (t, 2 H, J = 5.7 Hz), 2.10-1.15 (m, 6 H), 0.95 (t, 3 H, J = 5.4 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.4 (t, 2 F, J = 11.3 Hz), 108.1 (m, 2 F), 118.2 (s, 2 F); MS, m/z 353, 352, 351, 332, 316, 166 (100). Anal. Calcd for $C_{13}H_{16}ClF_6NO$: C, 44.44; H, 4.56; Cl, 10.11; F, 32.48. Found: C, 44.41; H, 4.82; Cl, 9.96; F, 31.97.

Registry No. **1**, 16486-97-8; **3** (R = H, n = 1)), 108836-15-3; **3** (R = H, n = 2), 108836-16-4; **3** (R = CH_3, n = 0), 107728-86-9; **3** (R = CH_3, n = 2), 108836-17-5; **3** (R = Et, n = 0), 107728-87-0; **4**, 307-22-2; **5**, 108836-18-6; **7**, 108836-19-7; **8**, 108836-20-0; **18**, 121-44-8; **19**, 98968-85-5; **20**, 3405-42-3; **21**, 108836-08-4; **22**, 927-62-8; **23**, 108836-21-1; **24**, 108836-12-0; **25**, 108836-22-2; **26**, 108836-13-1; **27**, 108836-23-3; **28**, 108868-11-7; **29**, 108836-14-2; **30**, 108836-24-4; **31**, 108836-25-5; **32**, 108868-12-8; **33**, 108836-26-6; **34**, 108836-27-7; **39** (R_F = $ClCCF_2)_3$), 108836-09-5; (n-Pr)$_3$N, 102-69-2; $(CH_3CH_2)_2NCH_3$, 616-39-7; (n-Pr)N$(CH_3)_2$, 926-63-0; $[(CH_3)_2CHCH_2]_2NCH_3$, 10471-20-2; (n-Pr)N$(C_2H_5)_2$, 4458-31-5; (n-Pr)$_2$NC_2H_5, 20634-92-8; $(CH_3)_2CHN(C_2H_5)_2$, 6006-15-1; (i-Pr)$_2$NCH_3, 10342-97-9; Ni$(PPh_3)_4$, 15133-82-1; Pd$(PPh_3)_4$, 14221-01-3; Pt$(PPh_3)_4$, 14221-02-4; $Cl(CF_2)_6PdI(PPh_3)_2$, 108894-59-3; $Cl(CF_2)_3CF_2I$, 5848-38-4; $CF_3(CF_2)_2CF_2CH$=CHNEt$_2$, 98968-83-3; $CF_3(CF_2)_4CF_2CH$=CHNEt$_2$, 107728-83-6; $ClCF_2CF_2CH$=CHNEt$_2$, 107728-84-7; $Cl(CF_2)_3CF_2CH$=CHNEt$_2$, 98968-84-4; $Cl(CF_2)_7CF_2CH$=CHNEt$_2$, 107728-85-8; CF_3-$(CF_2)_2COCH$=CHNEt$_2$, 22769-73-9; $CF_3(CF_2)_4COCH$=CHNEt$_2$, 107728-88-1; $ClCF_2COCH$=CHNEt$_2$, 107728-89-2; Cl-$(CF_2)_3COCH$=CHNEt$_2$, 98968-86-6; $Cl(CF_2)_3COCH$=CHN-(Et)Pr-n, 108836-03-9; $Cl(CF_2)_3COCH$=CHN(Pr-n)$_2$, 108836-04-0; $Cl(CF_2)_3COCH$=CHN(Et)C_5H_{11}, 108836-05-1; $Cl(CF_2)_5COCH$=CHNEt$_2$, 98968-87-7; $Cl(CF_2)_5COCH$=CHN(CH_3)Et, 108836-06-2; $Cl(CF_2)_5COCH$=CHN$(CH_3)_2$, 108836-07-3; $Cl(CF_2)_7COCH$=CHNEt$_2$, 107728-90-5; $Cl(CF_2)_5CF_2CH(CH_3)CHO$, 107728-91-6; $Cl(CF_2)_5CF_2CH(Et)CHO$, 107728-92-7; *N*-(1-butenyl)pyrrolidine, 13937-89-8; *N*,*N*-diethylcyclohexylamine, 91-65-6; *N*-methylpiperidine, 626-67-5; *N*-etylpiperidine, 766-09-6; *N*-*n*-butylpiperidine, 4945-48-6; *N*-ethyl-$\Delta^{\alpha,\beta}$-β-(ω-chlorohexafluoro-*n*-butyryl)piperidine, 108836-10-8; *N*-*n*-butyl-$\Delta^{\alpha,\beta}$-β-(ω-chlorohexafluoro-*n*-butyryl)piperidine, 108836-11-9.

Highly Stereoselective Synthesis of *Z*,*E* Conjugated Diene Type Sex Pheromones†

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Insect sex pheromones **1**-**4** which contain a *Z*,*E* conjugated diene were synthesized by using a new formyl-olefination method, followed by a Wittig reaction. Thus, the aldehydes **6a**-**c** reacted with (formylmethyl)triphenylarsonium bromide (**5**) in THF-ether (trace H_2O) in the presence of K_2CO_3 at room temperature to give *E*-α,β-unsaturated aldehydes **7a**-**c**. These reacted with alkylidene phosphorane generated with *n*-BuLi in THF-HMPA to afford (*Z*,*E*)-diene derivatives **1**-**4** in good overall yield and high stereoselectivity.

Conjugated diene compounds are an important class of sex attractants for insects. Among the four geometrical isomers, a great number of dienes with *Z*,*E* configuration have already been identified as the components of sex pheromones; for example, (3*Z*,5*E*)-3,5-tetradecadien-1-ol acetate (**1**) for the Carpenterworm moth (*Prionoxystus robiniae*),[1] (5*Z*,7*E*)-5,7-dodecadien-1-ol (**2**) for *Dendrolimus spectabilis*,[2] (5*Z*,7*E*)-5,7-dodecadien-1-ol acetate (**3**) for *Dendrolimus punctatus*,[3] and (5*E*,7*Z*)-5,7-dodecadienal (**4**) for *Malacosoma californicum*.[4] Compounds **1**, **2**, and **4** have been synthesized[1,5,6] by nonstereoselective Wittig reactions. Recently, compound **3** was obtained with 85% stereoselectivity and in 31% overall yield.[7] In our previous

Scheme I[a]

$[Ph_3AsCH_2CHO]^+Br^- + RCHO \xrightarrow{i} RCH$=CHCHO (*E* isomer, >98%)

5	**6a**	**7a**, R = $CH_3(CH_2)_7$
	b	**b**, R = $CH_3(CH_2)_3$
	c	**c**, R = $THPO(CH_2)_4$

yields: 75-90%

[a] (i) Et_2O-THF (7:3), trace H_2O/K_2CO_3, 20 °C, 18-24 h.

† This is paper 54 in the series on the application of organic compounds substituted with elements of groups 15 and 16 in organic synthesis.[11]

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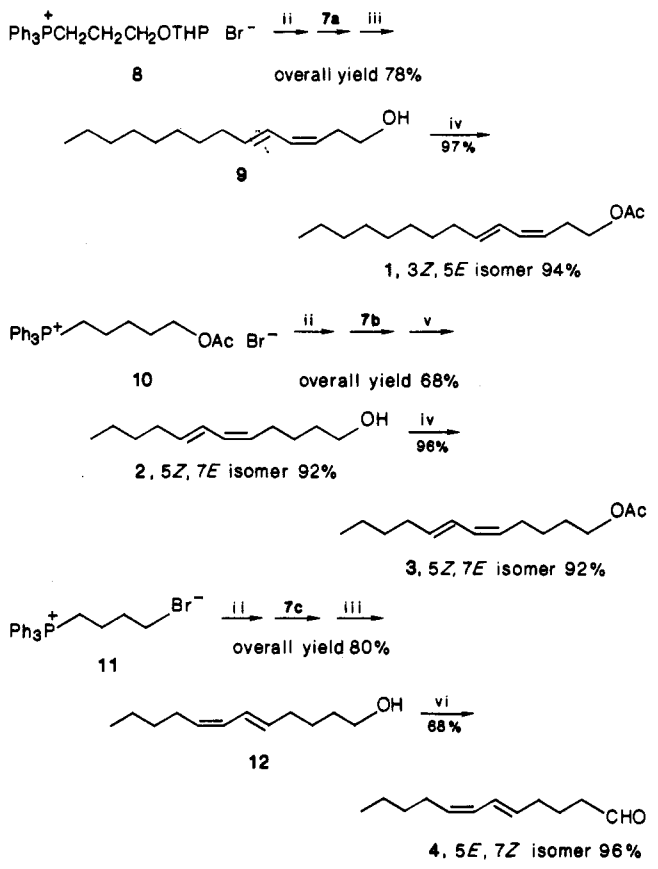
0022-3263/87/1952-3558$01.50/0

Scheme II[a]



[a] (ii) THF–HMPA (1:1)/*n*-BuLi, −30 °C, 2 h; (iii) MeOH/H^+, room temperature, 20 h; (iv) Ac_2O/Py, 5–10 °C, 8 h; (v) EtOH/OH^-, 24 h; (vi) PCC/CH_2Cl_2, 15 °C, 2 h.

paper,[8] we reported a facile stereoselective formylolefination of aldehydes by means of (formylmethyl)triphenylarsonium bromide (**5**) in a mixed solvent in the presence of potassium carbonate at room temperature, which furnished α,β-unsaturated aldehydes (*E* isomer, >98%) in excellent yields. We would like to report here the application of our method followed by the Wittig reaction for the synthesis of the above mentioned four pheromones as shown in Schemes I and II.

In comparison with the Wittig reaction[6,7] and the other method,[9] the high yield, experimental simplicity and *E* stereoselectivity on using arsonium salt (Scheme I) have made it the most satisfactory procedure for the preparation of the key intermediates of *Z,E* conjugated diene type sex pheromones. The conversion of *E*-α,β-unsaturated aldehydes into *Z,E* conjugated diene type sex pheromones according to silazide technique[7] is the best one of the known methods,[1,5,6] but the undesired *E,E* isomer still reaches 15%. However, when the *E*-α,β-unsaturated aldehydes **7** were reacted with phosphorane, generated from phosphonium salt (**8**, **10**, **11**) with *n*-butyllithium as base and HMPA as a cosolvent with THF, the desired *Z,E* conjugated diene compounds **1**–**4** were obtained in 50–70% overall yields (the desired *Z,E* isomers reached 92–96%). Therefore, our highly stereoselective procedure in good overall yield seems to hold much potential as a general route to *Z,E* conjugated diene type sex pheromones.

Experimental Section

Proton nuclear magnetic resonance (^1H NMR) spectra were determined with a Varian EM-360L (60 MHz) or XL-200 (200 MHz) spectrometer using tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on an IR-440 instrument. Mass spectral data were obtained with electron ionization (EI) on a Finnigan 402 spectrometer. GC/MS analyses were performed on a QP-1000 equipped with a PEG fused silica capillary column 50 m × 0.2 mm i.d. GC analyses were performed on an HP 5880 fitted with an FFAP capillary column 50 m × 0.3 mm i.d.

All reactions were carried out under nitrogen. All solvents were dried and redistilled before use. Boiling and melting points were uncorrected.

Materials. 3-(Tetrahydropyranyloxy)propyltriphenylphosphonium bromide (**8**) was prepared according to a known procedure.[10] [5-(Acetyloxy)pentyl]triphenylphosphonium bromide (**10**) and *n*-pentyltriphenylphosphonium bromide (**11**) were prepared by a reported procedure.[7] The aldehyde **6c** was obtained by the oxidation of 5-(tetrahydropyranyloxy)pentanol with PCC reagent in 53% yield.

(Formylmethyl)triphenylarsonium Bromide (5). A 150-mL round-bottomed flask equipped with a magnetic stirring bar was charged with triphenylarsine (13.40 g, 0.044 mol), bromoacetaldehyde–dioxane solution (10.40 g; containing bromoacetaldehyde, 4.44 g, 0.036 mol), and dry acetonitrile (30 mL). The mixture was stirred at 30 °C for 9 h and allowed to stand overnight at room temperature. The resulting solid **5** was collected by filtration, washed with ether, and dried in vacuo, affording the desired **5** (13.90 g, 90%): mp 160–161 °C.

(*E*)-2-Undecenal (7a). A mixture of 1-nonanal (**6a**) (286 mg, 2 mmol), (formylmethyl)triphenylarsonium bromide (**5**) (1.03 g, 2.4 mmol), potassium carbonate (331 mg, 2.4 mmol), and THF–Et_2O (20 mL, v/v 3:7, containing 90 μL of water) was stirred at 25 °C for 25 h. The solvent was evaporated under reduced pressure, and the residue was extracted with ether. The ethereal solution was passed through a short column of silica gel to remove most of triphenylarsine oxide. The remaining oil was chromatographed on silica gel (eluted with 10% ethyl acetate–petroleum ether) to separate the desired product **7a** (0.30 g, 90%). The purity of the desired isomer (*E* isomer, > 98%) was determined by GC analysis: IR (film) 1700, 985 cm^{-1}; MS, *m/z* (relative intensity) 168 (M^+, 14), 167 (M − 1, 100), 137 (10), 81 (18); ^1H NMR (60 MHz, CCl_4) δ 0.88 (t, 3 H), 1.29 (m, 12 H), 2.28 (m, 2 H), 5.96 (dd, *J* = 15.5, 7.5 Hz, 1 H), 6.40–6.90 (m, 1 H), 9.45 (d, *J* = 7.5 Hz, 1 H).

E-α,β-unsaturated aldehydes **7b** and **7c** were prepared in a similar manner.

(*E*)-2-Heptenal (7b): yield, 75%; IR (film) 1690, 975 cm^{-1}; MS, *m/z* (relative intensity) 111 (M^+ − 1), 96, 82 (100), 55; ^1H NMR (60 MHz, CCl_4) δ 0.93 (t, 3 H), 1.40 (m, 4 H), 2.32 (m, 2 H), 5.98 (dd, *J* = 15, 7.5 Hz, 1 H), 6.65 (m, 1 H), 9.42 (d, *J* = 7.5 Hz, 1 H).

7-(Tetrahydropyranyloxy)-(*E*)-2-heptenal (7c): yield, 84% IR (film) 1680, 1070, 1020, 970 cm^{-1}; MS, *m/z* (relative intensity) 213 (M^+ + 1, 4), 155 (6), 86 (100), 55 (17); ^1H NMR (60 MHz, CCl_4) δ 1.56 (m, 10 H), 2.28 (m, 2 H) 3.02–3.91 (m, 4 H), 4.39 (t, 1 H),

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(11) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

5.92 (dd, J = 15.5, 7.5 Hz, 1 H), 6.65 (dt, 1 H), 9.36 (d, J = 7.5 Hz, 1 H).

(3*Z*,5*E*)-3,5-Tetradecadien-1-ol (9). To a suspension of **8** (240 mg, 0.495 mmol) in THF (2 mL) was added dropwise *n*-BuLi (1.36 N hexane solution, 0.37 mL) at -30 °C. After the mixture was stirred for 1 h, HMPA (2 mL) was added, and then the aldehyde **7a** (67 mg, 0.40 mmol) was added at the same temperature. After being stirred for 1 h, the resulting mixture was quenched with water (4 mL) and extracted with petroleum ether, dried over sodium sulfate, and evaporated. To this concentrated solution was added methanol (10 mL) and HCl (2 N, 4 mL). The resulting solution was stirred at room temperature for 20 h and then shaken with $NaHCO_3$, and the organic layer was washed with water until neutral, dried over sodium sulfate, and evaporated. The crude product was purified by TLC (silica gel) eluting with 8:2 petroleum ether–ethyl acetate to afford 70 mg (80%) of **9**.

(3*Z*,5*E*)-3,5-Tetradecadien-1-ol Acetate (1). A solution of the dienol **9** (86 mg, 0.41 mmol), pyridine (1 mL), and acetic anhydride (50 mg) was stirred at 5–10 °C for 8 h and worked up. The crude mixture was purified by flash chromatography to give as an oil **1** (99 mg, 96%). This oil consists of three peaks (94.9%, 2.3%, 2.8%) in GC. MS data of these three components were shown as isomers [192 (M^+ - 60, 100%)]. The main isomer (3*Z*,5*E*)-**1** was identified by ^1H NMR: IR (film) 3032, 2936, 1763, 1234, 980, 945 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, H-14), 1.27 (m, 12 H, H-8,9,10,11,12,13), 2.04 (s, 3 H, H-2′), 2.08 (m, 2 H, H-7), 2.50 (dt, 2 H, H-2), 4.09 (t, J = 7.0 Hz, 2 H, H-1), 5.26 (dt, $J_{3,4}$ = 10.9 Hz, $J_{2,3}$ = 8.0 Hz, 1 H, H-3), 5.69 (dt, $J_{5,6}$ = 14.7 Hz, $J_{6,7}$ = 6.5 Hz, 1 H, H-6), 6.06 (dd, $J_{3,4}$ = 10.9 Hz, $J_{4,5}$ = 10.9 Hz, 1 H, H-4), 6.28 (dd, $J_{5,6}$ = 14.7 Hz, $J_{4,5}$ = 10.9 Hz, 1 H, H-5) [decoupling of H-2 and H-7 transformed H-3 to a doublet, $J_{3,4}$ = 10.9 Hz (cis), and H-6 to a doublet, $J_{5,6}$ = 14.7 Hz (trans)].

(5*Z*,7*E*)-5,7-Dodecadien-1-ol (2). The reaction conditions used for the Wittig transformation of **10** with **7b** were the same as described above. The crude product was mixed with potassium hydroxide (50 mg) in aqueous ethanol (3 mL, H_2O/EtOH = 1:2) and stirred at room temperature for 24 h. The reaction mixture was neutralized with 0.1 N HCl, extracted with ether, and washed with brine. The organic layer was dried over sodium sulfate and filtered, and the filtrate was concentrated in vacuo to afford a yellow oil. this crude product was purified by column chromatography (silica gel), eluting with 20% ethyl acetate–petroleum ether to afford a colorless oil (105 mg, 68%). The purity of the desired product **2** (5*Z*,7*E* form) determined by GC and GC/MS was 92%: MS, m/z 182 (M^+); IR (film) 3330 (br), 981, 950 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3 H, H-12), 1.26–1.68 (m, 9 H, H-2,3,10,11, OH), 2.06–2.26 (m, 4 H, H-4,9), 3.66 (t, J = 6 Hz, 2 H, H-1), 5.30 (dt, $J_{5,6}$ = 10.8 Hz, $J_{4,5}$ = 7.0 Hz, 1 H, H-5), 5.68 (dt, $J_{7,8}$ = 15.1 Hz, $J_{8,9}$ = 6 Hz, 1 H, H-8), 5.98 (dd, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 10.6 Hz, 1 H, H-6), 6.30 (dd, $J_{7,8}$ = 15.1 Hz, $J_{6,7}$ = 10.6 Hz, 1 H, H-7).

(5*Z*,7*E*)-5,7-Dodecadien-1-ol Acetate (3). The mixture of **2** (11 mg, 0,06 mmol), Ac_2O (12 mg, 0.11 mmol), and pyridine (1 mL) was stirred at 10 °C for 1 h. The resulting crude product was concentrated in vacuo and purified by TLC (silica gel), eluted with 20% ethyl acetate–petroleum ether, to afford as a colorless oil **3** (13 mg, 96%): IR (film) 1740, 1260, 1180, 990, 950 cm^{-1}; MS, m/z (relative intensity) 224 (M^+, 23); ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H, H-12), 1.20–1.72 (m, 8 H H-2,3,10,11), 2.05 (s, 3 H, H-2′), 2.09–2.26 (m, 4 H, H-4,9), 4.07 (t, J = 6.5 Hz, 2 H, H-1), 5.28 (dt, $J_{5,6}$ = 10.8 Hz, $J_{4,5}$ = 7.2 Hz, 1 H, H-5), 5.68 (dt, $J_{7,8}$ = 15.1 Hz, $J_{8,9}$ = 7.0 Hz, 1 H, H-8), 5.96 (dd, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 10.9 Hz, 1 H, H-6), 6.30 (dd, $J_{7,8}$ = 15.1 Hz, $J_{6,7}$ = 10.9 Hz, 1 H, H-7).

(5*E*,7*Z*)-Dodecadien-1-ol (12). The reaction conditions used for the Wittig transformation of **11** to **12** were the same as described for the prepartion of **9**. The purity of the desired **12** (5*E*,7*Z* isomer 92%) determined by GC and GC/MS as the same as in **1** was 92%, The other two isomers were 2% and 4%, respectively. ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H, H-12), 1.26–1.68 (m, 9 H, H-2,3,10,11, OH), 2.06-2.26 (m, 4 H, H-4,9), 3.66 (t, J = 6 Hz, 2 H, H-1), 5.30 (dt, $J_{5,6}$ = 10.8 Hz, $J_{4,5}$ = 7 Hz, 1 H, H-5), 5.68 (dt, $J_{7,8}$ = 15.1 Hz, $J_{8,9}$ = 6 Hz, 1 H, H-8), 5.98 (dd, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 10.6 Hz, 1 H, H-6), 6.30 (dd, $J_{7,8}$ = 15.1 Hz, $J_{6,7}$ = 10.6 Hz, 1 H, H-7).

(5*E*,7*Z*)-5,7-Dodecadienal (4). To a suspension of PCC (60 mg, 0.28 mmol) in CH_2Cl_2 (1 mL) solution was added **12** (31 mg, 0.17 mmol) quickly. The mixture was stirred at room temperature. After the mixture was stirred for 2 h, ether (10 mL) was added. The resulting mixture was filtered on a short column of silica gel (petroleum ether–ethyl acetate, 95:5) to give the product (21 mg, 68%). The purity of the desired isomer (5*E*,7*Z* form) **4**, identified by GC and GC/MS, was 96%. The other isomers were 2% and 2%, respectively. MS, M^+ of the three isomers were the same; IR (film) 1725, 985, 995 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3 H, H-12), 1.26–1.40 (m, 4 H, H-10,11), 1.75 (m, 2 H, H-3), 2.16 (m, 4 H, H-4, 9), 2.45 (dt, 2 H, H-2), 5.35 (dt, $J_{8,9}$ = 7.2 Hz, $J_{7,8}$ = 10.9 Hz, 1 H, H-8), 5.60 (dt, $J_{4,5}$ = 7.1 Hz, $J_{5,6}$ = 15.1 Hz, 1 H, H-5), 5.94 (dd, $J_{7,8}$ = 10.9 Hz, $J_{6,7}$ = 10.5 Hz, 1 H, H-7), 6.33 (dd, $J_{5,6}$ = 15.1 Hz, $J_{6,7}$ = 10.5 Hz, 1 H, for H-6), 9.77 (t, J = 1.7 Hz, 1 H for H-1).

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Registry No. **1**, 61360-84-7; **2**, 73416-71-4; **3**, 78350-11-5; **4**, 75539-65-0; **5**, 103698-50-6; **6a**, 124-19-6; **6b**, 110-62-3; **6c**, 124-19-6; **7a**, 53448-07-0; **7b**, 18829-55-5; **7c**, 78350-09-1; **8**, 70665-02-0; **9**, 102488-79-9; **10**, 83085-84-1; **11**, 21406-61-1; **12**, 72922-18-0; $THPO(CH_2)_5OH$, 76102-74-4; $BrCH_2CHO$, 17157-48-1; Ph_3As, 603-32-7.

Total Synthesis of Dihydrovitamin DHV_3 and Dihydrotachysterol DHT_3. Application of the Low-Valent Titanium-Induced Reductive Elimination

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Optically active ring A synthons **6**, **11**, **13**, and **14**, precursors of DHV_3 and DHT_3, were synthetized from (-)- and (+)-carvone. Application of the low-valent titanium-induced reductive elimination gave a new synthetic approach to vitamin D_3 analogues, as shown by an efficient preparation of DHT_3.

Synthetic efforts directed toward vitamin D_3 and its metabolites have been renewed since the discovery that specific hydroxylated derivatives are involved in a complex control of calcifiction processes. In contrast to the traditional passive characterization of vitamin D_3 as a vitamin, it is known[1] that vitamin D_3 acts like other classical steroid

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