Pergamon

Tetrahedron Vol. 51, No. 38, pp. 10433-10442, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00622-2

Syntheses of the Female Sex Pheromones of *Matsucoccus* Pine Scales Using the [2,3]-Wittig Rearrangement of a Bisallylic Tertiary Ether

Xiongwei Shi*, Francis X. Webster*, and Jerrold Meinwald†

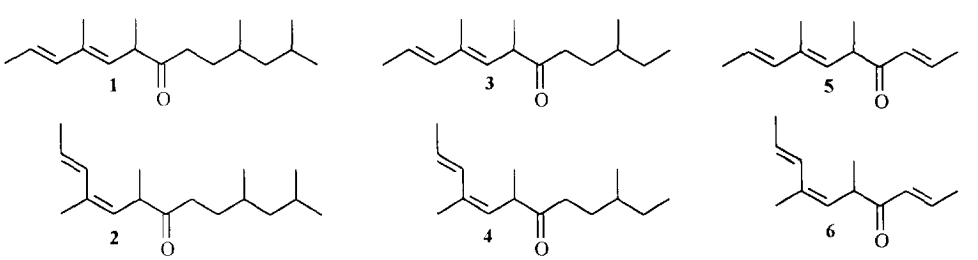
*Department of Chemistry, College of Environmental Science and Forestry,
State University of New York, Syracuse, NY 13210

†Department of Chemistry, Cornell University, Ithaca, NY 14853

Abstract: A convergent, general synthesis of (2*E*,4*E*)-4,6,10,12-tetramethyltrideca-2,4-dien-7-one (matsuone, **1**) and five closely related analogs (**2-6**), which serve as sex pheromone components of female *Matsucoccus* pine scales, is described. The aldehydes **8a** and **8b** were obtained via a reaction sequence in which the key step is a [2,3]-Wittig sigmatropic rearrangement of the oxazoline ether of bisallylic tertiary alcohol **11**. Coupling of **8** with the appropriate nucleophilic reagents, followed by oxidation of the resultant secondary alcohols, afforded the pheromone components **1-6**.

INTRODUCTION

Pine scales of the genus *Matsucoccus* devastate forestlands worldwide. In a search for an effective monitoring system for these pests, Lanier *et al.*[1] isolated and identified a cross-attractive female sex pheromone component, (2*E*,4*E*)-4,6,10,12-tetramethyltrideca-2,4-dien-7-one (matsuone, **1**), from *M. resinosae* (USA), *M. matsumurae* (China), and *M. thunbergianae* (South Korea). Subsequently, another sex pheromone

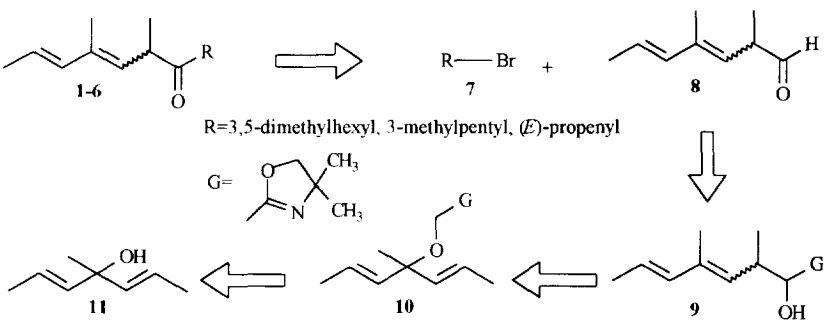


of this family was isolated from the maritime pine scale *M. feytaudi* (Africa and Europe) by Einhorn *et al.*[2] and characterized as a mixture of (8*E*,10*E*)-3,7,9-trimethyldodeca-8,10-dien-6-one (**3**) (major) and its (8*Z*,10*E*)-isomer **4** (minor). Two closely related compounds, (2*E*,6*E*,8*E*)-5,7-dimethyldeca-2,6,8-trien-4-one (**5**) (major) and its (2*E*,6*Z*,8*E*)-isomer **6** (minor) have also been reported as sex pheromone components of *M. josephi* (Israel)[3]. Interestingly, compound **2**, the geometric isomer of matsuone **1** corresponding to **4** and **6**, has not been isolated as a natural product.

Since all these compounds have the potential of serving as attractants in control programs for *Matsucoccus* scales, considerable synthetic effort has been reported for **1**[4-7], **3**[7-11], **5**[12], and a mixture of **5** and **6**[13]. Enantioselective syntheses of **1**, **3** and **5** have resulted in the assignment of the absolute configuration of matsuone (**1**) as (6*R*,10*R*)-**1**[7,14], that of the major pheromone component of *M. feytaudi* as (3*S*,7*R*)-**3**[15], and those of the major and minor pheromone components of *M. josephi* as (*R*)-**5** and (*R*)-**6**,[16] respectively. These investigations also revealed that the unnatural diastereomers (6*R*,10*S*)-**1**[7] and (3*R*,7*R*)-**3**[15] have pheromonal activities similar to those of the natural products, whereas other unnatural stereoisomers showed neither blocking nor synergistic effects. This has made it possible to use synthetic mixture of isomers for pest management. However, efficient syntheses leading to such mixtures for the major components have not been described. Moreover, no synthetic procedures for the preparation of pure samples of **2**, **4**, and **6** have been reported. We have now completed geometrically selective syntheses of compounds **1-6**, using the [2,3]-Wittig rearrangement of the tertiary oxazoline ether **15** as the key step.

RESULTS AND DISCUSSION

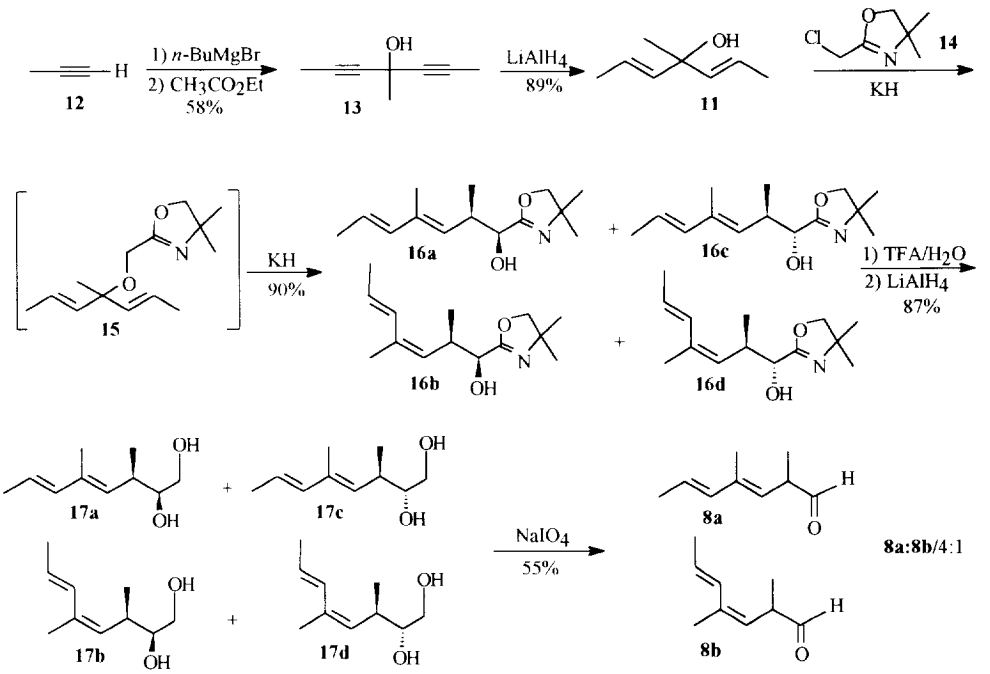
The strategy for the synthesis of compounds **1-6** is based on the [2,3]-Wittig rearrangement of tertiary ether **10** bearing a suitable migrating group (G) (**Scheme 1**). For the synthesis of **1**, **3**, and **5**, the (*E*,*E*)-subunit was elaborated from the corresponding (*E*,*E*)-dienol **9**. Similarly, the (*E*,*Z*)-framework of **2**, **4**, and **6** was constructed from the (*E*,*Z*)-isomers of **9**. A three-step sequence serves to degrade **9** to aldehyde **8.** The remainder of the carbon backbone of each pheromone component was then assembled by addition of a nucleophilic reagent derived from the corresponding bromide 7 to aldehyde **8**. The resulting alcohols were oxidized to give the pheromone components **1-6**.



Scheme 1

Aldehydes **8a** and **8b** were prepared as shown in **Scheme 2**. Methylacetylene (**12**) was converted to the corresponding Grignard reagent, followed by addition to ethyl acetate, to afford the crystalline diynol **13**. This

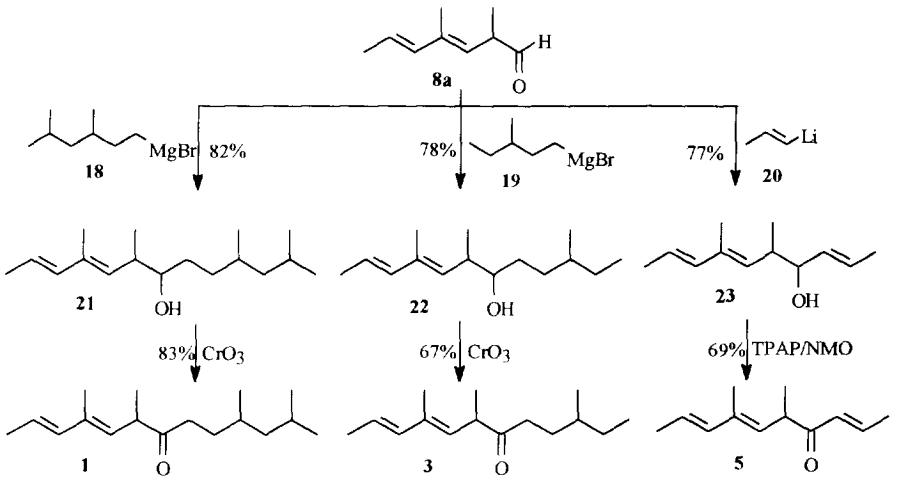
diynol was reduced in two steps with $LiAlH_4$ to dienol **11** in 89% yield. In the presence of two equivalents of KH, this tertiary alcohol was coupled with 2-chloromethyl-4,5-dihydro-4,4-dimethyloxazole (**14**)[17,18] to afford intermediate **15** which without isolation underwent the desired [2,3]-Wittig sigmatropic rearrangement to give a mixture of four racemic conjugated dienes **16a-d** in 90% overall yield.[19] Capillary GC analysis indicated that



Scheme 2

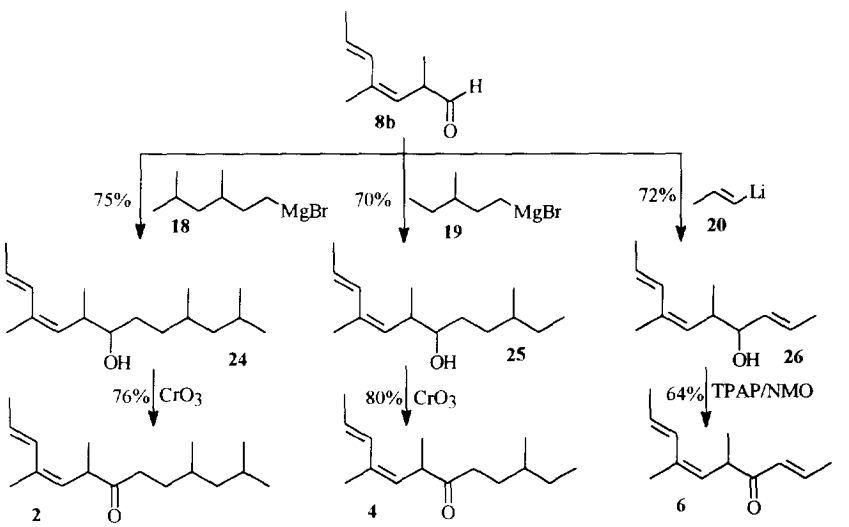
the ratio of the four isomers was *ca.* 1:1:1:7 (**16d**:**16c**:**16b**:**16a**), in order of increasing retention times. Since these isomers are difficult to separate by flash chromatography, the mixture was converted directly into the corresponding mixture of dienediols **17a-d** by hydrolysis and reduction in 87% overall yield. Periodate cleavage of this diol mixture afforded a mixture of aldehydes (55% yield) which were separated by flash chromatography over silica gel to give the desired **8a** and **8b** (**8a**:**8b**/4:1) in high stereochemical purity.

Addition of the Grignard or lithium reagents **18-20** derived from the corresponding bromides (racemic in the cases of **18** and **19**, *trans* in case of **20**)[7] to the (*E*,*E*)-aldehyde **8a** gave diastereomeric mixtures of alcohols **21-23** in good yield (**Scheme 3**). Oxidation of these alcohols yielded the geometrically pure final products **1**, **3**, and **5**. Similarly, the sex pheromone components **2**, **4**, and **6** were obtained, starting with the (*Z*,*E*)-aldehyde **8b**, as shown in **Scheme 4**. GC-MS, ^1H and ^{13}C NMR data obtained from the previously unreported compound **2** confirmed its structure unambiguously. The spectroscopic data of the other synthetic pheromone components are in good agreement with those reported.



Scheme 3

The convergent, flexible syntheses described above provide the naturally occurring sex pheromone components **1**, **3-6,** along with the possible pheromone component **2** in quantities sufficient for both laboratory and field tests. This [2,3]-Wittig rearrangement sequence offers a general synthetic approach to all of the identified *Matsucoccus* sex pheromones, as well as to any other natural products which incorporate a similar (*E,E*)- or (*E,Z*)-trisubstituted diene system.[20,21] Enantiospecific syntheses of *Matsucoccus* pine scale pheromones based on a similar strategy will be described in another publication.



Scheme 4

EXPERIMENTAL

General experimental procedure. -- NMR spectra were recorded on an AMX 300 Bruker NMR spectrometer. Proton NMR spectra were acquired at 300 MHz. ^{13}C NMR and DEPT spectra were acquired at 75 MHz. The low resolution EI and CI (CH_4) mass spectra were recorded on a Finnigan 4500 GC-MS spectrometer. The high resolution mass spectra were obtained in the mass spectrometry laboratory of the University of Illinois. IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer as films. Melting points were measured with a Thomas melting point apparatus and were uncorrected. Capillary gas chromatography was performed on a Varian 3700 gas chromatograph [DB-1, 30 m x 0.25 mm, temperature program: 80 °C, 4 °C/min, 200 °C (20 min)]. Flash column chromatography was performed over silica gel (Merck, grade 60, 230-240 mesh, 60 Å). Preparative column chromatography and reactions were monitored by TLC utilizing POLYGRAM SILG/UV254 precoated 0.25 mm silica gel with a fluorescent indicator. Solvents were distilled prior to use. All reactions were run under an argon atmosphere except as noted.

4-Methylhepta-2,5-diyn-4-ol (13).-- Gaseous methylacetylene (9.60 g, 0.24 mol) from a cylinder was condensed in a 100 ml flask cooled with a dry-ice/acetone bath, then warmed slowly and transferred into a solution of *n*-BuMgBr (0.2 mol) in THF/HMPA (4:1, 100 ml) at -78 °C over 3 h with vigorous stirring. Upon completion of the transfer, the mixture was stirred for 2 hr and warmed to 25 °C slowly. Ethyl acetate (8.80 g, 0.1 mol) was added dropwise over a period of 20 min. After stirring for an additional hour, the reaction mixture was quenched with a saturated solution of NH_4Cl (10 ml) and extracted with hexane (3 x 100 ml). The combined extract was washed with brine, dried over Na_2SO_4 and concentrated to give a yellow oil (12.1 g) which was purified by flash chromatography over silica gel (5:2/hexane:ethyl acetate) to afford **13** as white crystals (7.08g, 58%, m.p. 39-40 °C). EIMS *m/e* (%) 122(M$^+$, 0.45), 121 (5), 107(100), 77(35), 67(39), 43(65); ^1H NMR (C_6D_6) δ 1.43(6H, s), 1.81(3H, s), 2.40-2.60(OH, br); HREIMS *m/e* calcd for $C_8H_{10}O$ 122.0732, found 122.0732; ^{13}C NMR (C_6D_6) δ 3.1(CH_3), 32.6(CH_3), 60.3(C), 78.1(C), 82.5(C); IR (KBr) 3350, 2210, 1060 cm^{-1}.

(2*E*,5*E*)-4-Methylhepta-2,5-dien-4-ol (11).-- To a refluxing suspension of $LiAlH_4$ (11.40 g, 0.33 mol) in THF (500 ml) was added dropwise a solution of **13** (34.00 g, 279 mmol) in THF (500 ml) over 15 min. After stirring for 2 h, the reaction mixture was slowly quenched with water (50 ml) and extracted with hexane (3 x 250 ml). The combined extract was washed with brine, dried over $MgSO_4$ and concentrated to provide the partially reduced product (2*E*,4*RS*)-4-methyl-2-hepten-5-yn-4-ol (34.01 g, 98%). To a suspension of $LiAlH_4$ (11.40 g, 330 mmol) in dried THF (500 ml) was added dropwise a solution of the crude eneynol (15.00g, 120 mmol) in THF (300 ml) at room temperature over 1 h. After stirring for 16 h, the reaction mixture was quenched with water (30 ml), extracted with hexane (3 x 250 ml), dried over Na_2SO_4 and concentrated to give a yellow oil (14.50 g), which was purified by flash chromatography (ethyl acetate:hexane/5:95) to afford **11** (13.59 g, 90%) as a light yellow oil. EIMS *m/e* (%) 126(M$^+$, 1), 111(38), 97(8), 85(18), 83(25), 69(20), 67(22), 55(48), 43(100), 41(41); HREIMS *m/e* calcd for $C_8H_{14}O$ 126.1045, found 126.1044; ^1H NMR (C_6D_6) δ 1.27 (3H, s), 1.55 (6H, *J* = 6.8 Hz, d), 5.48-5.62 (m, 4H); ^{13}C NMR (C_6D_6) δ 17.6(CH_3), 28.7(CH_3), 72.3(CH_3), 122.4(CH), 138.5(CH).

4,5-Dihydro-4,4-dimethyl-2-(2,4-dimethyl-1-hydroxylhepta-3,5-dienyl)-oxazole (16a-d).-- To a stirred suspension of KH (150 mmol) in THF (50 ml) was slowly added a solution of **11** (9.0 g, 72 mmol) in THF (100 ml). After stirring for 1 h, 2-chloromethyl-4,5-dihydro-4,4-dimethyloxazole (**14**) (10.62 g, 72 mmol) in THF(100 ml) was added dropwise over 10 min. After stirring for an additional 9 h at room temperature, the mixture was quenched with water (20 ml) and extracted with ether (3 x 100 ml). The combined extract was washed with brine and dried over Na_2SO_4. Concentration and purification over silica gel (ethyl acetate:hexane/1:4) afforded an oil (15.36 g, 90%). GC analysis indicated the products contained four isomers with a ratio of 1:1:1:7, in order of increasing retention times. A small amount of the major product (m.p. 77-79 °C) was obtained by recrystallization from ether at -25 °C. For major product **16a**: EIMS *m/e* (%) 237(M^+, 5), 220(1), 164(4), 129(10), 109(100), 91(4), 81(12), 67(40), 55(27), 41(29); HREIMS *m/e* calcd for $C_{14}H_{23}O_2N$ 237.1729, found 237.1726; ^1H NMR (CDC_{13}) δ 1.01(3H, *J* = 6.8 Hz, d), 1.26(3H, s), 1.28(3H, s), 1.74(3H, *J* = 6.6, 1.3 Hz, dd), 1.75 (3H, *J* = 1.3 Hz, d), 2.8-3.0(1H, m), 2.7-2.9(1H, br), 3.99(2H, s), 4.13(1H, *J* = 4.6 Hz, d), 5.32(1H, *J* = 10 Hz, d), 5.61(1H, *J* = 15.6, 5.7 Hz, dq), 6.07(1H, *J* = 15.6, 0.7 Hz, dq); ^{13}C NMR ($CDCl_3$) δ 12.6(CH_3), 15.3(CH_3), 18.1(CH_3), 28.1(CH_3), 36.8(CH), 66.6(C), 71.0(CH), 79.9(CH_2), 123.1(CH), 130.5(CH), 134.5(CH), 134.1(C), 135.8(CH), 166.6(C); IR (film) 3210, 3030, 2940, 2910, 1650, 1440, 1380, 1360, 1290, 1060, 990, 960 cm^{-1}.

3,4-Dimethylocta-4,6-dien-1,2-diol (17a-d).-- To a stirred solution of oxazolines (**16a-d**) (8.0 g, 33.8 mmol) in THF (100 ml) were added TFA (3.85 g, 33.8 mmol) and water (0.6 g, 33.8 mmol). After stirring for 15 h at 25 °C, the solution was slowly added to a stirred suspension of $LiAlH_4$ (100 mmol) in THF (50 ml) at 0 °C. After stirring for additional 3 h at 0 °C, the solution was quenched with water (50 ml); the white precipitate was filtered off and washed by hexane (3 x 0.5 ml). The combined filtrate was washed with brine, dried over Na_2SO_4 and concentrated to give a colorless oil. The crude product was further purified by flash chromatography (ethyl acetate:hexane/1:1) over silica gel to afford an oil (**17a-d**) (5.01 g, 87%). In the same manner, a small amount of the pure major product of **17** was obtained using pure major product of **16**. For the major product **17a**: CIMS *m/e* 171(M^++1); HREIMS *m/e* calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1307; ^1H NMR (C_6D_6) δ 1.11(3H, *J* = 7 Hz, d), 1.65(3H, *J* = 6.6, 1.5 Hz, dd), 1.67(3H, *J* = 1.3 Hz, dd), 2.5-2.7(m, 1H), 2.8-3.4(2H, m), 3.3-3.5(2H, m). 3.5-3.7(1H, m), 5.13(1H, *J* = 10 Hz, d), 5.43-5.51(1H, *J* = 15.7, 6.7 Hz, dq), 6.06(1H, *J* = 15.7, 1.5 Hz, dd); ^{13}C NMR (C_6D_6) δ 13.0(CH_3), 17.4(CH_3), 18.2(CH_3), 36.30(CH), 65.6(CH_2), 76.6(CH), 122.7(CH), 132.3(CH), 134.1(C), 136.6(CH); IR (film) 3360, 3030, 1660, 1060, 1010, 960 cm^{-1}.

(3*E*,5*E*)-2,4-Dimethylhepta-3,5-dienal (8a) and **(3*Z*,5*E*)-2,4-Dimethylhepta-3,5-dienal (8b)**.-- To a stirred solution of $NaIO_4$ (8.0 g, 40 mmol) in a mixed solvent of 1,4-dioxane (40 ml) and water (40 ml) was added a solution of diols **17a-d** (4.80 g, 28 mmol) in 1,4-dioxane (5 ml) at room temperature. After stirring for 2 h, the reaction solution was extracted with pentane (3 x 150 ml). The combined extracts were dried and carefully concentrated under reduced pressure to afford a volatile oil which was purified by flash chromatography over silica gel (3% ether in pentane) to give a less polar (*E,Z*)-isomer **8b** (0.44 g, 11.4%) and more polar (*E,E*)-isomer **8a** (1.76 g, 45.6%). For (*E,Z*)-isomer **8b**: EIMS *m/e* (%) 138(M^+, 15), 109(81), 81(28), 67(100), 55(34), 43(33), 41(52); HREIMS *m/e* calcd for $C_9H_{14}O$ 138.1045, found 138.1045; ^1H NMR ($CDCl_3$) δ 1.17(3H, *J* = 6.9 Hz, d), 1.82(3H, *J* = 6.6, 1.2 Hz, dd), 1.87(1H, *J* = 1.2 Hz, d), 3.45-3.55(m, 1H), 5.01(1H, *J* = 9.3 Hz, d), 5.83(1H, *J* = 15.4, 6.7 Hz, dq), 6.40(1H, *J* = 15.4, 1.2 Hz, dq), 9.50(1H, *J* = 1.6 Hz,

d); ^{13}C NMR ($CDCl_3$) δ 14.21(CH_3), 20.72(CH_3), 22.30(CH_3), 45.53(CH), 122.87(CH), 125.25(C), 127.82(CH), 128.04(CH), 201.10(C=O). For (*E,E*)-isomer **8a**: HREIMS *m/e* calcd for $C_9H_{14}O$ 138.1045, found 138.1045; ^{1}H NMR ($CDCl_3$) δ 1.17(3H, *J* = 6.9 Hz, d), 1.76(3H, *J* = 6.6, 0.9 Hz, dd), 1.80(3H, *J* = 0.9 Hz, d), 3.31-3.39(1H, m), 5.13(1H, *J* = 9.1, 0.6 Hz, dd), 5.72(1H, *J* = 16.5, 6.6 Hz, dq), 6.10(1H, *J* = 16.5, 0.9 Hz, dq), 9.48(1H, *J* = 1.9 Hz, d); ^{13}C NMR ($CDCl_3$) δ 13.1(CH_3), 14.1(CH_3), 18.1(CH_3), 46.4(CH), 124.6(CH), 124.7(CH), 135.1(CH), 137.8(C), 200.8(C=O).

(2*E*,4*E*)-4,6,10,12-Tetramethyltrideca-2,4-dien-7-ol (21).-- To a stirred suspension of activated magnesium powder (583 mg, 24 mmol) in THF (10 ml) was slowly injected a solution of 3,5-dimethyl-1-bromohexane[7] (4.32 g, 24 mmol) in THF (10 ml). Upon completion of the reaction, **8a** (1.66 g, 12 mmol) was injected into the above solution. After stirring for an additional 1 h, the reaction solution was quenched with water (5 ml) and extracted with ether (3 x 100 ml). The combined extract was dried and concentrated to provide a crude product which was purified by chromatography over silica gel to afford a diastereomeric mixture of alcohols **21** (2.60 g, 83%). HREIMS *m/e* calcd for $C_{17}H_{32}O$ 252.2453, found 252.2456; ^{1}H NMR ($CDCl_3$) δ 0.81-0.84(9H, m), 1.05(3H, *J* = 6.6 Hz, 2d), 1.05-1.70(8H, m), 1.74-1.75(3H, 2s), 1.77(3H, *J* = 9.6, 1.8 Hz, d), 2.49-2.60(1H, m), 3.37(1H, br), 5.21(1H, *J* = 9.5 Hz, d), 5.61(1H, *J* = 15.6, 6.6 Hz, dq), 6.08(1H, *J* = 14.8 Hz, d); ^{13}C NMR ($CDCl_3$) δ 12.9(CH_3), (16.3, 16.1)(CH), 18.1(CH_3), (19.9, 19.6)(CH_3), 22.2(CH_3), (23.5, 23.4)(CH_3), (25.3)(CH), (30.5, 30.3)(CH), 32.0(CH), (33.6, 33.7)(CH_2), (38.6, 38.8)(CH_2), (46.7, 49.0)(CH_2), 76.4(CH), 122.7(CH), 132.4(CH), 133.8(C), 136.1(CH); IR (film) 3350, 3030, 2930, 2880, 1695, 1440, 1375, 1050, 960 cm^{-1}.

(8*E*,10*E*)-3,7,9-Trimethyldodeca-8,10-dien-6-ol (22) -- In the same manner, **22** (530 mg, 78%) was obtained from **8a**. EIMS *m/e* (%) 224(M^+, 0.31), 121(1), 110(41), 109(19), 95(100), 93(5), 81(7), 67(16), 55(28), 41(27); HREIMS *m/e* calcd for $C_{15}H_{28}O$ 224.2140, found 224.2139; ^{1}H NMR ($CDCl_3$) δ 0.80-0.92(3H, *J* = 7 Hz, dt), 1.02(3H, *J* = 7 Hz, d), 1.05-1.60(7H, m), 1.74(3H, *J* = 1.5 Hz, d), 1.75-1.80(6H, m), 2.5-2.7(1H, m), 3.30-3.5(1H, br), 5.22(1H, *J* = 9.5 Hz, d), 5.57-5.66(1H, *J* = 15.5, 1.3 Hz, dq), 6.08(1H, *J* = 15.5 Hz, d); ^{13}C NMR ($CDCl_3$) δ (11.3, 11.4)(CH_3), (12.9, 13.0)(CH_3), (16.0, 16.3 16.5)(CH_3), (18.2, 18.6)(CH_3), (19.1, 19.3)(CH_3), (29.3, 29.7)(CH_2), (32.1, 32.9)(CH_2), 34.1(CH_2), (34.4, 34.6)(CH_2), (38.7, 38.8)(CH), (76.1, 76.3, 76.4)(CH), 122.7(CH), 132.2(CH), 133.7(C), 136.1(CH); IR (film) 3350, 3030, 2970, 2930, 1450, 1375, 1075, 1030, 960 cm^{-1}.

(2*E*,6*E*,8*E*)-5,7-Dimethyldeca-2,6,8-trien-4-ol (23).[22]-- To a stirred solution of (*E*)-1-bromopropene (726 mg, 6 mmol) in THF/ether/pentane/ 4:1:1 (15 ml) at -115 °C (ethanol/liquid N_2) was injected *t*-BuLi (4 ml, 1.7 M). After stirred for 0.5 h, the mixture was allowed to warm up to - 78 °C. Li_2CuCl_4 (150 µl; 0.1 M in THF) and then aldehyde **8a** (438 mg, 3 mmol) were slowly injected into the solution. The reaction mixture was allowed to warm to 25 °C and quenched with water (2 ml). The organic phase was extracted with hexane (3 x 10 ml) and the combined extract was dried and concentrated to give a residue which was purified by flash chromatography to yield an oil (418 mg, 77%). EIMS *m/e* (%) 180(M^+, 0), 110(49), 109(78), 95(52), 81(37), 71(59), 67(100), 55(28), 43(48), 41(56); ^{1}H NMR (C_6D_6) δ 1.15(3H, *J* = 6.7 Hz, d), 1.48(3H, *J* = 6.7, 1.3 Hz, dd), 1.61(3H, *J* = 6.7, 1.6 Hz, dq), 1.67(3H, *J* = 1.3 Hz, d), 2.58(1H, m), 3.76(1H, m), 5.24(1H, *J* = 9.5 Hz, d), 5.45(3H, m), 6.10(1H, *J* = 15.3, 0.9 Hz, dq); ^{13}C NMR (C_6D_6) δ 8.6, 12.3, 13.2, 13.7, 34.8, 72.2, 117.9, 121.8, 128.0, 128.7, 132.4.

(2*E*,4*Z*)-4,6,10,12-Tetramethyltrideca-2,4-dien-7-ol (24).-- In the same manner, addition of the Grignard reagent derived from 3,5-dimethyl-1-bromohexane[7] (500 mg, 2.3 mmol) to **8b** (200 mg, 1.3 mmol) afforded **24** (248 mg, 75%). HREIMS *m/e* calcd for $C_{17}H_{32}O$ 252.2453, found 252.2456; ^{1}H NMR ($CDCl_3$) δ 0.82-0.87(9H, m), 1.05(3H, *J* = 6.6 Hz, 2d), 1.05-1.70(8H, m), 1.75-1.83(9H, m), 2.60-2.70(1H, m), 3.38(1H, m), 5.08(1H, *J* = 9.9 Hz, d), 5.73(1H, *J* = 15.6, 6.6 Hz, 2d), 6.44(1H, *J* = 15.6 Hz, d).

(8*Z*,10*E*)-3,7,9-Trimethyldodeca-8,10-dien-6-ol (25).--In the same manner, alcohol **25** (154 mg, 70%) was obtained from **8b**. EIMS *m/e* (%) 224 (M^+, 0.25), 121(1), 110(40), 109(18), 95(100), 93(6), 81(7), 67(15), 55(27), 41(27); HREIMS *m/e* calcd for $C_{15}H_{28}O$ 224.2140, found 224.2139; ^{1}H NMR ($CDCl_3$) δ 0.80-0.90(3H, m), 0.95(3H, *J* = 7 Hz, d), 1.00(3H, *J* = 7 Hz, d), 1.05-1.60(7H, m), 1.79-1.824(6H, t), 2.6-2.8(1H, m), 3.30-3.5(1H, m), 5.00-5.15(1H, *J* = 9.5 Hz, d), 5.65-5.82(1H, *J* = 15.5, 1.3 Hz, dq), 6.42(1H, *J* = 15.5 Hz, d).

(2*E*,6*Z*,8*E*)-5,7-Dimethyldeca-2,6,8-trien-4-ol (26).[22]-- As described in the preparation of **23**, alcohol **26** (195 mg, 72%) was obtained from **8b.** ^{1}H NMR (C_6D_6) δ 1.20(3H, *J* = 6.7 Hz, d), 1.44(3H, *J* = 6.7, 1.3 Hz, dd), 1.62(3H, *J* = 6.7, 1.6 Hz, dq), 1.76(3H, *J* = 1.3 Hz, d), 2.75(1H, m), 3.69(1H, m), 5.15(1H, *J* = 9.5 Hz, d), 5.57(3H, m), 6.56(1H, *J* = 15.3, 1.2 Hz, dq).

(2*E*,4*E*)-4,6,10,12-Tetramethyltrideca-2,4-dien-7-one (1).-- To a stirred solution of **21** (2.52 g, 10 mmol) in acetone (400 ml) was added Jones' reagent (3 ml, 8N) at 0 °C. After stirring for 5 min, the reaction solution was diluted with water (50 ml) and extracted by hexane (3 x 500 ml). The combined extract was washed with a solution of saturated $NaHCO_3$, brine and water, dried over Na_2SO_4, and concentrated to give 2.63 g of residue which was purified by flash chromatography (2% ethyl acetate in hexane) to afford **1** (2.06 g, 83%) as a colorless oil. EIMS *m/e* (%) 250(M^+, 4), 141(7), 123(35), 109(100), 81(22), 67(35), 57(23), 55(26); HREIMS *m/e* calcd for $C_{17}H_{30}O$ 250.2297, found 250.2296; ^{1}H NMR (C_6D_6) δ 0.75(3H, *J* = 6.9 Hz, d), 0.80(3H, *J* = 6.6 Hz, d), 0.84(3H, *J* = 6.6 Hz, d), 0.86-1.07(1H, m), 1.20(3H, *J* = 6.6 Hz, d) 1.60(3H, *J* = 6.6 Hz, d), 1.66(3H, s), 2.07-2.37(2H, s), 3.26-3.22(1H, *J* = 15.5, 6.6 Hz, q), 5.24(1H, *J* = 10 Hz, d), 5.48(1H, *J* = 15.5, 6.6 Hz, dq), 5.97-6.03(1H, *J* = 15.5, 0.6 Hz, dq); ^{13}C NMR (C_6D_6) δ 12.9(CH_3), 16.7(CH_3), 18.1(CH_3), (19.6, 19.8)(CH_3), (22.4)(CH_3), (23.0, 23.4)(CH_3), 25.5(CH), 30.2(CH), 31.3(CH_2), (38.4)(CH_2), (46.6, 46.7)(CH), (46.8, 46.9)(CH_2), 123.7(CH), 129.5(CH), 135.5(C), 136.1(CH), 209.5(C=O); IR (film) 3030, 2900, 1700, 1380, 1360, 960 cm^{-1}.

(2*E*,4*Z*)-4,6,10,12-Tetramethyltrideca-2,4-dien-7-one (2).-- In the same manner, alcohol **24** (250 mg, 1 mmol) gave ketone **2** (188 mg, 76%). EIMS *m/e* (%) 250(M^+, 4), 141(8), 123(34), 109(100), 81(22), 67(33), 57(22), 55(25.92); HREIMS *m/e* calcd for $C_{17}H_{30}O$ 250.2297, found 250.2296; ^{1}H NMR(C_6D_6) δ 0.81(d, *J* = 6.9 Hz, 3H), 0.86(3H, *J* = 6.6 Hz, d), 0.90(3H, *J* = 6.6 Hz, d), 0.86-1.07(1H, m), 1.21(3H, *J* = 6.6, 0.7 Hz, dd), 1.22-1.35(2H, m), 1.35-1.55(1H, m), 1.55-1.75(1H, m), 1.71(3H, *J*=6.6 Hz, d), 1.75(3H, s), 2.15-2.50(2H, m), 3.56(1H, *J* = 15.5, 6.6 Hz, 2q), 5.18(1H, *J* = 10 Hz, d), 5.68(1H, *J* = 15.5, 6.6 Hz, dq), 6.55(1H, *J* = 15.5 Hz, d); ^{13}C NMR (C_6D_6) δ 14.2(CH_3), (16.9)(CH_3), 18.6(CH3), (19.6, 19.7)(CH_3), (22.4, 22.6)(CH_3), (23.40)(CH_3), 25.5(CH), 30.2(CH), 31.4(CH_2), (38.3, 38.4)(CH_2), 45.8(CH), (46.8, 46.9)(CH2), 124.5(CH), 124.7(CH), 130.1(C), 134.2(CH), 209.6(C=O).

(8*E*,10*E*)-3,7,9-Trimethyldodeca-8,10-dien-6-one (3).-- Similarly, alcohol **22** (450 mg, 2 mmol) afforded ketone **3** (301 mg, 67%). EIMS *m/e* (%) 222(M^+, 5), 113(17), 109(100), 95(43), 81(14), 79(11),

69(15), 67(40), 57(17), 55(23), 43(64), 41(48); HREIMS *m/e* calcd for $C_{15}H_{26}O$ 222.1984, found 222.1984; ^{1}H NMR (C_6D_6) δ 0.75(3H, *J* = 6.6 Hz, d), 0.79(3H, *J* = 7.2 Hz, t), 0.97-1.07(1H, m), 1.16-1.27(1H, m), 1.31-1.44(1H, m), 1.20(3H, *J* = 6.7 Hz, d), 1.60(3H, *J* = 6.6, 1.3 Hz, dd), 1.66(3H, *J* = 1.3 Hz, d), 1.62-1.67(1H, m), 2.06-2.35(2H, m), 3.23-3.34(1H, *J* = 8.0, 14.0 Hz, dq), 5.34(1H, *J* = 10.0 Hz, d), 5.47(1H, *J* = 15.0, 7.5 Hz, dq), 5.97(1H, *J* = 15.0, 0.5 Hz, dd); ^{13}C NMR (C_6D_6) δ 11.5(CH_3), 12.9(CH_3), (16.7)(CH_3), 18.2(CH_3), (19.0, 19.1)(CH_3), (29.5, 29.7)(CH_2), 30.7(CH_2), 34.3(CH), 38.6(CH_2), (46.6)(CH), 123.7(CH), 129.6(CH), 135.5(C), 136.1(CH), 209.5(C=O); IR (film) 3030, 2940, 2900, 2850, 1700, 1440, 1370, 960 cm^{-1}.

(8*Z*,10*E*)-3,7,9-Trimethyldodeca-8,10-dien-6-one (4).-- In the same manner, alcohol **25** (225 mg, 1 mmol) gave ketone **4** (179 mg, 80%). EIMS *m/e* (%) 222(M$^+$, 4), 113(19), 109(100), 95(41), 81(13), 79(11), 69(14), 67(41), 57(17), 55(23), 43(67), 41(49); HREIMS *m/e* calcd for $C_{15}H_{26}O$ 222.1984, found 222.1984; ^{1}H NMR (C_6D_6) δ 0.81(3H, *J* = 6.6 Hz, d), 0.85(3H, *J* = 7.2 Hz, t), 0.97-1.07(1H, m), 1.16-1.27(1H, m), 1.20 (3H, *J* = 6.7 Hz, d), 1.20-1.35(2H, m), 1.71(3H, *J* = 6.6, 1.3 Hz, dd), 1.78(3H, *J* = 1.0 Hz, d), 2.06-2.45(2H, m), 3.56(1H, *J* = 8.0, 14.0 Hz, dq), 5.18(1H, *J* = 10.0 Hz, d), 5.67(1H, *J* = 15.2, 7.5 Hz, dq), 6.55(1H, *J* = 15.0 Hz, d); ^{13}C NMR (C_6D_6) δ 11.4(CH_3), 15.5(CH_3), 16.9(CH_3), 18.6(CH_3), (19.0, 19.1)(CH_3), (29.5, 29.7)(CH), 30.7(CH_2), (34.3, 34.4)(CH), 38.5(CH_2), 45.8(CH), 124.6(CH), 124.8(CH), 130.1(C), 134.1(CH), 209.5(C=O).

(2*E*,6*E*,8*E*)-5,7-Dimethyl-2,6,8-decatrien-4-one (5).-- To a stirred solution of **23** (180 mg, 1 mmol) in CH_2Cl_2 (5 ml) were added 4-methylmorpholine N-oxide (200 mg, 1.7 mmol), tetrapropylammonium perruthenate (16 mg, 0.05 mmol), and several 4Å molecular sieves. After stirring for 0.5 h, the reaction mixture was subjected to column chromatography over silica gel (pentane:ether/15:1) to give an oily product (125 mg, 69%). EIMS *m/e* (%) 178(M$^+$, 6), 163(4), 109(100), 81(14), 67(37), 55(6), 41(38); HREIMS *m/e* calcd for $C_{12}H_{18}O$ 178.1358, found 178.1355; ^{1}H NMR ($CDCl_3$) δ 1.18(3H, *J* = 6.7 Hz, d), 1.77(3H, *J* = 6.7, 1.6 Hz, dd), 1.81(3H, *J* = 1.3 Hz, d), 1.86 (3H, *J* = 6.7, 1.6 Hz, dq), 3.61(1H, *J* = 9.8, 6.7 Hz, dq), 5.25(1H, *J* = 9.8 Hz, d), 5.68(1H, *J* = 15.3, 6.7 Hz, dq), 6.07(1H, *J* = 15.5, 0.9 Hz, dq), 6.17(1H, *J* = 15.5, 1.8 Hz, d), 6.86(1H, *J*=15.3, 6.7 Hz, dq); ^{13}C NMR ($CDCl_3$) δ 12.9, 16.6, 18.1, 18.2, 44.6, 124.0, 128.5, 129.8, 135.5, 135.5, 142.5, 200.3(C=O).

(2*E*,6*Z*,8*E*)-5,7-Dimethyldeca-2,6,8-trien-4-one (6).-- In the same manner, alcohol **26** (180 mg, 1 mmol) gave ketone **6** (115 mg, 64%). EIMS *m/e* (%) 178(M$^+$, 4), 163(3), 109(100), 81(12), 67(39), 55(7), 41(30); HREIMS *m/e* calcd for $C_{12}H_{18}O$ 178.1358, found 178.1355; ^{1}H NMR ($CDCl_3$) δ 1.17(3H, *J* = 6.7 Hz, d), 1.82(3H, *J* = 6.7, 1.6 Hz, dd), 1.84(3H, *J* = 6.7 Hz, d), 1.87 (3H, *J* = 15.3, 6.7 Hz, dq), 3.75(1H, *J*=9.8, 6.7 Hz, dq), 6.07(1H, *J* = 15.5, 0.9 Hz, dq), 5.11(1H, *J* = 10.4 Hz, d), 5.81(1H, *J* = 15.6, 6.7 Hz, dq), 6.18(1H, *J* = 15.6, 1.5 Hz, d), 6.46(1H, *J* = 15.5 Hz, d), 6.89(1H, *J* = 15.5, 6.7 Hz, dq); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.9, 20.8, 22.6, 43.7, 126.6, 126.9, 127.4, 127.9, 142.5, 200.3.

ACKNOWLEDGMENTS

We thank Mr. David Kiemle for performing GC-MS and NMR analyses. We gratefully acknowledge financial support by the NSF (Grant DCB8608077) and the NIH (Grant AI 12020).

REFERENCES AND NOTES

1. Lanier, G. N.; Qi;, Y.-T.; West, J. R.; Park, S. C.; Webster, F. X.; Silverstein, R. M. *J. Chem. Ecol.*, **1989** *15*, 1645-1659.
2. Einhorn, J.; Menussieu, P.; Malosse, C.; Ducrot, P. H. *Tetrahedron Lett.*, **1990**, *31*, 6633-6636.
3. Dunkelblum, Z.; Mendel, Z.; Assael, F.; Harel, M.; Kerhoas, L.; Einhorn, J. *Tetrahedron Lett.*, **1993**, *34*, 2805-2808.
4. Cywin, C. L.; Webster, F. X.; Kallmerten, J. *J. Org.Chem.*, **1991**, *56*, 2953-2955.
5. Lin, G.-q.; Xu, W.-c. *Tetrahedron Lett.*, **1993**, *34*, 5931-5934.
6. Mori, K.; Harashima, S. *Liebigs Ann. Chem.* **1993**, 993-1001.
7. Shi, X. *Application of [2,3]-Wittig Rearrangement to the Syntheses of Matsucoccus Sex Pheromones and Related Natural Products*, State University of New York, College of Environmental Science and Forestry 1994.
8. Cywin, C. L.; Kallmerten, J. *J. Nat. Prod.*, **1991**, *54*, 1664-1667.
9. Mori, K.; Harashima, S. *Tetrahedron Lett.*, **1991**, *32*, 5995-5998.
10. Mori, K.; Harashima, S. *Liebigs Ann. Chem.* **1993**, 391-401.
11. Mori, K.; Furuuchi, T.; Kiyota, H. *Liebigs Ann. Chem.* **1994**, 971-974.
12. Mori, K.; Amaike, M. *J. Chem. Soc. Perkin Trans. I* **1994**, 2727-2733.
13. Zegelman, L; Hassner, A; Mendel, Z.; Dunkelblum, E. *Tetrahedron Lett.* **1993**, *34*, 5641-5644.
14. Park, S. C.;Wi, A. J.; Kim, H. S. *J. Chem. Ecol.* **1994**, *20*, 2185-2195.
15. Jactel; H.; Menassieu, P.; Lettere, M; Mori, K.; Einhorn, J. *J. Chem. Ecol.* **1994**, *20*, 2159-2170.
16. Dunkelblum, E.; Gries, R.; Gries, G.; Mori, K.; Mendel, Z. *J. Chem. Ecol.* **1995**, *21*, 849-858.
17. Lendon, N. P.; George, M. *J. Heterocyclic Chem.*, **1983**, *20*, 1223-1230.
18. Snyder, E. I. *J. Org. Chem.*, **1972**, *37*, 1466-1466.
19. (a) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885-902; (b) Mikami, K.; Nakai, T. *Syntheis* **1991**, 594-604; (c) Isomer **16a** was isolated by recrystallizing the mixture from ether and **16b-d** were separated by preparative GC. Their relative configurations indicated in **Scheme 2** were determined by ^{1}H NMR analysis and degradation studies (see reference 7).
20. Mori, K.; Itou, M. *Liebigs Ann. Chem.* **1992**, 87-93.
21. Mori; K.; Itou, M. *Liebigs Ann. Chem.* **1990**, 1249-1255.
22. Neither HREIMS nor HRCIMS showed M^+ or $(M+1)^+$ for **23** and **26**.

(*Received in USA* 10 *July* 1995; *accepted* 26 *July* 1995)