Oxidation[9] of **9** was performed by the slow addition of a solution containing 2.9 mL (2.3 mmol) of 0.8 N NaOCl (Chlorox) and 0.8 mL of 2 N NaOH to 418 mg (0.85 mmol) of **9** in 12 mL of acetonitrile followed by stirring for 2.5 h at 20 °C. The mixture was saturated with $NaHSO_3$ and evaporated to dryness under reduced pressure. The residue was dissolved in 5 mL of water and brought to pH 10 with 2 N NaOH, extracted with ether, acidified with concentrated HCl, and again extracted with ether. Solvent removal from the dried extracts gave 107 mg (78%) of *trans*-2-phenylcyclopropanecarboxylic acid: mp 93 °C (from water) (lit.[19] mp 93 °C).

Ethyl 3-[*trans*-2-(1,3-Dithianyl)cyclopropyl]-3-oxo-2-(triphenylphosphoranylidene)propanoate (10). A solution of 2-lithio-1,3-dithiane[20] (0.36 mmol) was prepared by adding 0.3 mL of 1.24 M *n*-BuLi to 43 mg of 1,3-dithiane in 3 mL of THF at −20 °C followed by stirring at −20 °C for 1.5 h. To this solution was added 135 mg (0.3 mmol) of **1** in 3 mL of THF. After 10 min the mixture was brought to 25 °C and stirred for 15 min and then treated with 6 mL of water. The mixture was extracted with ether (2 × 20 mL), and the extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on 12 g of silica (1:3 EtOAc–hexane) gave 126 mg of **10**: mp 70–71 °C (from EtOHc–hexane); ^1H NMR ($CDCl_3$) δ 0.8–1.3 (m, 2 H), 1.4–2.3 (m, 1 H), 2.02 (m, 2 H), 2.81 (m, 4 H), 3.5–3.9 (m, 4 H), 7.3–7.8 (m, 15 H). Anal. Calcd for $C_{30}H_{31}O_3PS_2$: C, 67.39; H, 5.84. Found: C, 67.45; H, 6.10.

Ethyl 3-[*trans*-2-((*tert*-butoxycarbonyl)methyl)cyclopropyl]-3-oxo-2-(triphenylphosphoranylidene)propanoate (11). A solution of *tert*-butyl lithioacetate[21] (0.36 mmol) was prepared by adding 49 μL of *tert*-butyl acetate to a solution containing 0.36 mmol of LDA in 3 mL of THF at −20 °C. After 10 min, a solution containing 135 mg (0.3 mmol) of **1** in 3 mL of THF was added with continued stirring for 20 min. The mixture was treated with 6 mL of water and extracted with ether (2 × 20 mL), and the extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on 12 g of silica (1:3 EtOAc–hexane) gave 145 mg (91%) of **11** as a pale yellow oil: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.65 (t, 3 H, J = 7 Hz), 1.43 (s, 9 H), 0.7–1.6 (m, 3 H), 2.25 (m, 2 H), 3.23 (m, 1 H), 3.73 (q, 2 H, J = 7 Hz), 7.3–7.8 (m, 15 Hz).

***tert*-Butyl 4-Chloro-2-butenoate (12).**[22] To a solution containing 19.4 g (0.052 mol) of *tert*-butyl (triphenylphosphoranylidene)acetate[10a] in 60 mL of CH_2Cl_2 was added over 1 h at 25 °C a solution containing 4.53 g (0.058 mol) of freshly distilled anhydrous chloroacetaldehyde[11] in 40 mL of CH_2Cl_2. After an additional 40 min the mixture was heated under reflux for 2 h. Solvent was removed under reduced pressure, and the residue was triturated with 250 mL of pentane. After standing overnight, triphenylphosphine oxide was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography on 250 g of silica gave, upon elution with 5:1 petroleum ether–CH_2Cl_2, 1.4 g (16%) of **12Z** followed by 6.4 g (70%) of **12E**. **12Z**: bp 69–70 °C (4.5 mm); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.49 (s, 9 H), 4.63 (dd, 2 H, J = 6.8, 1.5 Hz), 5.76 (dt, 1 H, J = 11.5, 1.5 Hz), 6.22 (dt, 1 H, J = 11.5, 6.8 Hz). Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.80; H, 7.85. **12E**: bp 95–97 °C (15 mm); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.49 (s, 9 H), 4.14 (dd, 2 H, J = 6.1, 1.7 Hz), 6.01 (td, 1 H, J = 15.4, 1.7 Hz), 6.87 (td, 1 H, J = 15.4, 6.1 Hz). Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.22; H, 7.34.

***tert*-Butyl *trans*-2-Butylcyclopropanecarboxylate (13, R = *n*-Bu).** To a solution containing 271 mg (1.53 mmol) of **12E** in 5 mL of THF at 78 °C was slowly added 1.06 mL (1.7 mmol) of 1.6 M *n*-BuLi in hexane. After 20 min water was added along with 100 μL of undecane (GC standard). GC analysis showed the presence of **13** (R = Bu) in 34% yield. The mixture was treated with 10 mL of water and extracted with ether (2 × 15 mL). The dried extracts ($MgSO_4$) gave after concentration and chromatography on 15 g of silica (4:1 petroleum ether–CH_2Cl_2) 66 mg (22%) of **13** (R = Bu). An analytical sample was obtained by bulb-to-bulb distillation (130 °C, 0.5 mm): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.44 (s, 9 H), 0.5–2.0 (m, 13 H). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.84; H, 11.11.

***tert*-Butyl *trans*-2-Isobutenylcyclopropanecarboxylate (13, R = $(CH_3)_2C{=}CH$).** To a solution of 9.3 g (69 mmol) of isobutenyl bromide in 100 mL of ether at −78 °C was added dropwise over 20 min 84 mL (69 mmol) of 0.82 M *t*-BuLi in pentane. The mixture was stirred for 10 min at −78 °C and for 20 min at 0 °C and then recooled to −78 °C, whereupon a solution containing 4.21 g (24 mmol) of **12E** in 25 mL of THF was added over 3 min. After 20 min the mixture was warmed to 20 °C, stirred for 20 min and then treated with 30 mL of water. The mixture was extracted with ether (3 × 50 mL), and the extracts were washed with brine and dried over Na_2SO_4. Removal of solvent under reduced pressure gave an oil, which upon chromatography on 150 g silica (3:1 petroleum ether–CH_2Cl_2) gave 2.29 g (51%) of **13** (R = $(CH_3)_2C{=}CH$). An analytical sample was obtained by bulb-to-bulb distillation [130 °C (1 mm)]: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.66–1.55 (m, 3 H), 1.45 (s, 9 H), 1.68 (br s, 3 H), 1.74 (br s, 3 H), 2.0 (m, 1 H), 4.60 (d, 1 H, J = 8.5 Hz). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.34.

***tert*-Butyl *trans*-2-Phenylcyclopropanecarboxylate (13, R = Ph).** A solution of 177 mg (1.0 mmol) of **12E** in 4 mL of THF was cooled to −78 °C and treated dropwise with 0.82 mL (1.1 mmol) of 1.35 M PhLi in cyclohexane–ether. After 20 min, the mixture was brought to 25 °C, stirred for 10 min, and then treated with 5 mL of wet ether. GC analysis with the aid of 100 μL of added pentadecane indicated the presence of **13** in 64% yield. Concentration of the mixture followed by chromatography of the residue on 15 g of silica (petroleum ether followed by 3:1 petroleum ether–CH_2Cl_2) and bulb-to-bulb distillation [135 °C (0.02 mm)] gave 121 mg (56%) of **13** (R = Ph) as an oil:[16] ^1H NMR ($CDCl_3$, 90 MHz) δ 1.1–1.6 (m, 2 H), 1.46 (s, 9 H), 1.80 (m, 1 H), 2.40 (m, 1 H), 7.15 (m, 5 H). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.93; H, 8.40.

Acknowledgment. We thank the National Science Foundation for support of this work.

Registry No. **1**, 100207-37-2; **4**, 78980-76-4; **5**, 100207-38-3; **6**, 100207-39-4; **7**, 100207-40-7; **8**, 100207-41-8; **9**, 100229-26-3; **10**, 100207-42-9; **11**, 100207-43-0; **12E**, 56905-09-0; **12Z**, 56904-91-7; **13** (R = Ph), 5279-78-7; **13** (R = *n*-Bu), 100207-44-1; **13** (R = $(CH_3)_2C{=}CH$), 100207-45-2; *tert*-butyl (triphenylphosphoranylidene)acetate, 35000-38-5; chloroacetaldehyde, 107-20-0; *trans*-2-phenylcyclopropanecarboxylic acid, 939-90-2; isobutenyl bromide, 3017-69-4.

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Synthesis of the Aggregation Pheromone of the Square-Necked Grain Beetle *Cathartus quadricollis*

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Received July 10, 1985

The square-necked grain beetle (*Cathartus quadricollis* (Guêr.)) is one of the most common beetles found in stored corn in the southern United States.[1] In cornfields, it is almost always found on damaged or exposed ears. This beetle resembles, in morphology and habit, other grain-infesting beetles in the genera *Cryptolestes*[2–5] and *Ory-*

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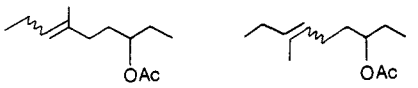
zaephilus,[6,7] whose chemical communication systems have been under investigation in our laboratory. Extension of the techniques of pheromone detection and isolation utilized previously[3,8] to the square-necked beetle confirmed the presence of a pheromone.[9] Trapping of male or mixed sex volatiles and the bioassay of fractionated components led to the isolation of microgram amounts of a male-produced pheromone attractive to both sexes (aggregation pheromone).

Analysis of the aggregation pheromone by high-field ^1H NMR and GC/MS indicated the structure to be either 4-methyl-7-acetoxy-3-nonene (**1**) or 3-methyl-7-acetoxy-3-nonene (**2**). Since the amount of isolated material was

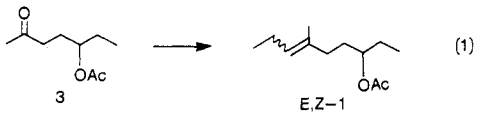


1 **2**

insufficient for definite structural assignment, syntheses of **1** and **2** were undertaken. Because possible structures **1** and **2** can both exist as geometric isomers, initial synthetic approaches were designed to produce mixtures of geometric isomers in order to facilitate comparison with the natural material.

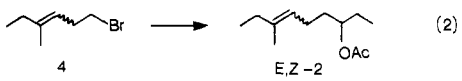
Results and Discussion

The synthesis of an *E,Z* mixture of **1** was accomplished by the Wittig reaction shown in eq 1.[10] ^1H NMR and capillary GC comparison of the synthetic material to the natural pheromone proved that neither geometric isomer of **1** corresponded to the insect-produced compound.



3 **E,Z-1** (1)

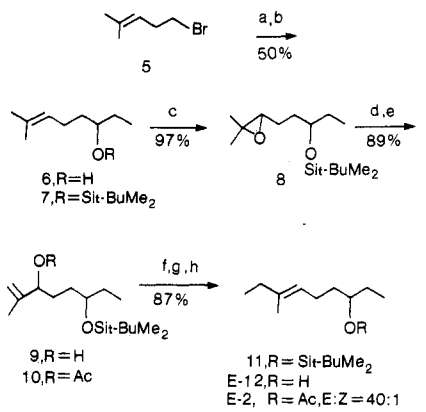
The synthesis of an *E,Z* mixture of **2** proceeded through the Grignard reaction of a 3:1 *E,Z* mixture of 1-bromo-4-methyl-3-hexene (**4**)[12] with propanal, eq 2. Acetylation of the derived alcohol yielded an *E,Z* mixture of **2**. Comparison with the natural material by capillary GC and ^1H NMR confirmed the structure of the pheromone to be (*E*)-**2**.



4 **E,Z-2** (2)

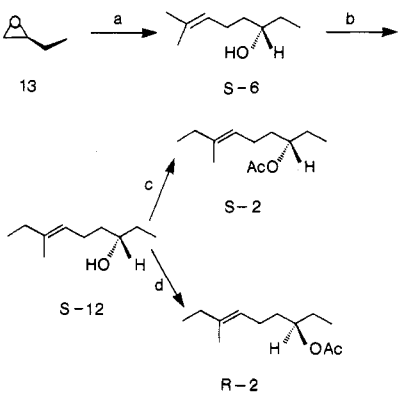
The stereoselective synthesis of (*E*)-**2** outlined in Scheme I produced (*E*)-**2** of >97% geometric purity. The key reaction in this sequence was the coupling of allylic acetate **10** with lithium dimethylcuprate to yield trisubstituted alkene **11**. The *E* stereoselectivity of this type of reaction has been previously demonstrated to be ≥95% in studies directed toward juvenile hormone synthesis.[13] The necessary allylic alcohol precursor **9** was assembled in a series of standard synthetic procedures. Thus, alcohol **6** was synthesized by the Grignard reaction of bromide **5** with propanal. Protection of the alcohol as the silyl ether[14] and peracid epoxidation yielded epoxide **8**. Base isomerization[15] of this epoxide was selective for the formation of secondary allylic alcohol **9**. Lithium dimethylcuprate S_N2' displacement of the acetate **10** proceeded as expected[13] to yield **11** with an *E:Z* ratio of 40:1. Removal of the protecting group and acetylation gave (*E*)-**2** in 50% overall yield from **6**.

Scheme I[a]



[a] Reagents: (a) i, Mg, Et_2O; ii, CH_3CH_2CHO; (b) *t*-Bu(Me)$_2$SiCl, DMF, imidazole; (c) *m*-CPBA; (d) LDA, THF; (e) Ac_2O, pyridine; (f) Me_2CuLi, Et_2O; (g) H^+; (h) Ac_2O, pyridine.

Scheme II[a]



[a] Reagents: (a) $(CH_3)_2C{=}CHCH_2MgCl$, CuI; (b) see Scheme I; (c) Ac_2O, pyridine; (d) i, MsCl, Et_3N, CH_2Cl_2; ii, KOAc, DMF.

Finally, a chiral synthesis of (*S*)-**2** was performed as outlined in Scheme II. (*S*)-Ethyloxirane[16] (**13**) provided the chiral template. Cuprous iodide catalyzed opening[17] of this epoxide by (dimethylallyl)magnesium chloride produced (*S*)-**6**. We have previously applied this reaction with (*R*)- or (*S*)-propylene oxide in the chiral synthesis of the bark beetle pheromone 6-methyl-5-hepten-2-ol (sulcatol), a lower homologue of **6**.[18] The remainder of the

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synthesis proceeded through the same reactions used for the racemic sequence outlined in Scheme I. Analysis, by ^1H NMR, of the diastereomeric esters of (*S*)-**6** and (*S*)-**12**, derived from reaction of the alcohols with (+)-α-(methoxy(trifluoromethyl)phenylacetyl chloride ((+)-MTPA-Cl)[19], allowed an estimate of the chiral purity at >98% ee.

The *R* enantiomer of **2** ((*R*)-**2**) is conceptually available from the same series of reactions, beginning with (*R*)-ethyloxirane.[20] The length of the synthetic sequence was such that a more attractive option appeared to be the production of the enantiomer by inversion of alcohol (*S*)-**12**. Of the several general methods for chiral secondary alcohol inversion,[21] we chose S_N2 displacement of the mesylate derivative with acetate anion. Although cesium carboxylates have been advocated as being superior to their sodium or potassium counterparts in this reaction,[21d] we found that, at least for this case, potassium acetate served the purpose satisfactorily. Thus, (*S*)-**12** was treated with methanesulfonyl chloride and triethylamine to produce the mesylate. The mesyloxy group was then displaced by reaction with excess potassium acetate in dimethylformamide at 100 °C (Scheme II). NMR and GC/MS analysis of the crude reaction mixture indicated a mixture of acetate (*R*)-**2** with the corresponding formate ester (≈10:1 ratio). Purification by silica gel chromatography yielded pure (*R*)-**2** in 44% overall yield from (*S*)-**12**. The enantiomeric excess was estimated at ≥97% by ^1H NMR analysis of the (+)-MTPA ester of (*R*)-**12** (obtained by hydride reaction of (*R*)-**2**).

In summary, the structure of the beetle-produced aggregation pheromone of *Cathartus quadricollis* has been demonstrated to be (*E*)-3-methyl-7-acetoxy-3-nonene ((*E*)-**2**)) by synthesis and comparison to the natural material. Additionally, a chiral synthesis of the *S* and *R* enantiomers of (*E*)-**2** from readily available (*S*)-ethyloxirane in good overall yield has been developed. Details of the response of insects to the synthetic compounds will be published separately.

Experimental Section

Gas chromatographic analyses were on a Hewlett-Packard 5880A or 5890 instrument equipped with J+W fused silica DB-1 capillary columns (15 m × 0.25 mm), a flame ionization detector, and suitable linear temperature gradient.

Tetrahydrofuran was distilled from Na or K benzophenone ketyl. Methylene chloride was distilled from CaH_2. Anhydrous ether (Fisher) was used as received from freshly opened cans. All reactions involving air or moisture reagents were performed under an argon atmosphere.

7-Methyl-6-octen-3-ol (6). Magnesium (4.86 g, 200 mmol) was stirred with dry ether (100 mL). After initiation with a small amount of ethylene dibromide, a solution of **5** (15.0 g, 92.0 mmol) in dry ether (300 mL) was added dropwise with ice bath cooling over 1 h. The Grignard solution was stirred a further 1.5 h at ambient temperature and propanal (6.00 g, 103 mmol) was added dropwise over 0.5 h. After a further 0.5 h, the reaction mixture was poured into cold saturated NH_4Cl solution (200 mL) and extracted with ether (3 × 100 mL). The ether extracts were washed with water (50 mL) and saturated NaCl solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate, 4:1) to yield pure **6** (9.40 g, 76%): bp 45–46 °C (0.5 mmHg); IR (neat film) 3360 (s), 2985 (s), 2930 (s), 2885 (s), 1450 (m), 1380 (m), 1113 (m), 972 (m), 937 (m), 835 (m) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.14 (1 H, vinyl H, m), 3.54 (1 H, OCH, pentet, J = 7.0 Hz), 2.09 (2 H, allylic CH_2, m), 1.63 (6 H, allylic CH_3, s), 1.6–1.1 (4 H, 2-CH_2, m), 0.94 (3 H, CH_3, t, J = 6.5 Hz); mass spectrum, m/e (relative intensity) 142 (3, M^+), 95 (33), 82 (10), 69 (42), 67 (32), 59 (13), 57 (22), 55 (18), 53 (13), 43 (58), 41 (100); CI (isobutane) 143 (100, $M^+ + 1$), 125 (60). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.94; H, 13.03.

2-Methyl-6-[(*tert*-butyldimethylsilyl)oxy]-2-octene (7). A solution of alcohol **6** (2.60 g, 18.3 mmol) in dry DMF (30 mL) was treated with imidazole (4.0 g, 59 mmol) and *tert*-butyldimethylsilyl chloride (3.50 g, 23.3 mmol) for 1 h at ambient temperature. The reaction was poured into ice water and extracted with methylene chloride (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was distilled to yield **7** (3.22 g, 69%): bp 64–65 °C (0.05 mmHg); IR (neat film) 2970 (s), 2940 (s), 2870 (s), 1468 (m), 1381 (m), 1368 (m), 1260 (s), 1082 (m), 1056 (s), 1012 (m), 843 (s), 780 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (1 H, vinyl H, t, J = 5 Hz), 3.58 (1 H, OCH, pentet, J = 6 Hz), 2.1–1.8 (2 H, allylic CH_2, m), 1.68 (3 H, allylic CH_3, s), 1.60 (3 H, allylic CH_3, s), 1.5–1.4 (4 H, 2-CH_2, m), 0.89 (9 H, $SiC(CH_3)_3$, s), 0.86 (3 H, CH_3, t, J = 7.5 Hz), 0.04 (3 H, $SiCH_3$, s); mass spectrum, m/e (relative intensity) 199 (22), 129 (11), 117 (62), 95 (12), 75 (100), 73 (24), 69 (17), 41 (13); CI (isobutane) 257 (10, $M^+ + 1$), 199 (11), 125 (100). Anal. Calcd for $C_{15}H_{32}OSi$: C, 70.24; H, 12.58. Found: C, 70.01; H, 12.65.

2,3-Epoxy-2-methyl-6-[(*tert*-butyldimethylsilyl)oxy]octane (8). A solution of alkene **7** (3.20 g, 12.5 mmol) in dry CH_2Cl_2 (50 mL) was stirred with ice-bath cooling while 85% *m*-chloroperoxybenzoic acid (3.5 g, ≈ 17 mmol) was added in portions over 0.5 h. The reaction was stirred 0.5 h at ambient temperature, poured into saturated $NaHCO_3$ solution (100 mL), and extracted with CH_2Cl_2 (3 × 50 mL). Drying ($MgSO_4$), removal of solvent in vacuo, and purification by chromatography on silica gel (hexane/ethyl acetate, 10:1) yielded **8** (3.29 g, 97%). This material appeared to be homogeneous by GC and TLC but a mixture of diastereomers by NMR. The relative stereochemistry was not determined: IR (neat film) 2970 (s), 2940 (s), 2895 (m), 2870 (m), 1469 (m), 1384 (m), 1260 (m), 1125 (m), 1060 (m), 1013 (m), 843 (s), 781 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.60 (1 H, CHOSi, m), 2.71 (1 H, CHO, m), 1.7–1.4 (6 H, 3-CH_2, m), 1.30 (3 H, CH_3, s), 1.26 (3 H, CH_3, s), 0.88 (9 H, $SiC(CH_3)_3$, s), 0.86 (3 H, CH_3, m), 0.04 (6 H, $Si(CH_3)_2$, s); mass spectrum, m/e (relative intensity) 215 (17), 173 (19), 159 (66), 81 (28), 75 (100), 73 (47), 69 (12), 59 (12), 41 (12); CI (isobutane) 273 (3, $M^+ + 1$), 215 (7), 141 (100). Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 66.33; H, 11.99.

2-Methyl-3-acetoxy-6-[(*tert*-butyldimethylsilyl)oxy]-1-octene (10). Diisopropylamine (2.50 g, 24.7 mmol) in dry THF (30 mL) was cooled with an ice bath while a 2.1 M solution of *n*-butyllithium in hexane (10 mL, 21 mmol) was added dropwise over 5 min. After a further 10 min, epoxide **8** (3.20 g, 11.8 mmol) in THF (15 mL) was added dropwise over 10 min. The reaction mixture was stirred 16 h at ambient temperature, poured into ice water (100 mL), and extracted with ether (3 × 50 mL). The combined extracts were washed with water (50 mL) and saturated NaCl solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude alcohol **9** was dissolved in pyridine (30 mL). Acetic anhydride (10 mL, ≈100 mmol) was then added and the mixture kept at 50–60 °C for 4 h. The reaction mixture was poured into ice water (150 mL) and extracted with ether (3 × 75 mL). The combined extracts were washed with water (2 × 50 mL) and saturated NaCl solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography on silica gel (hexane/ethyl acetate, 20:1) to yield **10** (3.31 g, 90% from **8**): IR (neat film) 2970 (s), 2940 (s), 2900 (m), 2870 (m), 1748 (s), 1657 (m), 1466 (m), 1373 (m), 1245 (s), 1060 (m), 1025 (m), 908 (m), 845 (s), 783 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (1 H, CHOAc, m), 4.93 (1 H, vinyl H, br s), 4.88 (1 H, vinyl H, br s), 3.58 (1 H, CHOSi, six-line multiplet), 2.05 (3 H, $COCH_3$, s), 1.71

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(3 H, allylic CH_3, brs), 1.7-1.3 (6H, 3 × CH_2, m), 0.88 (9H, $SiC(CH_3)_3$, s), 0.85 (3 H, CH_3, m), 0.03 (6 H, $Si(CH_3)_2$, s); mass spectrum, *m/e* (relative intensity) 123 (44), 117 (70), 81 (100), 75 (54), 73 (36), 67 (13), 57 (10), 43 (21); CI (isobutane) 315 (12, $M^+ + 1$), 255 (15), 173 (10), 123 (100). Anal. Calcd for $C_{17}H_{34}O_3Si$: C, 64.92; H, 10.90. Found: C, 65.22; H, 11.11.

(*E*)-3-Methyl-7-[(*tert*-butyldimethylsilyl)oxy]-3-nonene (11). A suspension of CuI (2.75 g, 14.4 mmol) in dry ether (50 mL) was cooled to −20 °C. A solution of MeLi in ether (18.0 mL, 28.8 mmol) was added dropwise over 5 min. After 15 min, acetate **10** (2.72 g, 8.66 mmol) in ether (10 mL) was added dropwise over 10 min. The reaction was stirred for 45 min at −20 °C to −30 °C and poured into saturated NH_4Cl solution (100 mL). The insoluble copper salts were removed by filtration and the aqueous phase further extracted with ether (2 × 50 mL). The combined ether extracts were washed with saturated NaCl solution (2 × 20 mL), dried ($MgSO_4$), and concentrated to a syrup. Purification by silica gel chromatography (hexane/ethyl acetate, 10:1) yielded **11** (2.21 g, 94%). Capillary GC analysis indicated a *E*:*Z* ratio of 40:1: IR (neat film) 2975 (s), 2945 (s), 2890 (m), 2870 (m), 1470 (m), 1385 (m), 1368 (m), 1263 (m), 1090 (m), 1062 (m), 1014 (m), 847 (s), 783 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (1 H, vinyl H, m), 3.58 (1 H, CHOSi, pentet, *J* = 6 Hz), 1.97 (4 H, allylic CH_2, m), 1.59 (3 H, allylic CH_3, br s), 1.45 (4 H, 2 × CH_2, m), 0.98 (3 H, CH_3, t, *J* = 7.5 Hz), 0.89 (9 H, $SiC(CH_3)_3$, s), 0.86 (3 H, CH_3, t, *J* = 7.5 Hz), 0.04 (6 H, $Si(CH_3)_2$, s); mass spectrum, *m/e* (relative intensity) 213 (26), 138 (18), 129 (11), 117 (82), 109 (19), 83 (13), 75 (100), 73 (24), 55 (11); CI (isobutane) 271 (12, $M^+ + 1$), 213 (18), 139 (100). Anal. Calcd for $C_{16}H_{34}OSi$: C, 71.04; H, 12.67. Found: C, 70.98; H, 12.68.

(*E*)-7-Methyl-6-nonen-3-ol ((*E*)-12)). A mixture of **11** (2.00 g, 7.41 mmol), MeOH (50 mL) and *p*-toluenesulfonic acid (100 mg) was stirred at room temperature for 1 h. The solvent was removed on a rotary evaporator at <35 °C. The residue was partitioned between ether (100 mL) and saturated $NaHCO_3$ solution (30 mL). The aqueous phase was extracted with ether (50 mL) and the combined extracts were dried ($MgSO_4$) and concentrated to a syrup. Bulb-to-bulb distillation yielded (*E*)-**12** (1.12 g, 97%): bp 60–70 °C bath temperature (0.5 mmHg). Capillary GC analysis indicated an *E*:*Z* ratio of 40:1: IR (neat film) 3360 (m), 2975 (s), 2940 (s), 2885 (s), 1460 (m), 1380 (m), 1120 (m), 970 (m), 850 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (1 H, vinyl H, m), 3.53 (1 H, CHO, m), 2.15–2.00 (2 H, allylic CH_2, m), 1.98 (2 H, allylic CH_2, q, *J* = 7.5 Hz), 1.62 (3 H, allylic CH_3, br s), 1.6–1.4 (4 H, 2 × CH_2, m), 0.98 (3 H, CH_3, t, *J* = 7.5 Hz), 0.94 (3H, CH_3, t, *J* = 7.5 Hz); mass spectrum, *m/e* (relative intensity) 138 (10, $M^+ - H_2O$) 127 (33), 109 (100), 95 (17), 85 (31), 83 (22), 82 (34), 81 (43), 72 (12), 69 (20), 68 (18), 67 (71), 59 (18), 57 (27), 55 (61), 43 (20), 41 (27); CI (isobutane 157 (100, $M^+ + 1$) 155 (20), 139 (46), 137 (21), 127 (20), 109 (12). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.86. Found: C, 76.54; H, 13.14.

(*E*)-3-Methyl-7-acetoxy-3-nonene ((*E*)-2). Conversion of alcohol (*E*)-**12** to the acetate (*E*)-**2** using acetic anhydride in pyridine yielded (*E*)-**2** in 96% yield. Capillary GC indicated a 40:1 *E*:*Z* mixture: IR (neat film) 2975 (s), 2940 (m), 2885 (m), 1735 (s), 1455 (m), 1375 (m), 1250 (s), 1020 (m), 955 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (1 H, vinyl H, m), 4.81 (1 H, CHO, pentet, *J* = 7 Hz), 2.04 (3 H, $COCH_3$, s), 2.0–1.9 (4 H, allylic CH_2, m), 1.6–1.5 (4 H, 2 × CH_2, m), 0.97 (3 H, CH_3, t, *J* = 7.5 Hz), 0.88 (3 H, CH_3, t, *J* = 7.5 Hz); mass spectrum, *m/e* (relative intensity) 138 (12, M^+ − HOAc) 127 (31), 109 (100), 95 (15), 85 (32), 83 (23), 82 (35), 81 (43), 67 (72), 55 (60), 43 (20), 41 (28); CI (isobutane) 199 ($M^+ + 1$, 5) 139 (100). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.82; H, 11.40.

(*S*)-7-Methyl-6-octen-3-ol ((*S*)-6). A Grignard solution was prepared from 1-chloro-3-methyl-2-butene (2.08 g, 20 mmol) and magnesium (0.72 g, 30 mmol) as described previously.[18] Addition of CuI (0.38 g, 20 mmol) and (*S*)-(+)-ethyloxirane (0.68 g, 12 mmol) followed by aqueous extractive workup yielded crude (*S*)-**6**. Purification by chromatography on silica gel gave pure (*S*)-**6** (1.32 g, 77%). Spectral data were identical with (*R*,*S*)-**6**. Preparation of the (+)-MTPA esters of (*S*)-**6** and (*R*,*S*)-**6** by the standard method[19] and analysis by ^1H NMR (400 MHz) indicated ≥99% ee (Δδ for C_1 protons = 0.11 ppm).

(*S*)-(*E*)-3-Methyl-7-acetoxy-3-nonene ((*S*)-2). Conversion of (*S*)-**6** to (*S*)-**2** by the sequence of reactions described for the racemic material yielded (*S*)-**2** in an overall yield of 33% for seven steps. Preparation of the (+)-MTPA esters[19] of (*S*)-**12** and (*R*,*S*)-**12** and analysis by 400-MHz NMR indicated an ee of ≥99%, indicating that no racemization occurred.

(*R*)-(*E*)-3-Methyl-7-acetoxy-3-nonene ((*R*)-2). Alcohol (*S*)-**12** (0.312 g, 2.00 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and cooled in an ice bath. Triethylamine (0.7 mL, 5 mmol) and methanesulfonyl chloride (0.3 mL, 4 mmol) were added and the reaction mixture was stirred for 0.5 h. Ice water (5 mL) was added and the organic phase washed with water (3 × 5 mL), dried ($MgSO_4$) and concentrated to a light yellow syrup. This crude mesylate was dissolved in dry DMF (10 mL), KOAc (1.0 g, 10 mmol) was added, and the reaction was stirred at 100 °C for 2 h. After cooling, dilution with water (60 mL), extraction with hexane (3 × 20 mL), washing with saturated NaCl solution (10 mL), drying ($MgSO_4$), and removal of solvent, the crude product was shown by capillary GC to be a 10:1 mixture of two compounds. Silica gel chromatography (hexane/ethyl acetate, 20:1) resulted in partial separation of the two components. A 97% pure fraction of (*R*)-**2** (178 mg, 44%), having an *E*:*Z* ratio of 35:1, was isolated. In addition, a less pure fraction (126 mg) consisting of a mixture of the two components (≈75% (*R*)-**2**) was obtained. Analysis of this mixture by GC/MS and ^1H NMR (δ 8.13) indicated the minor component to be the formate ester of alcohol **12**. A small sample of (*R*)-**2** was reduced with lithium aluminum hydride in ether to yield (*R*)-**12**, which was analyzed by ^1H NMR of the (+)-MTPA ester to be ≥97% ee.

Acknowledgment. This work was supported through a Natural Sciences and Engineering Research Council of Canada Operating Grant to A.C.O. (A0851) and Strategic (Agriculture) Grant 60958. The scientific collaboration of Professor J. H. Borden, Dr. H. D. Pierce, Jr., and Dr. A. M. Pierce is gratefully acknowledged.