dropwise to a stirred suspension of CuCN (172 mg, 1.92 mmol) in THF (10 mL) at -78 °C. The resulting tan-colored slurry was allowed to warm to -10 °C to produce a clear tan solution. After the mixture was cooled to -78 °C, a solution of VSP **6** (200 mg, 0.48 mmol) in THF (1 mL) was added, and the reaction mixture was left to warm to room temperature overnight. Workup and purification as described above afforded compound **7c** (85 mg, 72%): ^{1}H NMR δ 7.29–7.22 (m, 5 H), 5.57 (s, 1 H), 2.47 (s, 2 H), 0.81 (s, 9 H), -0.13 (s, 9 H); ^{13}C NMR δ 157.8, 145.4, 131.9, 128.3, 127.6, 126.8, 56.6, 31.9, 30.1, 0.24; EIMS, *m/z* (relative intensity) 246 (M$^+$, 0.3), 231 (0.5), 135 (8), 73 (32), 57 (100), 41 (46); HRMS calcd for $C_{16}H_{26}Si$ 246.1804, found 246.1798. Irradiation of the resonance at 2.47 ppm results in a 10% enhancement of the resonance at 5.57 ppm, supporting assignment as the *Z* isomer.

Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 8. Solutions of VSP **8** (325 mg, 0.74 mmol) and the higher order phenyl cuprate (2.97 mmol) in THF (3 and 15 mL, respectively) were allowed to react via the general procedure above to obtain vinyl silane **9c** (91 mg, 46%): ^{1}H NMR δ 7.26–7.10 (m, 10 H), 1.82 (s, 3 H), -0.14 (s, 9 H); ^{13}C NMR δ 152.3, 145.3, 143.5, 135.6, 129.6, 129.2, 127.8, 127.7, 126.8, 126.3, 20.7, -0.2; EIMS, *m/z* (relative intensity) 266 (M$^+$, 27), 251 (57), 135 (100), 115 (9), 105 (4), 91 (6), 73 (27). Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.43; H, 8.35.

Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 10. According to the general procedure, vinyl silane **11c** was prepared from the VSP **10** (250 mg, 0.62 mmol) and the higher order phenyl cuprate (2.48 mmol) with THF as solvent (5 and 10 mL, respectively). The desired vinyl silane **11c** was obtained as a colorless oil (54 mg, 38%): ^{1}H NMR δ 7.27–7.19 (m, 3 H), 7.09 (d, 2 H, J = 8.0 Hz), 2.26–2.22 (m, 2 H), 2.17–2.13 (m, 2 H), 1.73–1.60 (m, 4 H), -0.26 (s, 9 H); ^{13}C NMR δ 148.9, 146.7, 133.5, 128.4, 127.7, 126.4, 34.5, 29.0, 23.3, 22.8, -0.4; EIMS, *m/z* (relative intensity) 230 (M$^+$, 8), 215 (21), 156 (53), 135 (11), 91 (11), 73 (100), 59 (21); HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1490.

Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 12. VSP **12** (300 mg, 0.72 mmol) was treated with the higher order phenyl cuprate (2.88 mmol) in THF (12 mL) to obtain vinyl silane **13c** (44 mg, 25%): ^{1}H NMR δ 7.31–7.08 (m, 5 H), 2.50–1.25 (m, 7 H), 1.10 (d, 3 H, J = 6.9 Hz), -0.23 (s, 9 H); ^{13}C NMR δ 149.4, 146.7, 138.8, 128.4, 127.7, 126.4, 34.6, 31.9, 30.6, 22.0, 19.0, 1.0; EIMS, *m/z* (relative intensity) 244 (M$^+$, 5), 229 (9), 170 (100), 155 (18), 135 (25), 91 (22), 73 (92); HRMS calcd for $C_{16}H_{24}Si$ 244.1647, found 244.1613.

Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 14. The general procedure was repeated with the higher order phenyl cuprate (1.77 mmol) and VSP **14** (200 mg, 0.44 mmol) in THF (10 mL) to obtain vinyl silane **15c** (57 mg, 47%): ^{1}H NMR δ 7.36–7.01 (m, 8 H), 6.65 (d, 1 H, J = 7.6 Hz), 2.78 (m, 2 H), 2.41 (m, 2 H), -0.18 (s, 9 H); ^{13}C NMR δ 147.1, 141.8, 137.7, 136.5, 136.4, 130.4, 127.9, 127.0, 126.96, 126.9, 126.2, 125.8, 28.3, 26.9, -0.4; EIMS, *m/z* (relative intensity) 278 (M$^+$, 5), 204 (29), 189 (5), 128 (5), 73 (100), 59 (40); HRMS calcd for $C_{19}H_{22}Si$ 278.1491, found 278.1498.

Acknowledgment. We gratefully acknowledge the University of Iowa Faculty Scholars Program for the research leave during which this work was conducted (1985–1988) and the Alfred P. Sloan Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No. **2**, 118297-83-9; **3a**, 71814-07-8; **3b**, 118298-71-8; **3c**, 51318-08-2; **4**, 118297-82-8; **5a**, 68669-68-1; **5b**, 118226-86-1; **5c**, 51318-07-1; **6**, 118297-91-9; **7a**, 118298-72-9; **7b**, 118317-81-0; **7c**, 118298-73-0; **8**, 118297-87-3; **9a**, 118298-74-1; **9b**, 118298-75-2; **9c**, 87729-76-8; **10**, 118297-88-4; **11a**, 55860-92-9; **11b**, 118298-76-3; **11c**, 118298-77-4; **12**, 118297-89-5; **13a**, 118298-78-5; **13b**, 118298-79-6; **13c**, 118298-80-9; **14**, 118297-84-0; **15a**, 118298-81-0; **15b**, 118298-82-1; **15c**, 118298-83-2; **16**, 118297-85-1; **17**, 118298-84-3; **18**, 118298-85-4; **20**, 118297-92-0; **21**, 118298-86-5; $(CH_3)_2CuLi$, 15681-48-8; $(CH_3)_2Cu(CN)_2Li_2$, 118298-87-6; $(n\text{-}Bu)_2Cu(CN)_2Li_2$, 118317-82-1; $(C_6H_5)_2Cu(CN)_2Li_2$, 118298-88-7.

Chemistry of Cyclic Phosphorus Compounds. 3. Synthesis of Pheromones Having an γ,δ-Unsaturated Ketone System from 1,1-Diphenylphospholanium Perchlorate

Iwao Yamamoto,* Satoshi Tanaka, Tetsuya Fujimoto, and Kazuchika Ohta

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan

Received August 10, 1988

1,1-Diphenylphospholanium perchlorate (**1**) was converted into the sex pheromones **5a,b** of the Japanese female peach fruit moth by use of tandem Wittig reactions. The ylide of **1** formed with potassium *tert*-butoxide reacted with heptanal to give *Z* phosphine oxide **2** with stereoselectivity. The reaction of the anion of **2** with dimethyl disulfide followed by the Horner–Wittig reaction with nonanal or octanal gave the corresponding diene derivatives **4a,b**. Hydrolysis of **4a,b** afforded the desired *Z* γ,δ-unsaturated ketones **5a,b**. On the other hand, the conversion of **9**, which was derived from methylthio-substituted compound **6**, gave an *E* and *Z* isomeric mixture of **5b** (4:5).

Tandem Wittig reactions with the same phosphorous atom from a cyclic phosphonium salt provide a versatile procedure for syntheses of dienes or enones. However, to our knowledge, only few examples of their use have been reported.[1,2] We have previously reported the synthesis of 1,6-diene derivatives by tandem Wittig reactions[3] and application of the method to a synthesis of the sex pheromone of Douglas Fir Tussock moth.[4] In connection with our continuing interest in the utilization of these reactions, we applied the method to a synthesis of γ,δ-unsaturated ketones: the sex pheromones of the Japanese female peach

---

[1] (a) Lednicer, D. *J. Org. Chem.* **1970**, *35*, 2307. (b) Lednicer, D. *J. Org. Chem.* **1971**, *36*, 3473.

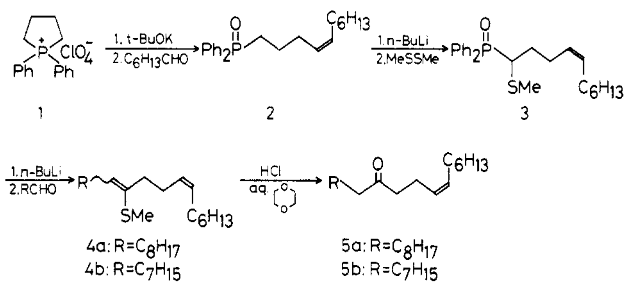
[2] Muchowski, J. M.; Venuti, M. C. *J. Org. Chem.* **1981**, *46*, 459.

[3] Yamamoto, I.; Fujimoto, T.; Ohta, K.; Matsuzaki, K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1537.

[4] Yamamoto, I.; Tanaka, S.; Fujimoto, T.; Ohta, K.; Matsuzaki, K. *Nippon Kagaku Kaishi* **1987**, 1227.

0022-3263/89/1954-0747$01.50/0 © 1989 American Chemical Society

Scheme I



fruit moth (*Carposina niponensis* Walshingham).[5]

Results and Discussion

The desired pheromone is a mixture of (*Z*)-13-eicosen-10-one (**5a**) and (*Z*)-12-nonadecen-9-one (**5b**), with the strongest biological activity exhibited by a 20:1 mixture. Muchowski et al.[2] reported that the Wittig reaction of a five-membered cyclic phosphonium salt with potassium *tert*-butoxide as base in tetrahydrofuran (THF) gave only *Z* olefins. Recently, Vedejs et al.[6] observed the same results and rationalized them by refining the description of the transition state. Accordingly, the phosphonium salt **1**[7] was treated with heptanal in the presence of potassium *tert*-butoxide to afford the corresponding olefin **2** (Scheme I).

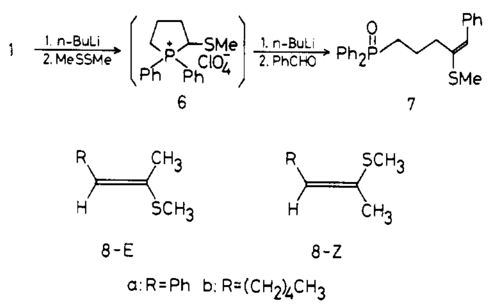
The configuration of the double bond was determined by comparing the ^{13}C NMR chemical shifts of the allylic carbon atoms with those of the analogous (*Z*)-4-octene and (*E*)-4-octene. As expected, the *Z* isomer was the sole product. By contrast, the Wittig reaction with *n*-butyllithium under the same reaction conditions provided a mixture of *Z* and *E* isomers (6:1).

The anion from the *Z* phosphine oxide **2**, formed with *n*-butyllithium at −78 °C, reacted with dimethyl disulfide to give the sulfenylated phosphine oxide **3** in 30% yield after purification by column chromatography on silica gel. A considerable amount of a bis(methylthio) derivative was also obtained.

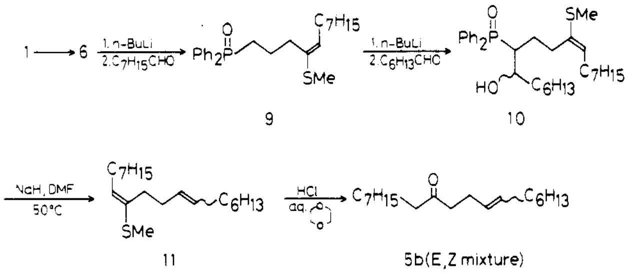
Phosphine oxides with anion-stabilizing substituents such as methylthio and vinyl groups give one-step olefination in high yields[8,9a] and especially those substituted with methyl- or phenylthio group act as acyl anion equivalents.[9]

The mono(methylthio) derivative **3**, which is a common intermediate for synthesis of both major and minor components of the sex pheromone of peach fruit moth on treatment with nonanal furnished the corresponding vinyl sulfide **4a** in 75% yield. Similarly, Horner–Wittig olefination of **3** with octanal afforded the vinyl sulfide **4b** in 39% yield where the vinyl sulfide moiety was an *E*,*Z* mixture (51:49). Finally, acid-catalyzed hydrolysis of **4a** and **4b** at 60 °C in dioxane[10] gave in high yield the γ,δ-unsaturated ketones **5a**, **5b** corresponding to the major and minor components of the sex pheromone.

Scheme II



Scheme III



The ^{13}C NMR spectra showed that only the *Z* isomers were present:[5c] δ 127.85, 131.26 for **5a** and δ 127.85, 131.25 for **5b**. The ^{1}H NMR, IR, and high-resolution mass spectra also supported the structures.

The stereoselective synthesis of the sex pheromone of the Japanese female peach fruit moth was then accomplished. However, there is an alternative route for obtaining the desired pheromone with the cyclic phosphonium salt **1**, namely, construction of a vinyl sulfide by a Wittig reaction, followed by a Horner–Wittig reaction of the resulting phosphine oxide.

As a preliminary experiment, we attempted a Wittig reaction of the methylthio-substituted compound **6** with benzaldehyde in the presence of *n*-butyllithium in the expectation that **6** was unstable[4] and that an investigation of the reaction conditions was needed (Scheme II). Treatment of **1** with *n*-butyllithium and dimethyl disulfide at −78 °C in THF, followed by deprotonation of the resulting **6** with *n*-butyllithium and condensation with benzaldehyde, gave vinyl sulfide **7** in 66% yield based on **1**. Assignment of *E* geometry to **7** was based on the chemical shift of its vinylic proton (a singlet at δ 6.15) in analogy with that of **8a-E** (δ 6.12).[11]

The same procedure was employed for a synthesis of the minor component **5b** in the sex pheromones. Treatment of **6** with *n*-butyllithium at −78 °C, followed by addition of octanal at room temperature under nitrogen atmosphere, gave phosphine oxide **9** in 30% yield (Scheme III). In the ^{1}H NMR spectrum of **9**, the chemical shift of its vinylic proton (a triplet at δ 5.15) was fully consistent with that of **8b-E** (δ 5.17)[11] and the corresponding *Z* vinylic proton was not observed.

Lithium salts of diphenylphosphinyl compounds undergo condensation with aldehydes and ketones to produce alcohol intermediates. These carbinols can be converted into the olefins by using sodium hydride or potassium *tert*-butoxide.[12] Also, the carbinol intermediates obtained

---

(5) (a) Tamaki, Y.; Honma, K.; Kawasaki, K. *Appl. Entmol. Zool.* **1977**, *12*, 60. (b) Tamada, S.; Mori, K.; Matsui, M. *Agric. Biol. Chem.* **1978**, *42*, 191. (c) Naoshima, Y.; Kawakubo, M.; Wakabayashi, S.; Hayashi, S. *Agric. Biol. Chem.* **1981**, *45*, 439. (d) Shirasaki, S.; Yamada, M.; Saito, R.; Yanaginuma, K.; Kumakura, M.; Tamaki, Y. *Nippon Oyo Dobutsu Konchu Gakkai Shi* **1979**, *23*, 240. (e) Yoshida, T.; Saito, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3047. (f) Vig, O. P.; Sharma, M. L.; Taneja, K. C.; Malik, N. *Indian J. Chem.* **1981**, *20B*, 863. (g) Yamashita, M.; Matsumiya, K.; Murakami, K.; Suemitsu, R. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3368.

(6) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1988**, *110*, 3948.

(7) (a) Märkl, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 620. (b) Purdum, W. R.; Berlin, K. D. *J. Org. Chem.* **1975**, *40*, 2801.

(8) (a) Lythgoe, B.; Moran, T. A.; Nambudiry, M. E. N.; Ruston, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2386. (b) Schlosser, M.; Tuong, H. B. *Chimia (Switz)* **1976**, *30*, 197.

(9) (a) Grayson, J. I.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2263. (b) Green, M. *J. Chem. Soc.* **1963**, *1324*. (c) McGuire, H. M.; Odon, H. C.; Pinder, A. R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1879.

(10) Marino, J. P.; Landick, R. C. *Tetrahedron Lett.* **1975**, 4531.

(11) Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777.

by using *n*-butyllithium in THF are predominantly *erythro* and these lead to *Z* olefins with stereospecific elimination of $Ph_2PO_2^-$.[12] Thus, the Horner–Wittig reaction of **9** with heptanal in the presence of *n*-butyllithium in THF afforded carbinol **10** in 77% yield. The ^{1}H NMR spectrum (250 MHz) of **10** was very complicated. However, two triplets at δ 4.97 and δ 5.09 in a 7:6 ratio could be assigned to the vinylic protons in the diastereomers. This diastereomeric mixture was dephosphorylated by sodium hydride in *N,N*-dimethylformamide (DMF) at 50 °C[12] to give diene **11** in 31% yield as a mixture of *E,E* and *Z,E* isomers.

Finally, acid-catalyzed hydrolysis of **11** afforded a mixture of *E* and *Z* γ,δ-unsaturated ketone **5b**. The structure of **5b** was confirmed by ^{1}H NMR, ^{13}C NMR, IR, and high-resolution mass spectrometry. Furthermore, the ratio of *E* and *Z* isomers was shown to be 4:5 by capillary GC and an inverse gated heteronuclear decoupling ^{13}C NMR measurement.

Experimental Section

Melting points were taken with a Yanagimoto micro-melting point apparatus. IR spectra were obtained on a JASCO A-100 spectrometer. ^{1}H NMR spectra were recorded on either a Bruker AC-250 or a JEOL PMX-60SI spectrometer and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer. All chemical shifts were reported in ppm from tetramethylsilane as internal standard. Mass spectra were obtained with a JEOL JMS-01SG-2 spectrometer on-line to a JEOL-JEC-6 spectrum computer. High-resolution mass spectra were taken with a HITACHI M-80B spectrometer. Capillary gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph using a DB-1 megabore column (30 m × 0.53 mm).

(*Z*)-11-(Diphenylphosphinyl)-7-undecene (2). A mixture of phosphonium salt **1**[7] (4.00 g, 11.8 mmol) and potassium *tert*-butoxide (1.35 g, 12.0 mmol) in dry THF (70 mL) was stirred at room temperature for 1 h. To the mixture was slowly added a solution of heptanal (1.01 g, 8.85 mmol) in dry THF (10 mL), and the resulting mixture was stirred overnight at room temperature. After being quenched with water, the mixture was extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation (180 °C at 0.2 mmHg) to yield **2** (2.64 g, 84%) as a colorless syrup: IR (neat) 1600 (C=C), 1185 cm^{-1} (P=O); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.86 (t, 3 H, $\mathrm{C}H_3$), 1.25 (m, 8 H, $\mathrm{C}H_2$), 1.69 (m, 2 H, $\mathrm{PCC}H_2$), 1.96 (m, 2 H, $\mathrm{C{=}CC}H_2$) 2.12 (m, 2 H, $\mathrm{PCCC}H_2$), 2.25 (m, 2 H, $\mathrm{PC}H_2$), 5.21–5.46 (m, 2 H, $\mathrm{C}H{=}\mathrm{C}H$), 7.40–7.50 (m, 6 H, P(O)Ph-*m* and -*p*), 7.68–7.78 (m, 4 H, P(O)Ph-*o*); ^{13}C NMR ($CDCl_3$) δ 14.10 (C_1), 21.47 (J_{PC} = 3.6 Hz, C_{10}), 22.61 (C_2), 28.96, 29.63, 31.75 (C_3, C_4, C_5), 27.30 (C_6), 28.19 (J_{PC} = 15.1 Hz, C_9), 29.18 (J_{PC} = 72.3 Hz, C_{11}), 127.97, 131.58 (vinylic carbons), 128.62 (J_{PC} = 11.5 Hz, C_m), 130.77 (J_{PC} = 9.1 Hz, C_o), 131.65 (J_{PC} = 2.6 Hz, C_p), 133.11 (J_{PC} = 97.9 Hz, C_s); MS (75 eV), *m/z* 354 (M^+).

Wittig Reaction of 1 by Use of *n*-BuLi as Base. In a similar manner, **1** (2.7 g, 8.0 mmol) was treated with *n*-BuLi (5.1 mL, 15% in hexane, 8.0 mmol) and heptanal (0.82 g, 7.2 mmol) to give a mixture of *E/Z* isomers (1/6) of **2** (1.7 g, 66%): ^{13}C NMR ($CDCl_3$) δ 27.31 (*Z*), 32.55 (*E*) (allylic carbons), 127.97 (*Z*), 128.53 (*E*), 131.59 (*Z*), 132.19 (*E*) (vinylic carbons). The ratio of *E/Z* isomers was determined from peak intensities of allylic carbons in the inverse gated heteronuclear decoupling ^{13}C NMR spectrum.

(*Z*)-11-(Diphenylphosphinyl)-11-(methylthio)-7-undecene (3). A solution of *n*-BuLi (2.2 mL, 15% in hexane, 3.4 mmol) was added dropwise to a solution of **2** (1.3 g, 3.6 mmol) in dry THF (35 mL) at −78 °C under a nitrogen atmosphere. After 20 min, a solution of dimethyl disulfide (0.33 g, 3.6 mmol) in dry THF (10 mL) was added and the resulting mixture was stirred for 2 h. After being warmed to room temperature, the mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using ethyl acetate–benzene (1/1) to give 0.42 g of sulfide **3** (30% yield) as white crystals: mp 72.5–73.0 °C; IR (neat) 1600 (C=C), 1185 cm^{-1} (P=O); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3 H, $\mathrm{C}H_3$), 1.26 (m, 8 H, $\mathrm{C}H_2$), 1.83 (m, 2 H, $\mathrm{PCC}H_2$), 1.99 (m, 2 H, $\mathrm{C{=}CC}H_2$), 2.01 (s, 3 H, $\mathrm{SC}H_3$), 2.33 (m, 2 H, $\mathrm{C}H_2\mathrm{C{=}C}$), 3.02 (ddd, 1 H, $\mathrm{PC}H$, J_{PH} = 11 Hz, J_{HH} = 7.5, 3.4 Hz), 5.21–5.47 (m, 2 H, $\mathrm{C}H{=}\mathrm{C}H$), 7.42–7.55 (m, 6 H, P(O)Ph-*m* and -*p*), 7.74–7.92 (m, 4 H, P(O)Ph-*o*); MS (75 eV), *m/z* 400 (M^+). Anal. Calcd for $C_{24}H_{33}OPS$: C, 71.96; H, 8.30. Found: C, 71.81; H, 8.41.

(7*Z*,11*E*)- and (7*Z*,11*Z*)-11-(Methylthio)-7,11-eicosadiene (4a). To a solution of **3** (0.29 g, 0.72 mmol) in dry THF (25 mL) was added a solution of *n*-BuLi (0.52 mL, 15% in hexane, 0.83 mmol) at −78 °C under a nitrogen atmosphere. After 30 min, a solution of nonanal (0.12 g, 0.84 mmol) in dry THF (3 mL) was added. After 2 h, the mixture was warmed to room temperature, quenched with saturated aqueous NH_4Cl, and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using carbon tetrachloride to give 175 mg (75%) of diene **4a** as a colorless syrup: IR (neat) 1630 cm^{-1} (C=C); HRMS, *m/z* 324.2872 (calcd for $C_{21}H_{40}S$, 324.2848).

(7*Z*,11*E*)- and (7*Z*,11*Z*)-11-(Methylthio)-7,11-nonadecadiene (4b). In a manner analogous to the preparation of **4a**, 0.34 g (0.85 mmol) of **3** was converted to 103 mg (39%) of **4b**: IR (neat) 1630 cm^{-1} (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 6 H, $\mathrm{C}H_3$), 1.27 (m, 18 H, $\mathrm{C}H_2$), 2.02–2.19 (m, 6 H, $\mathrm{SCC}H_2\mathrm{C}H_2\mathrm{C{=}CC}H_2$), 2.17 (s, 3 H, $\mathrm{SC}H_3$), 2.24–2.26 (m, 2 H, $\mathrm{SC{=}CC}H_2$), 5.36 (m, 2 H, $\mathrm{C}H{=}\mathrm{C}H$), 5.13 (*E*), 5.52 (*Z*) (t and t, 1 H, $\mathrm{C}H{=}\mathrm{CS}$); MS (75 eV), *m/z* 310 (M^+); HRMS, *m/z* 310.2646 (calcd for $C_{20}H_{38}S$, 310.2693).

(*Z*)-13-Eicosen-10-one (5a). A mixture of the compound **4a** (170 mg, 0.52 mmol) and 20% hydrochloric acid (2 mL) in 1,4-dioxane (3 mL) was stirred at 60 °C for 16 h. After being cooled to room temperature, the solution was neutralized with saturated aqueous $NaHCO_3$ and extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel by using ether–petroleum ether (1/4) to give 132 mg (86%) of **5a** as a pale yellow syrup: IR (neat) 1725 cm^{-1} (C=O); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, 6 H, $\mathrm{C}H_3$), 1.26 (m, 20 H, $\mathrm{C}H_2$), 1.58 (m, 2 H, $\mathrm{C}H_2\mathrm{CCO}$), 2.01 (m, 2 H, $\mathrm{C{=}CC}H_2$), 2.28 (m, 2 H, $\mathrm{C{=}CC}H_2\mathrm{CCO}$), 2.40 (m, 4 H, $\mathrm{C}H_2\mathrm{COC}H_2$), 5.34 (m, 2 H, $\mathrm{C}H{=}\mathrm{C}H$); ^{13}C NMR ($CDCl_3$) δ 127.85, 131.26 (vinylic carbons), 210.98 (carbonyl carbon); MS (75 eV), *m/z* 294 (M^+).

(*Z*)-12-Nonadecen-9-one (5b). In a manner analogous to the preparation of **5a**, 75 mg (0.24 mmol) of **4b** was converted to 50 mg (75%) of **5b**; IR (neat) 1725 cm^{-1} (C=O); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, 6 H, $\mathrm{C}H_3$), 1.26 (m, 18 H, $\mathrm{C}H_2$), 1.56 (m, 2 H, $\mathrm{C}H_2\mathrm{CCO}$), 2.01, (m, 2 H, $\mathrm{C{=}CC}H_2$), 2.28 (m, 2 H, $\mathrm{C{=}CC}H_2\mathrm{CCO}$), 2.41 (m, 4 H, $\mathrm{C}H_2\mathrm{COC}H_2$), 5.34 (m, 2 H, $\mathrm{C}H{=}\mathrm{C}H$); ^{13}C NMR ($CDCl_3$) δ 127.85, 131.25 (vinylic carbons), 210.95 (carbonyl carbon); MS (75 eV), *m/z* 280 (M^+).

(*E*)-5-(Diphenylphosphinyl)-2-(methylthio)-1-phenyl-1-pentene (7). A solution of *n*-BuLi (3.5 mL, 15% in hexane, 5.5 mmol) was added dropwise to a suspension of 1,1-diphenylphospholanium perchlorate (**1**) (1.7 g, 5.0 mmol) in dry THF (50 mL) at room temperature under a nitrogen atmosphere. After 30 min, the wine red solution was cooled to −78 °C and a solution of dimethyl disulfide (0.52 g, 5.5 mmol) in dry THF (5 mL) was added dropwise. After the mixture was stirred for 1 h at this temperature, a solution of *n*-BuLi (3.5 mL, 5.5 mmol) was added dropwise and the resulting solution was slowly warmed to room temperature. After addition of a solution of benzaldehyde (0.58 g, 5.5 mmol) in dry THF (5 mL), the mixture was stirred for 1 h, quenched with water, and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel by using ethyl acetate to give 1.29 g of pure pentene **7** (66% yield): IR (neat) 1610, 1580 cm^{-1} (conjugated C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.82–2.03 (m, 2 H, $\mathrm{C}H_2$), 2.09–2.26 (m, 2 H, $\mathrm{PC}H_2$), 2.28 (s, 3 H, $\mathrm{SC}H_3$), 2.55 (t, 2 H, $\mathrm{C}H_2\mathrm{C{=}C}$, *J* = 7.4 Hz), 6.15 (s, 1 H, $\mathrm{C{=}C}H\mathrm{Ph}$), 7.09–7.31 (m, 5 H, $\mathrm{C{=}C}Ph$),

---

[12] (a) Buss, A. D.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1981**, 100. (b) Buss, A. D.; Cruse, W. B.; Kennard, O.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1984**, 243. (c) Buss, A. D.; Warren, S. *Tetrahedron Lett.* **1983**, *24*, 3931. (d) Buss, A. D.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2307.

7.39–7.49 (m, 6 H, P(O)Ph-*m* and -*p*), 7.64–7.74 (m, 4 H, P(O)-Ph-*o*); ^{13}C NMR ($CDCl_3$) δ 14.80 (SCH_3), 29.09 (J_{PC} = 71.7 Hz, C_5), 21.08 (J_{PC} = 3.1 Hz, C_4), 33.08 (J_{PC} = 15.7 Hz, C_3), 121.56 (C_1), 126.25, 128.34, 128.37, 137.38 (aromatic C), 128.61 (J_{PC} = 11.3 Hz, C_m), 130.78 (J_{PC} = 8.8 Hz, C_o), 131.68 (J_{PC} = 2.5 Hz, C_p), 132.83 (J_{PC} = 98.7 Hz, C_s), 139.74 (C_2); MS (75 eV), *m/z* 392 (M^+).

(*E*)-12-(Diphenylphosphinyl)-9-(methylthio)-8-dodecene (9). A solution of *n*-BuLi (5.6 mL, 15% in hexane, 8.8 mmol) was added dropwise to a suspension of phosphonium salt 1 (2.73 g, 8.0 mmol) in dry THF (60 mL) at room temperature under a nitrogen atmosphere and the mixture was stirred for 30 min. The wine red solution was cooled in an ice bath and a solution of dimethyl disulfide (0.83 g, 8.8 mmol) in dry THF (5 mL) was added dropwise. After 1 h, a solution of *n*-BuLi (5.6 mL, 8.8 mmol) was added dropwise, and the resulting solution was stirred for 30 min and warmed to room temperature. After addition of a solution of octanal (1.13 g, 8.8 mmol) in dry THF (5 mL), the mixture was stirred for 1 h, quenched with water, and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel by using ethyl acetate to give dodecene **9** (0.98 g) in 30% yield as a colorless syrup: IR (neat) 1630 cm^{-1} (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.85 (m, 2 H, PCH_2), 2.00 (m, 2 H, C=CCH_2), 2.15 (s, 3 H, SCH_3), 2.31 (m, 4 H, PCH_2CCH_2), 5.15 (t, 1 H, C=C*H*), 7.48 (m, 6 H, P(O)Ph-*m* and -*p*), 7.74 (m, 4 H, P(O)Ph-*o*).

(*E*)-8-(Diphenylphosphinyl)-11-(methylthio)-11-nonadecen-7-ol (10). A solution of *n*-BuLi (1.7 mL, 15% in hexane, 2.6 mmol) was added to a solution of **9** (0.98 g, 2.3 mmol) in dry THF (25 mL) at −78 °C under a nitrogen atmosphere. After the clear red solution was stirred for 30 min, a solution of heptanal (0.3 g, 2.6 mmol) in dry THF (5 mL) was added at −78 °C and the mixture was stirred for 1 h. After being warmed to room temperature, the mixture was quenched with water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using benzene–THF (1/1) to give pure alcohol **10** (0.95 g) in 77% yield as a colorless syrup: IR (neat) 3350 (OH), 1630 cm^{-1} (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (m, 6 H, CH_3), 1.13–1.25 (m, 18 H, CH_2), 1.46 (m, 2 H, HOCCH_2), 1.60–2.26 (m, 9 H, CH_2 and SCH_3), 2.28–2.63 (m, 1 H, PC*H*), 3.88–4.09 (m, 1 H, HOC*H*), 4.29 (br s, 1 H, O*H*), 4.97, 5.09 [t and t, 1 H, vinylic protons, *J* = 7.3 Hz (the ratio of their peaks was 7:6)], 7.49 (m, 6 H, P(O)Ph-*m* and -*p*), 7.86 (m, 4 H, P(O)Ph-*o*).

(7*E*,11*E*)- and (7*Z*,11*E*)-11-(Methylthio)-7,11-nonadecadiene (11). A solution of **10** (0.87 g, 1.7 mmol) in dry *N*,*N*-dimethylformamide (DMF, 20 mL) was added dropwise to a suspension of sodium hydride (0.1 g, approximately 60% in oil, washed with hexane, 2.5 mmol) in dry DMF (5 mL) under a nitrogen atmosphere and the mixture was stirred at 50 °C for 3 h. After being cooled to room temperature, the mixture was quenched with water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel by using hexane to afford 0.16 g (31%) of diene **11** as a colorless syrup: IR (neat) 1630 cm^{-1} (C=C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.87 (t, 6 H, CH_3), 1.26 (m, 18 H, CH_2), 1.80–2.40 (m, 11 H, allylic protons and SCH_3), 5.14 (t, 1 H, *H*C=CS), 5.37 (m, 2 H, HC=C*H*); MS (75 eV), *m/z* 310 (M^+).

(*E*)- and (*Z*)-12-Nonadecen-9-one (5b). A mixture of compound **11** (0.15 g, 0.48 mmol) and 20% aqueous hydrochloric acid (5 mL) in 1,4-dioxane (7 mL) was stirred at 60 °C for 4 h. After being cooled to room temperature, the solution was neutralized with sodium bicarbonate and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using benzene–hexane (3/7) to give enone **5b** in 63% yield (89 mg) as a pale yellow syrup: IR (neat) 2950, 1715, 1480, 1420, 1380, 1090, 720 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (br t, 6 H, CH_3), 1.26 (m, 18 H, CH_2), 1.56 (m, 2 H, CH_2CCO), 1.99 (m, 2 H, C=CCH_2), 2.25 (m, 2 H, COCCH_2C=C), 2.40 (m, 4 H, CH_2COCH_2), 5.36 (m, 2 H, C*H*=C*H*); ^{13}C NMR ($CDCl_3$) δ 127.81 (*Z*), 128.36 (*E*), 131.22 (*Z*), 131.57 (*E*) (vinylic carbons), 210.90 (*Z*), 210.94 (*E*) (carbonyl carbons); MS (75 eV), *m/z* 280 (M^+). The peak intensities of vinylic carbons in an inverse gated heteronuclear decoupling ^{13}C NMR spectrum and capillary GC (initial time = 1 min; initial temp = 180 °C; rate = 2.0 °C/min; final temp = 230 °C; He flow rate = 78.6 mL/min) indicated a 4:5 mixture of *E* and *Z* isomers (retention times: *E*, 26.73 min; *Z*, 26.52 min).

Acknowledgment. We thank Dr. R. Irie of the Faculty of Agriculture, Shinshu University, for 250-MHz NMR spectral measurements. We also thank T. Yanagisawa of Kotobuki Seiyaku Co., Ltd., for high-resolution mass spectral measurements. This work was partially supported by a Grant-in-Aid for Scientific Research No. 6355619 from the Ministry of Education, Science, and Culture to I.Y.

Registry No. 1, 55759-75-6; (*Z*)-**2**, 118377-29-0; (*E*)-**2**, 118377-30-3; **3**, 118377-31-4; (*E*,*Z*)-**4a**, 118377-32-5; (*Z*,*Z*)-**4a**, 118377-33-6; (*E*,*Z*)-**4b**, 118377-34-7; (*Z*,*Z*)-**4b**, 118377-35-8; **5a**, 63408-44-6; (*Z*)-**5b**, 63408-45-7; (*E*)-**5b**, 63408-51-5; **7**, 118377-36-9; **9**, 118377-37-0; **10**, 118398-10-0; (*E*,*E*)-**11**, 118377-38-1; heptanal, 111-71-7; nonanal, 124-19-6; octanal, 124-13-0; benzaldehyde, 100-52-7.