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# Stereoselective Syntheses of *E*- and *Z*-9,11-Dodecadien-1-yl Acetates: The Major Sex Pheromones of the Red Bollworm Moth

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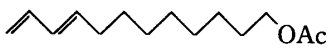
The sex pheromones **1** and **2** of the red bollworm moth were synthesized in a highly stereoselective manner. The key step of their syntheses was the olefination reaction of *E*- and *Z*-allyl phenyl sulfones **8** and **12**, affording the corresponding dienes **9** and **15**, respectively.

**Keywords**——*E*-9,11-dodecadien-1-yl acetate; *Z*-9,11-dodecadien-1-yl acetate; sex pheromone; red bollworm moth; allyl sulfone; tri-*n*-butylstannylmethyl iodide

The most potent of the sex pheromones produced by the virgin female of the red bollworm moth (*Diparopsis castanea* HMPS.), which does substantial damage to the cotton crop, has been shown to be *E*-9,11-dodecadien-1-yl acetate (**1**). Its stereoisomer, *Z*-9,11-dodecadien-1-yl acetate (**2**), was also found to be one of the components of the phromones.[1] Several syntheses of **1** have been reported,[2] and **2** was synthesized stereoselectively by Rossi and co-workers.[3] We wish to report our new approach for the highly stereoselective syntheses of these conjugated dienic pheromones **1** and **2**.

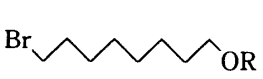
Recently we developed a general method for the synthesis of 1,3-dienes by the reaction of lithium salts of allyl phenyl sulfones or allyl 2-pyridyl sulfides with tri-*n*-buthylstannylmethyl iodide.[4] Allyl phenyl sulfones **8** and **12** seemed to be suitable key intermediates for the syntheses of the dienic pheromones **1** and **2** by the application of this method. Both of these allyl sulfones may be easily derived stereoselectively from the acetylenic derivative **5**.

The tetrahydropyranyl ether **4** was prepared by the known method:[5] this tetrahydropyranyl ether **4** of 8-bromo-1-octanol (**3**) [prepared from commercially available 1,8-octanediol], on treatment with the dilithio derivative of propargyl alcohol in hexamethylphosphortriamide, afforded a 54% yield of the acetylenic compound **5**, a common intermediate for the syntheses of **1** and **2**.

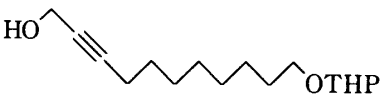



**1**


**2**




**3**: R=H
**4**: R=THP

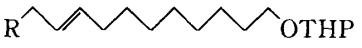



**5**

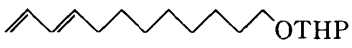
## Synthesis of *E*-Diene 1

The acetylenic compound **5** was effectively transformed into the *E*-allyl phenyl sulfone **8** in 71% overall yield: stereoselective reduction of **5** with lithium aluminium hydride,[6] followed by the treatment of the resulting *E*-allyl alcohol **6** with *n*-buthyllithium, *p*-toluenesulfonyl chloride, and lithium chloride afforded **7**, which was converted to the sulfone **8** by using benzenesulfinate dihydrate and tetrabutylammonium bromide according to the slightly modified

procedure of Vennstra and Zwanenburg.[7] The *E*-allyl phenyl sulfone **8** on treatment with *n*-butyllithium in tetrahydrofuran and then with tri-*n*-butylstannylmethyl iodide at −70°C gave the terminal conjugated diene **9** in 71% yield, along with 22% recovery of the starting sulfone. The direct conversion of the tetrahydropyranyl ether **9** into the acetate **1** has been reported by Rossi and co-workers,[2i] but we found that the reaction was accompanied by some isomerization of *E*-diene to *Z*-diene: on treatment with acetic anhydride in acetic acid at 80°C, **9** afforded a mixture of **1** and **2** in a ratio of 79: 21. Finally, the *E*-diene **1** was successfully obtained in 93% stereoisomeric purity from **9** by hydrolysis using pyridinium *p*-toluenesulfonate (PPTS),[8] a milder acid, in ethanol at room temperature followed by acetylation.



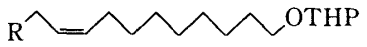
**6**: R=OH
**7**: R=Cl
**8**: R=$SO_2C_6H_5$



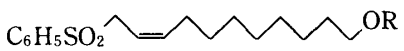
**9**

**Synthesis of *Z*-Diene 2**

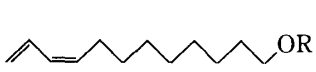
The acetylenic compound **5** was reduced to the *Z*-allyl alcohol **10** using Lindlar catalyst,[9] and **10** was converted to the allyl sulfone **12** *via* the chloride **11** in good yield in the same manner as described for the synthesis of **8**. The *Z*-conjugated diene **15** was obtained in 73% yield by olefination of the allyl sulfone **12** with *n*-butyllithium and tri-*n*-butylstannylmethyl iodide. The attempted direct conversion of **15** to the acetate **2** was also fruitless because of the considerable stereoisomerization of the *Z*-double bond: the diene **15** on treatment with acetic anhydride in acetic acid at 80°C afforded a mixture of **1** and **2** in a ratio of 65: 35. On the other hand, the tetrahydropyranyl ether **15**, on PPTS-catalyzed hydrolysis in ethanol followed by acetylation, gave the *Z*-diene **2** in 58% yield, and its stereoisomeric purity was shown to be higher than 98%.



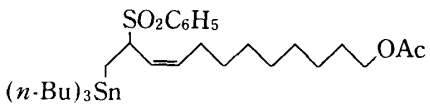
**10**: R=OH
**11**: R=Cl
**12**: R=$SO_2C_6H_5$



**13**: R=H
**14**: R=Si(Me)$_2$-*tert*-Bu



**15**: R=THP
**16**: R=Si(Me)$_2$-*tert*-Bu



**17**

Another synthetic procedure leading to the desired compound **2** *via* an alternative protection of the alcohol **13** was tried with success. Since the 1,3-dienes **1** and **2** were shown to be labile under acidic conditions, the use of a dimethyl-*tert*-butylsilyl group, which is deprotected under basic conditions,[10] as a protecting group for the alcohol **13** must be preferable. The dimethyl-*tert*-butylsilyl ether **14** was obtained in good yield from the tetrahydropyranyl ether **12** by successive hydrolysis and reprotection. The crude reaction mixture obtained from the treatment of the silyl ether **14** with *n*-butyllithium and tri-*n*-butylstannylmethyl iodide at −70°C was shown to consist of the β-tri-*n*-butylstannyl sulfone **17** contaminated with the unreacted starting sulfone **14**. The structure of **17** was deduced from the diagnostic signals of vinylic protons in its proton magnetic resonance (PMR) spectrum: the C-9- and C-10-vinylic

protons appeared at $\delta$ 5.56 (1H, dt, $J$=11,7 Hz) and 5.12 (1H, t, $J$=11 Hz), respectively. The reaction mixture on treatment with silica gel in chloroform afforded the diene **16** smoothly, accompanied by the recovery of some starting materials. Protodesilylation of **16** under basic conditions using tetra-*n*-butylammonium fluoride followed by acetylation gave the desired diene **2** in quantitative yield. Its stereoisomeric purity was shown to be higher than 98%.

Thus, we achieved a highly stereoselective synthesis of both stereoisomers **1** and **2** through a new approach using olefination reactions of the *E*- and *Z*-allyl sulfones.

## Experimental

Infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer. PMR spectra were obtained with a JEOL JNM-FX 100 or a JEOL JNM-PMX 60 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a JEOL JMS-DX-300 spectrometer. High performance liquid chromatography was performed on a JASCO apparatus (Tri Rotar). Column chromatography was carried out on Merck Silica-gel 60. Preparative thin layer chromatography (TLC) was carried out on Merck DC-Fertigplatten (Kieselgel 60 F-254).

**8-Bromo-1-(2-tetrahydropyranyloxy)octane (4)**——According to the procedure described in the literature,[2d,5] 8-bromo-1-octanol (3) was prepared from 1,8-octanediol in 89% yield. 3: IR $\nu_{max}^{film}$ cm$^{-1}$: 3350, 1460, 1055. MS *m/e*: 190 (M$^+$−$H_2O$), 164, 162, 150, 148, 83 (base peak), 69. PMR ($CDCl_3$) $\delta$: 1.0—2.0 (13H, m), 3.42 (2H, t, $J$=6 Hz), 3.64 (2H, t, $J$=6 Hz). Dihydropyran (2.02 g, 24 mmol) was added to a stirred solution of 3 (4.18 g, 20 mmol) in chloroform (50 ml) (pre-dried with phosphorus pentoxide),[11] and the mixture was stirred for 10 min. It was made alkaline by adding aqueous sodium carbonate and extracted with dichloromethane. The organic layer was washed with water and dried. Evaporation left an oil, which was distilled to give the tetrahydropyranyl ether **4** (4.9 g, 84%), bp 123—125°C (0.3 mmHg) [lit.[5] bp 97—100°C (0.008 mmHg)]. IR $\nu_{max}^{film}$ cm$^{-1}$: 1030. MS *m/e*: 293, 291, 115 (base peak), 101, 86, 84. PMR ($CDCl_3$) $\delta$: 3.2—4.0 (6H, m), 4.58 (1H, m).

**Preparation of Alcohol 5**——*n*-Butyllithium (1.5 M in hexane) (15.6 ml, 23.4 mmol) was added slowly to a solution of propargyl alcohol (655 mg, 11.7 mmol) in hexamethylphosphortriamide (60 ml) at about 5°C under argon, and the solution was stirred for 15 min. A solution of the bromide **4** (2.29 g, 7.8 mmol) in hexamethylphosphortriamide (10 ml) was then added over 20 min. After being stirred for 1 h at the same temperature (5°C), the reaction mixture was quenched with water, and extracted with ether. The organic layer was washed with water and dried. Evaporation left an oil, which was chromatographed on a column of silica gel using ethyl acetate–hexane (2: 8) to give alcohol **5** (1.45 g, 54%). IR $\nu_{max}^{film}$ cm$^{-1}$: 3440, 2230, 1020 cm$^{-1}$. MS *m/e*: 268 (M$^+$), 267, 237, 101 (base peak), 85. PMR ($CDCl_3$) $\delta$: 1.1—1.9 (18H, m), 2.1—2.3 (2H, m), 3.2—4.0 (4H, m), 4.1—4.3 (2H), 4.5—4.6 (1H, m). *Anal.* Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.48; H, 10.50.

**Preparation of *E*-Allyl Phenyl Sulfone 8**——A solution of the alcohol **5** (898 mg, 3.35 mmol) in ether (5 ml) was added to a stirred suspension of lithium aluminium hydride (64 mg, 1.68 mmol) in ether (5 ml) at −70°C under argon. The mixture was stirred for 15 min, then the cooling bath was removed and the mixture was allowed to warm up. It was heated for 4 h under reflux. The mixture, after cooling, was added to ethyl acetate, washed with water, and dried. The solvent was evaporated off to give the crude product **6** (886 mg), which was used without further purification. A small portion of the crude reduction product **6** (270 mg) was dissolved in ether (1 ml) and hexamethylphosphortriamide (0.5 ml). *n*-Butyllithium (1.55 M in hexane) (0.65 ml, 1 mmol) was added to the solution at 0°C as described by Stork and co-workers.[12] After being stirred for 10 min at room temperature, the mixture was cooled again to 0°C and a solution of *p*-toluenesulfonyl chloride (210 mg, 1.1 mmol) in ether (1 ml) and hexamethylphosphortriamide (0.5 ml) was added. Then lithium chloride (127 mg, 3 mmol) was added. After being stirred overnight at room temperature, the mixture was poured into water and extracted with ether. The organic layer was washed with water and dried. Evaporation left the crude *E*-allyl chloride **7**. The crude product **7** was dissolved in tetrahydrofuran (10 ml). After the addition of tetrabutylammonium bromide (645 mg, 2 mmol) and benzenesulfinate dihydrate (414 mg, 2 mmol), the reaction mixture was stirred for 2 d at room temperature. The mixture was poured into water and extracted with ether. The organic layer was washed with water, dried, and concentrated to give an oil, which was chromatographed on a column of silica gel using hexane–ethyl acetate (8: 2) to give the *E*-allyl phenyl sulfone **8** (320 mg, 80%). IR $\nu_{max}^{film}$ cm$^{-1}$: 1660, 1440, 1315, 1300, 1140, 1020, 725, 685. MS *m/e*: 394 (M$^+$), 393, 311, 151, 143, 109 (base peak), 101, 95. High resolution MS: Found 394.2186. Calcd for $C_{22}H_{34}O_4S$ (M$^+$) 394.2178. PMR ($CDCl_3$) $\delta$: 3.2—4.2 (6H, m), 4.54 (1H, br s), 5.2—5.7 (2H, m), 7.4—7.9 (5H, m).

**Preparation of the *E*-Diene 9**——*n*-Butyllithium (1.55 M in hexane) (0.056 ml, 0.087 mmol) was added to a stirred solution of the sulfone **8** (31 mg, 0.079 mmol) in tetrahydrofuran (1 ml) at −70°C under argon and the resulting yellow solution was stirred for 1 h at the same temperature. A solution of tri-*n*-butyl-

stannylmethyl iodide (40 mg, 0.088 mmol) in tetrahydrofuran (3 ml) was added dropwise to the yellow solution over 30 min. After being stirred for 2 h at −70°C, the reaction mixture was quenched with saturated aqueous $NH_4Cl$ solution and extracted with ether. The extract was washed with water, and dried. The solvent was removed to leave an oil. On preparative TLC (hexane–ethyl acetate (8: 2)), the *E*-diene **9** (15 mg, 71%) and the starting sulfone **8** (7 mg) were isolated. **9**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1650, 1600, 1020, 890 MS *m/e*: 266 ($M^+$), 248, 101, 85, 67 (base peak). High resolution MS: Found 266.2188. Calcd for $C_{17}H_{30}O_2$ ($M^+$) 266.2245. PMR ($CDCl_3$) $\delta$: 1.0—2.2 (20H, m), 3.2—4.0 (4H, m), 4.54 (1H, br s), 4.8—5.2 (2H, m), 5.5—6.5 (3H, m).

**Attempted Direct Conversion of 9 to Acetate 1**——A solution of **9** (3.5 mg, 0.013 mmol) in acetic anhydride (0.17 ml) and acetic acid (0.3 ml) was heated at 80°C for 12 h. Evaporation left an oil. On preparative TLC (hexane–ethyl acetate (8: 2)), a mixture of the *E*-diene **1** and the *Z*-diene **2** (3 mg, 100%) was separated, and their ratio was determined to be 79: 21, according to the procedure developed by Rossi and co-workers.[3,13]

**Preparation of Acetate 1**——A solution of **9** (7 mg, 0.026 mmol) and PPTS (1.3 mg, 0.005 mmol) in ethanol (0.4 ml) was stirred for 5 d at room temperature. The mixture was poured into water and extracted with ether. After being washed with water and dried, the organic layer was concentrated to give an oil. On preparative TLC (hexane–ethyl acetate (7: 3)), compound (4 mg) with *Rf* 0.22 was isolated. It was dissolved in pyridine (0.5 ml) and acetic anhydride (0.2 ml). The mixture was stirred overnight, then the solvent was evaporated off to give an oil. On preparative TLC (hexane–ethyl acetate (8: 2)), the *E*-diene **1** (4.8 mg, 83%) was isolated, and its stereoisomeric purity was shown to be higher than 93%.[13] **1**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1740, 1650, 1605, 1240, 1005, 900. MS *m/e*: 224 ($M^+$), 164, 149, 135, 121, 80, 67, 43. High resolution MS: Found 224.1784. Calcd for $C_{14}H_{24}O_2$ ($M^+$) 224.1777. PMR ($CDCl_3$) $\delta$: 2.05 (3H, s), 4.07 (2H, t, $J$=7 Hz), 4.9—5.2 (2H, m), 5.5—6.5 (3H, m).

**Preparation of the Chloride 11**——The alcohol **5** (536 mg, 2 mmol) was dissolved in hexane (5 ml) and quinoline (0.1 ml), and hydrogenated over Lindlar catalyst (20 mg) for 35 min. The mixture was filtered and concentrated to give the crude alcohol **10**. The crude product **10** was converted to the allyl chloride **11** by the same method as described for the synthesis of **7**. Chromatography on a column of silica gel using hexane–ethyl acetate (9: 1) afforded **11** (500 mg, 87%). IR $\nu_{max}^{film}$ $cm^{-1}$: 1650, 1450, 1110, 1025, 900, 865, 810. MS *m/e*: 288 ($M^+$), 287, 253, 215, 151, 109, 101, 95, 85, 41 (base peak). PMR ($CDCl_3$) $\delta$: 1.2—2.0 (18H, m), 2.0—2.3 (2H, m), 3.3—4.0 (4H, m), 4.0—4.3 (2H, m), 4.57 (1H, m), 5.5—5.9 (2H, m). *Anal.* Calcd for $C_{16}H_{29}ClO_2$: C, 66.53; H, 10.12. Found: C, 66.61; H, 10.19.

**Preparation of the *Z*-Allyl Phenyl Sulfone 12**——The chloride **11** (360 mg, 1.25 mmol) was converted to the sulfone **12** (448 mg, 91%) using tetrabutylammonium bromide (806 mg, 2.5 mmol) and benzenesulfinate dihydrate (518 mg, 2.5 mmol) by the same method as described for the synthesis of the sulfone **8**. **12**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1650, 1585, 1445, 1310, 1140, 1020, 715, 685. MS *m/e*: 393, 310, 309, 253, 168, 151, 143 (base peak), 109, 101, 95, 85, 67. High resolution MS: Found 393.2071. Calcd for $C_{22}H_{33}O_4S$ ($M^+$−H) 393.2099. PMR ($CDCl_3$) $\delta$: 1.0—2.0 (20H, m), 3.3—4.1 (6H, m), 4.58 (1H, m), 5.3—5.9 (2H, m), 7.5—8.0 (5H, m).

**Preparation of the *Z*-Diene 15**——The sulfone **12** (55 mg, 0.14 mmol) was converted to the diene **15** (27 mg, 73%), with partial recovery of the starting sulfone **12** (7 mg), using *n*-butyllithium (1.55 M in hexane) (0.1 ml, 0.155 mmol) and tri-*n*-butylstannylmethyl iodide (67 mg, 0.155 mmol) by the same method as described for the synthesis of the diene **9**. **15**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1640, 1595, 1350, 1120, 1030, 900, 815. MS *m/e*: 266, 265, 101, 85, 67, 55, 41 (base peak). High resolution MS: Found 266.2230. Calcd for $C_{17}H_{30}O_2$ ($M^+$) 266.2245. PMR ($CDCl_3$) $\delta$: 1.0—2.0 (18H, m), 2.0—2.4 (2H, m), 3.3—4.1 (4H, m), 4.57 (1H, m), 5.0—5.7 (3H, m), 6.01 (1H, t, $J$=11 Hz), 6.67 (1H, dt, $J$=17, 11 Hz).

**Attempted Direct Conversion of 15 to the Acetate 2**——A solution of **15** (8 mg, 0.03 mmol) in acetic anhydride (0.28 ml) and acetic acid (0.5 ml) was heated at 80°C for 12 h. Evaporation left an oil. On preparative TLC (hexane–ethyl acetate (8: 2)) a mixture of the *E*-diene **1** and the *Z*-diene **2** (6.5 mg, 97%) was obtained in a ratio of 65: 35.[13]

**Preparation of the Acetate 2**——Hydrolysis of **15** (6.1 mg, 0.023 mmol) using PPTS (0.6 mg, 0.0023 mmol) followed by acetylation afforded the *Z*-diene **2** (3 mg, 58%) by the same method as described for the synthesis of the *E*-diene **1**. Its stereoisomeric purity was shown to be higher than 98%.[13] **2**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1740, 1640, 1370, 1240, 1000, 905. MS *m/e*: 224 ($M^+$), 164, 135, 121, 80, 68 (base peak). High resolution MS: Found 224.1812. Calcd for $C_{14}H_{24}O_2$ ($M^+$) 224.1777. PMR ($CDCl_3$) $\delta$: 2.05 (3H, s), 4.07 (2H, t, $J$= 7 Hz), 5.0—5.7 (3H, m), 6.03 (1H, t, $J$=11 Hz), 6.68 (1H, dt, $J$=17, 11 Hz).

**Preparation of the Silyl Ether 14**——A solution of the sulfone **12** (142 mg, 0.36 mmol) and PPTS (9 mg, 0.036 mmol) in ethanol (4 ml) was heated at 50°C for 4 h. After the evaporation of the solvent and addition of water, the mixture was extracted with ether. The organic layer was washed with water and dried. Evaporation left a crude alcohol **13**. The crude **13** was dissolved in dimethylformamide (0.5 ml). After the addition of dimethyl-*t*-butylsilyl chloride (55 mg, 0.363 mmol) and imidazole (59 mg, 0.863 mmol), the mixture was stirred for 12 h at room temperature. After the addition of water, the mixture was extracted with ether, washed with water, and dried. Evaporation left a crude oil. On preparative TLC (hexane–ethyl acetate (7: 3)), the silyl ether **14** (150 mg, 98%) was isolated. **14**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1650, 1320, 1145, 1090, 835, 775. MS *m/e*: 425, 409, 368 (base peak), 367, 217, 201, 200, 151, 101. High resolution MS: Found 409.2277. Calcd for $C_{22}H_{37}O_3SiS$ ($M^+$−Me) 409.2233. PMR ($CDCl_3$) $\delta$: 0.04 (6H, s), 0.89 (9H, s),

1.0—1.8 (14H, m), 3.61 (2H, t, $J$=6 Hz), 3.87 (2H, d, $J$=7 Hz), 5.3—5.9 (2H, m), 7.4—8.0 (5H, m).

**Preparation of the *Z*-Diene 16**——*n*-Butyllithium (1.55 M in hexane) (0.091 ml, 0.142 mmol) was added to a stirred solution of the sulfone **14** (50 mg, 0.118 mmol) in tetrahydrofuran (2 ml) at −70°C under argon and the resulting yellow solution was stirred for 2 h at −70°C. A solution of tri-*n*-butylstannylmethyl iodide (61 mg, 0.142 mmol) in tetrahydrofuran (5 ml) was added very slowly to the yellow solution over 1 h. After being stirred for 5 h at −70°C, the reaction mixture was quenched with water and extracted with ether. The extract was washed with water, dried, and concentrated to give a crude oil, which was shown to be a mixture of the β-tri-*n*-butylstannyl sulfone **17** and the starting sulfone **14** by inspection of its PMR spectrum. **17**: PMR ($CDCl_3$) δ: *ca.* 4.0 (1H, m), 5.12 (1H, t, $J$=11 Hz), 5.56 (1H, dt, $J$=11, 7 Hz). The crude product **17** was dissolved in chloroform (5 ml). After the addition of silica gel (1 g), the mixture was stirred for 1 h at room temperature. Filtration followed by evaporation left an oil. On preparative TLC (hexane–ethyl acetate (95: 5)) the *Z*-diene **16** (23.5 mg, 67%) and the sulfone **14** (7 mg) were isolated. **16**: IR $\nu_{max}^{film}$ $cm^{-1}$: 1640, 1595, 1460, 1250, 1100, 900, 835, 775. MS *m/e*: 296 ($M^+$), 281, 240 (base peak), 239, 211, 115, 101, 73, 67. High resolution MS: Found 296.2528. Calcd for $C_{18}H_{36}OSi$ ($M^+$) 296.2534. PMR ($CDCl_3$) δ: 0.04 (6H, s), 0.90 (9H, s), 1.1—1.6 (12H, m), 2.0—2.3 (2H, m), 3.61 (2H, t, $J$=6 Hz), 5.0—5.6 (3H, m), 6.02 (1H, t, $J$=11 Hz), 6.68 (1H, dt, $J$=17, 11 Hz).

**Synthesis of the *Z*-Diene 2 from 16**——A solution of **16** (6 mg, 0.02 mmol) and tetrabutylammonium fluoride (10 mg, 0.04 mmol) in tetrahydrofuran (2 ml) was stirred for 2 h at room temperature. After addition of water, the mixture was extracted with ether. The extract was washed with water, dried, and concentrated to give a crude oil. The crude product was dissolved in pyridine (0.5 ml) and acetic anhydride (0.2 ml). The solution was stirred for 12 h at room temperature and the solvent was removed to leave an oil. On preparative TLC (hexane–ethyl acetate (8: 2)), the *Z*-diene **2** (4.8 mg, 100%) was isolated and its stereoisomeric purity was shown to be higher than 98%.[13]

## References and Notes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