Stereoselective Synthesis of Some Isomers of Dodecadien-1-ol: Compounds Related to the Pine Moth Sex Pheromone

Tetsu ANDO,* Manh Huynh VU, Shigeo YOSHIDA and Nobutaka TAKAHASHI†

Department of Agricultural Chemistry, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
**The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan*

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Four isomers of 5,7-dodecadien-1-ol were previously proposed as being the sex pheromone of the pine moth. The isomers were stereoselectively synthesized from 1-hexyne and tetrahydropyranyl ether of 5-hexyn-1-ol. The (5*Z*, 7*Z*)-isomer was synthesized by a Chodkiewic Cadiot reaction followed by hydroboration, and other three isomers by novel synthetic methods including the addition of zirconocene hydride [Schwarz's reagent $(C_5H_5)_2Zn(H)Cl$] to control the regioselective coupling reaction. The 5,8- and 5,9-dodecadien-1-ols were also synthesized by similar methods for comparison of their characteristics with the endogenous sex pheromone.

As described in the preceding paper,[1] the sex pheromone of the pine moth, *Dendrolimus spectabilis*, was confirmed to be (5*E*,7*Z*)-5,7-dodecadien-1-ol (**11**). For the identification of this sex pheromone, a comparison of the spectroscopic natures, retention times on gas chromatography and field attractiveness of its geometrical and positional isomers were essential. In this paper we describe the synthesis of four geometrical isomers of 5,7-dodecadien-1-ol together with (5*E*,8*E*) and (5*Z*,9*Z*) isomers, where the stereospecific introduction of double bonds was achieved by new methods containing the modified Chodkiewics Cadiot reaction, hydrozirconation, coupling reactions by palladium catalysts and selective hydrogenations.

*(5Z,7Z)-5,7-Dodecadien-1-ol (**6**)* (Scheme 1)

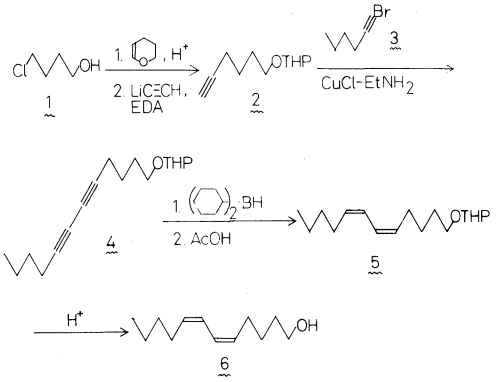
Tetrahydropyranyl ether of commercially available 4-chloro-1-butanol (**1**) was coupled with a lithium acetylide-ethylenediamine complex in dimethyl sulfoxide (DMSO)[2] to give 5-hexyn-1-ol tetrahydropyranyl (THP) ether (**2**) in a 70% yield. After the synthesis of 1-bromohexyne (**3**) from 1-hexyne using the reported reaction,[3] a Chodkiewics Cadiot reaction[3] between this 1-bromoacetylene (**3**) and the above acetylene (**2**) gave 5,7-dodecadiyn-1-ol THP ether (**4**) in a 53% yield. This diyne was treated with dicyclohexylborane in tetrahydrofuran (THF)[4] and then with glacial acetic acid to yield stereoselectively (5*Z*,7*Z*)-5,7-dodecadien-1-ol THF ether (**5**) in a quantitative yield. (5*Z*,7*Z*)-5,7-Dodecadien-1-ol (**6**) was obtained by the solvolysis of the THP ether (**5**) with *p*-toluenesulfonic acid in methanol.

*(5Z,7E)-5,7-Dodecadien-1-ol (**11**)* (Scheme 2)

It has been reported that the reaction of zirconocene monohydride (Schwartz's reagent, $(C_5H_5)_2Zr(H)Cl$* with 1-alkyne gives (*E*)-1-alkenylzirconium compound which establishes that a Zr-H addition (hydrozirconation) to the acetylene occurs regioselectively *cis*, and that the bond of Zr and carbon is easily attacked by iodine (I_2) to give (*E*)-1-iodo-1-alkene.[6] Therefore, a pure sample of (*E*)-1-iodo-1-

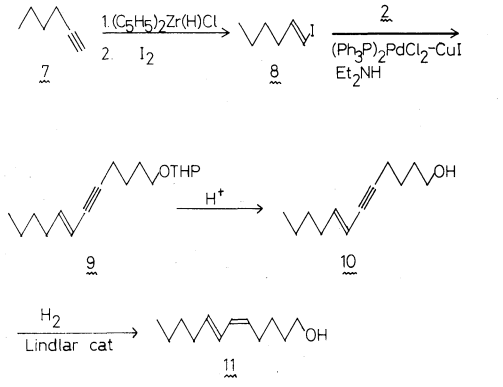
† To whom correspondence should be addressed.

* This reagent is commercially available from Alfa Products (Massachusetts, U.S.A.). But it can be easily prepared from Zirconocene dichloride, $(C_5H_5)_2ZrCl_2$.[5]



SCHEME 1. Synthesis of (5*Z*,7*Z*)-5,7-Dodecadien-1-ol.

hexene (**8**) was obtained by the successive treatment of 1-hexyne (**7**) with $(C_5H_5)_2Zr(H)Cl$ and I_2 in benzene in a 86% yield. This iodide (**8**) was coupled with 5-hexyn-1-ol THP ether (**2**) in the presence of bis(triphenylphosphine)palladium dichloride ($(Ph_3P)_2PdCl_2$)[7] and cuprous iodide (CuI) in diethylamine[8] to give (*E*)-7-dodecen-5-yn-1-ol THP ether (**9**) in a 76% yield, which was converted to (*E*)-7-dodecen-5-yn-1-ol (**10**) by removal of the THP protective group. It was difficult to hydrogenate the conjugated triple bond of the enyne (**10**) selectively to obtain (5*Z*,7*E*)-5,7-dodecadien-1-ol (**11**). Hydrogenation of the enyne (**10**) over a Lindlar catalyst (Pd-$CaCO_3$-PbO) further poisoned with quinoline in *n*-hexane gave a mixture of unhydrogenated enyne (**10**) (5%), diene (**11**) (71%) and monoene compounds (24%). Stereochemically pure (5*Z*,7*E*)-5,7-dodeca-

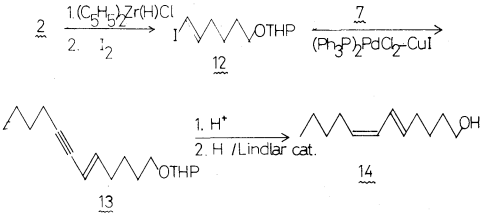


SCHEME 2. Synthesis of (5*Z*,7*E*)-5,7-Dodecadien-1-ol.

diene-1-ol (**11**) was obtained by means of a silica gel column impregnated with 20% silver nitrate ($AgNO_3$).

*(5E,7Z)-5,7-Dodecadien-1-ol (**14**)* (Scheme 3)

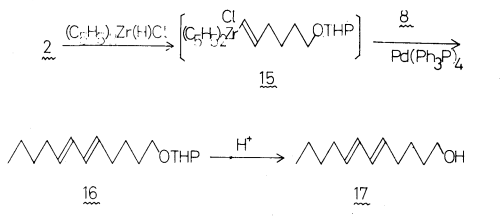
5-Hexyn-1-ol THP ether (**2**) was converted to (*E*)-6-iodo-5-hexen-1-ol THP ether (**12**) in an 80% yield by successive treatment with $(C_5H_5)_2Zr(H)Cl$ and I_2. The coupling of this iodide (**12**) with 1-hexyne (**7**), in the same manner as the synthesis of (**9**), afforded (*E*)-5-dodecen-7-yn-1-ol THP ether (**13**) in a 62% yield. The removal of the THP group followed by hydrogenation over Pd-$CaCO_3$-PbO poisoned with quinoline gave (5*E*,7*Z*)-5,7-dodecadien-1-ol (**14**).



SCHEME 3. Synthesis of (5*E*,7*Z*)-5,7-Dodecadien-1-ol.

*(5E,7E)-5,7-Dodecadien-1-ol (**17**)* (Scheme 4)

5-Hexyn-1-ol THP ether (**2**) was converted to the (*E*)-zirconium intermediate (**15**) by hydrozirconation in benzene. After replacing the benzene with THF, this zirconium derivative (**15**) was treated with (*E*)-1-iodo-1-hexene (**8**) using tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$)[9] as a catalyst[10] to give (5*E*,7*E*)-5,7-dodecadien-1-ol THP ether (**16**) in a 59% yield. The removal of the protective group afforded a stereochemically pure sample of (5*E*,7*E*)-5,7-dodecadien-1-ol (**17**).



SCHEME 4. Synthesis of (5*E*,7*E*)-5,7-Dodecadien-1-ol.

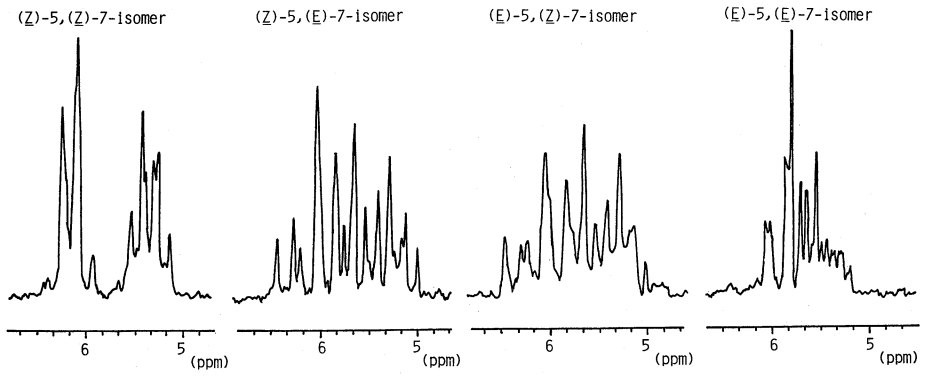


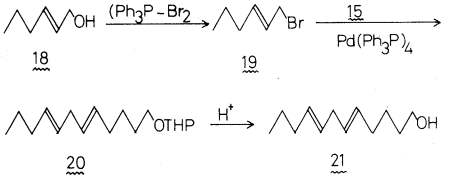
FIG. 1. NMR Spectra of Olefinic Proteins of Synthetic 5,7-Dodecadien-1-ol.

The expected geometries of these dienols were supported by IR absorption-bands at 720 and 980 cm^{-1} (see EXPERIMENTAL). The NMR spectra of four isomers of 5,7-dodecadien-1-ol were almost indistinguishable except for the parts of the olefinic proton signals in each geometrical isomer as shown in Fig. 1.

Separation of four geometrical isomers of the conjugated diene system is difficult even using preparative thin-layer chromatography (TLC) with silica gel plates impregnated with $AgNO_3$. The *Rf* values of the four isomers are very close while geometrical isomers of the monoene alcohols generally show appreciable differences in their *Rf* values. Benzene–ethyl acetate (3 : 1) as a developing solvent on TLC gave the following *Rf* values for these compounds: (*Z*),(*Z*)-isomer: *Rf* 0.52, (*Z*),(*E*)-isomer: *Rf* 0.54, (*E*),(*Z*)-isomer: *Rf* 0.54, (*E*),(*E*)-isomer: *Rf* 0.57, (*Z*)-5-dodecen-1-ol: *Rf* 0.48 and (*E*)-5-dodecen-1-ol: *Rf* 0.59. From this aspect, our methods were shown to be useful for the syntheses of stereochemically pure conjugated diene pheromones.

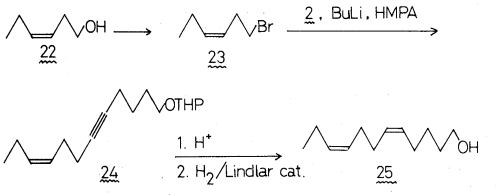
Syntheses of some other dodecadien-1-ols seemed to be necessary for the identification of the pine moth sex pheromone, so that (5*E*,8*E*)-5,8- and (5*Z*,9*Z*)-5,9-dodecadien-1-ols were synthesized as model compounds of the homo- and non-conjugated diene dodecanols respectively.

*(5E,8E)-5,8-Dodecadien-1-ol (**22**)* (Scheme 5) Commercially available (*E*)-2-hexen-1-ol (**18**) was converted to (*E*)-1-bromo-2-hexene (**19**) by bromination with bromine-triphenylphosphine in acetonitrile. This bromide (**19**) was coupled with 6-zirconium-(*E*)-5-hexen-1-ol THP ether (**20**), which was prepared with (**2**) and $(C_5H_5)_2Zr(H)Cl$, using $Pd(Ph_3P)_4$ as a catalyst in THF to give (5*E*,8*E*)-5,8-dodecadien-1-ol THP ether (**21**). Removal of the protective group from (**21**) gave (5*E*,8*E*)-5,8-dodecadien-1-ol (**22**).



SCHEME 5. Synthesis of (5*E*,8*E*)-5,8-Dodecadien-1-ol.

*(5Z,9Z)-5,9-Dodecadien-1-ol (**26**)* (Scheme 6) 5-Hexyn-1-ol THP ether (**2**) was coupled with (*Z*)-1-bromo-3-hexene (**24**), which was derived from commercially available (*Z*)-3-hexen-1-ol (**23**), using *n*-butyllithium in THF-hexamethylphosphoric triamide (HMPA) to give (*Z*)-9-dodecen-5-yn-1-ol THP ether (**25**).



SCHEME 6. Synthesis of (5*Z*,9*Z*)-5,9-Dodecadien-1-ol.

This non-conjugated enyne compound was hydrolyzed and the alcohol was quantitatively hydrogenated over a Lindlar catalyst in *n*-hexane to give only (5*Z*,9*Z*)-5,9-dodecadien-1-ol (**26**).

Significant differences of mass spectra between the conjugated and non-conjugated dodecadien-1-ols were indicated (see the preceding paper[1]). Furthermore it was observed that the retention times of the unconjugated alcohols in GC were much shorter than those of the 5,7-diene alcohols.[1] These analyses were quite helpful for identification of the pine moth sex pheromone.

EXPERIMENTAL

IR spectra were obtained on a Shimadzu IR-27G spectrometer referring to films. NMR spectra were recorded in CCl_4, with TMS as an internal standard, on a Joel JNM-PMX60 NMR spectrometer. GC-MS and GC-high MS were obtained with a Hitachi RMU-6MG and a Hitachi M-80 spectrometer respectively.

5-Hexyn-1-ol THP ether (**2**). 2,3-Dihydropyran (0.3 mol, 25.0 g) was added dropwise to a stirred 4-chlorobutan-1-ol (**1**) (0.3 mol, 32.6 g) at 10~15°C. After addition, the mixture was stirred for 3 hr at room temperature to give 4-chloro-1-butanol THP ether. Without purification, this crude halo ether was added dropwise to a stirred suspension of lithium acetylide-ethylenediamine complex (0.32 mol, 29.4 g) in DMSO (300 ml) under a dry nitrogen stream at 15~20°C. The mixture was stirred at room temperature for 2 hr, then poured into ice-water and extracted with *n*-hexane. After washing with water, 1 N hydrochloric acid and a sodium bicarbonate solution, the extract was dried over anhydrous magnesium sulfate and then concentrated *in vacuo* to give 38.2 g of **2**: IR ν_{max} cm^{-1}: 3300 (s), 2950 (s), 2880 (s), 2120 (w), 1140 (s), 1120 (s), 1080 (s), 1030 (s), 630 (br. s); NMR δ: 1.3~1.9 (10H, m), 1.9 (1H, t, J=3 Hz), 2.0~2.4 (2H, m), 3.1~4.0 (4H, m), 4.5 (1H, br, s); GC-high MS: M^+ m/z 182.1363, Calcd. for $C_{11}H_{18}O_2$ 182.1307.

1-Bromohexyne (**3**). Bromine (0.3 mol, 47.9 g) was added dropwise to a stirred and ice-cooled mixture of 1-hexyne (**7**) (0.1 mol, 8.2 g) and 3 N potassium hydroxide solution (400 ml). After addition the mixture was stirred overnight at room temperature. As the product **3** began to condense, the aqueous layer was removed and the colorless lower layer washed with water and dried with anhydrous magnesium sulfate. Distillation under nitrogen atmosphere gave 7.4 g (46%) of **3**: bp 60°C (39 mmHg); n_D^{25} 1.4649; IR ν_{max} cm^{-1}: 2990 (s), 2970 (s), 2890 (s), 1470 (s), 1465 (sh), 1430 (m), 1390 (m), 1120 (m), 780 (m), 700 (m); NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.2~1.7 (4H, m), 2.2 (2H, distorted t, J=6 Hz); GC-MS m/z 160.

5,7-Dodecadieyn-1-ol THP ether (**4**). A solution of **2** (18 mmol, 3.3 g) in methanol (25 ml) was stirred with cuprous chloride (40 mg) and 30% aqueous ethylamine (6 ml) at 16°C. Then a solution of **3** (20 mmol, 3.2 g) in methanol (10 ml) was slowly added at 25°C. A small amount of powdered hydroxylamine hydrochloride was added as required to discharge the blue color. After 1 hr a solution of potassium cyanide (100 mg) in water (2 ml) and water (25 ml) were successively added and the product **4** extracted with *n*-hexane. This extract was concentrated *in vacuo* after the usual work up. Purification with a silica gel column gave 2.5 g (55% from 2) of **4**; IR ν_{max} cm^{-1}: 2950 (s), 2880 (s), 1140 (s), 1120 (s), 1080 (s), 1040 (s); NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.2~1.9 (14H, m), 2.1~2.5 (4H, m), 3.1~4.0 (4H, m), 4.4 (1H, br. s); GC-high MS: M^+ m/z 262.1891, Calcd. for $C_{17}H_{26}O_2$ 262.1931.

(5Z,7Z)-5,7-Dodecadien-1-ol THP ether (**5**). To a stirred and ice-cooled solution of dicyclohexylborane in THF (1 M solution, 10 ml), a solution of **4** (4.5 mmol, 1.18 g) in THF (20 ml) was added dropwise at 0°C. The reaction mixture was maintained at room temperature for 5 hr, diluted with 2 ml of glacial acetic acid, and then heated at 60°C for 5 hr. Oxidation of the resulting dicyclohexylborinate was achieved by adding 6 N sodium hydroxide (7 ml) followed by the dropwise addition of 2 ml of 30% hydrogen peroxide at 30°C. The mixture was then stirred for an additional 30 min before working up. The crude product **5** was extracted with *n*-hexane and the extract was concentrated *in vacuo* after the usual work up. The residue was chromatographed over a silica gel column impregnated with 20% $AgNO_3$ to give 1.10 g of purified **5** (92% from 4); IR ν_{max} cm^{-1}: 3050 (m), 2980 (sh), 2890 (s), 1140 (s), 1120 (s), 1080 (s), 1040 (s), 720 (m); NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.1~1.8 (14H, m), 1.9~2.3 (4H, m), 3.1~4.0 (4H, m), 4.5 (1H, br. s), 5.1~6.4 (4H, m); GC-high MS: M^+ m/z 266.2252, Calcd. for $C_{17}H_{30}O_2$ 266.2245.

(5Z,7Z)-5,7-Dodecadien-1-ol (**6**). *p*-Toluenesulfonic acid (0.1 g) was added to a solution of **5** (1.1 g) in methanol (30 ml). The mixture was stirred for 1 hr at 60°C and then concentrated *in vacuo*. The residue was diluted with *n*-hexane (20 ml). The *n*-hexane solution was concentrated *in vacuo* after the usual work up. The residue was column-chromatographed on silica gel impregnated with 20% $AgNO_3$ to give 0.67 g of pure **6** (89% from **5**); IR ν_{max} cm^{-1}: 3300 (br. s), 3050 (m), 2980 (sh), 2960 (s), 2890 (s), 1650 (w), 1470 (sh), 1460 (m), 1440 (sh), 1380 (w), 1060 (m), 1040 (sh), 720 (m), NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.1~1.8 (8H, m), 1.9~2.4 (4H, m), 2.6 (1H, s), 3.5 (2H, t, J=6 Hz), 5.1~6.4 (4H, m); GC-high MS: M^+ m/z 182.1674, Calcd. for $C_{12}H_{22}O$ 182.1670.

(E)-1-Iodo-1-hexene (**8**). To a solution of the zirconocene hydride, $(C_5H_5)_2Zr(H)Cl$ (0.1 mol, 25.8 g) in dry benzene (100 ml), **7** (0.1 mol, 8.2 g) was added at room temperature under dry nitrogen. After stirring for 4 hr, sufficient iodine (*ca.* 22 g) was added to maintain the purplish red color of iodine. The mixture was poured into strongly stirred *n*-hexane (1 liter), and after the brown precipitate was removed, the solution was concentrated *in vacuo*. The residue was diluted with *n*-hexane (100 ml). The *n*-hexane solution was washed with sodium thiosulfate and sodium chloride solutions successively, dried with anhydrous magnesium sulfate and concentrated *in vacuo* to give 18.2 g of crude **8** (86% from **7**); IR ν_{max} cm^{-1}: 3060 (m), 2980 (s), 2950 (s), 2880 (s), 1616 (m), 1470 (s), 1220 (m), 1180 (m), 670 (s); NMR δ: 0.9 (3H, distorted t, J= 6 Hz), 1.1 ~ 1.7 (4H, m), 1.8 ~ 2.3 (2H, m), 5.9 (1H, distorted d, J=14 Hz), 6.5 (1H, m, J=14 and 7 Hz); MS: M^+ m/z 210. This was used for the next step without further purification.

(E)-7-Dodecen-5-yn-1-ol THP ether (**9**). To a stirred solution of **2** (30 mmol, 5.5 g), $(Ph_3P)_2PdCl_2$ (0.3 mmol, 0.2 g) and CuI (0.3 mmol, 57 mg) in diethylamine (60 ml), crude **8** (33 mmol, 7.0 g) was added at room temperature under dry nitrogen and stirred overnight. The mixture was then poured into ice-water (150 ml) and extracted with *n*-hexane. The *n*-hexane solution was concentrated *in vacuo* after the usual work up. The residue was chromatographed on a silica gel column impregnated with 20% $AgNO_3$ to give 6.0 g of **9** (76% from **2**); IR ν_{max} cm^{-1}: 3050 (w), 2980 (s), 2960 (sh), 2890 (s), 1140 (s), 1120 (s), 1080 (s), 1040 (s), 960 (m); NMR δ: 0.9 (3H, distorted t, J= 6 Hz), 1.1 ~ 1.9 (14H, m), 1.9 ~ 2.4 (4H, m), 3.1 ~ 4.0 (4H, m), 4.5 (1H, bs), 5.3 (1H, distorted d, J=16 Hz), 6.0 (1H, m, J=16 Hz, 7 Hz); GC-high MS: M^+ m/z 264.2090, Calcd. for $C_{17}H_{28}O_2$ 264.2088.

(E)-7-Dodecen-5-yn-1-ol (**10**). The THP protective group of **9** (6.0 g) was removed using the same procedure as in the synthesis of **6**, and after purification with a silica gel column, 3.7 g of **10** (90%) was obtained. IR ν_{max} cm^{-1}: 3300 (br, s), 3050 (w), 2980 (sh), 2960 (s), 2890 (s), 1470 (sh), 1460 (m), 1440 (m), 1380 (w), 1060 (s), 1040 (m), 960 (s); NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.2 ~ 1.8 (8H, m), 1.9 ~ 2.4 (4H, m), 3.0 (1H, s), 3.5 (2H, t, J=6 Hz), 5.4 (1H, distorted d, J=16 Hz), 6.0 (1H, m, J=16 Hz, 7 Hz); GC-high MS: M^+ m/z 180.1508, Calcd. for $C_{12}H_{20}O$ 180.1512.

(5Z,7E)-5,7-Dodecadien-1-ol (**11**). Lindlar catalyst (Pd-$CaCO_3$-PbO, 0.3 g) and quinoline (1 drop) were added to a solution of **10** (1 g) in *n*-hexane (10 ml). The mixture was strongly stirred under a hydrogen atmosphere (1 atm at room temperature) and the hydrogenated products analyzed by GC every hour. After 15 hr it was observed that the mixture contained unhydrogenated enyne (**10**), the required diene (**11**) and monoene alcohols in the ratio of 5 : 71 : 24. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was carefully chromatographed over a silica gel column impregnated with 20% $AgNO_3$ to give pure **11**; IR ν_{max} cm^{-1}: 3300 (br. s), 3050 (m), 2980 (sh), 2960 (s), 2890 (s), 1650 (w), 1470 (sh), 1460 (m), 1440 (sh), 1380 (w), 1060 (m), 1040 (sh), 980 (m), 720 (w); NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.2 ~ 1.8 (8H, m), 1.9 ~ 2.4 (4H, m), 2.6 (1H, s), 3.5 (2H, t, J=6 Hz), 5.0 ~ 6.5 (4H, m); GC-high MS: M^+ m/z 182.1677, Calcd. for $C_{12}H_{22}O$ 182.1670.

(E)-6-Iodo-5-hexen-1-ol THP ether (**12**). This synthesis was completed from **2** in the same manner as the synthesis of **8** to give crude **12** in an 88% yield, which was used for the next step without further purification. IR ν_{max} cm^{-1}: 2950 (s), 2880 (s), 1610 (w), 1140 (s), 1120 (s), 1080 (s), 1030 (s); NMR δ: 1.3 ~ 1.9 (10H, m), 1.9 ~ 2.3 (2H, m), 3.1 ~ 4.0 (4H, m), 4.5 (1H, br. s), 6.0 (1H, distorted d, J= 14 Hz), 6.5 (1H, m, J=14 Hz, 7 Hz); GC-MS: M^+ m/z 310.

(E)-5-Dodecen-7-yn-1-ol THP ether (**13**). This synthesis was completed from **7** and **12** in the same manner as the synthesis of **9**. Pure **13** was obtained in a 62% yield from **12** after column chromatography using silica gel impregnated with 20% $AgNO_3$. IR ν_{max} cm^{-1}: 3050 (w), 2980 (sh), 2960 (s), 2890 (s), 1140 (s), 1120 (s), 1080 (s), 1040 (s), 960 (m),; NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.1 ~ 1.9 (14H, m), 1.9 ~ 2.4 (4H, m), 3.1 ~ 4.0 (4H, m), 4.5 (1H, bs), 5.3 (1H, distorted bd, J=16 Hz), 6.0 (1H, m, J= 16 Hz, 7 Hz); GC-high MS: M^+ m/z 264.2082, Calcd. for $C_{17}H_{28}O_2$ 264.2088.

(5E,7Z)-5,7-Dodecadien-1-ol (**14**). The THP protective group of **13** was removed in the usual manner, and after chromatography with a silica gel column, the purified enyne compound was hydrogenated in the same manner described in the synthesis of **11** to give **14**. The hydrogenated product was also a mixture of enyne, diene (**14**) and monoene alcohols in a ratio of 9 : 68 : 23. A column chromatography using silica gel impregnated with 20% $AgNO_3$ gave pure diene **14**; IR ν_{max} cm^{-1}: 3300 (br. s), 3050 (m), 2980 (sh), 2960 (s), 1650 (w), 1470 (sh), 1460 (m), 1440 (sh), 1380 (w), 1060 (m), 1040 (sh), 980 (m), 720 (w), NMR δ: 0.9 (3H, distorted t, J=6 Hz), 1.2 ~ 1.9 (8H, m), 1.9 ~ 2.4 (4H, m), 3.3 (1H, s), 3.5 (2H, t, J=6 Hz), 5.0 ~ 6.5 (4H, m); GC-high MS: M^+ m/z 182.1664, Calcd. for $C_{12}H_{22}O$ 182.1670.

(5E,7E)-5,7-Dodecadien-1-ol THP ether (**16**). To a stirred solution of zirconocene hydride ($(C_5H_5)_2Zr(H)Cl$, 30 mmol, 7.7 g) in dry benzene (30 ml), **2** (30 mmol, 5.5 g) was added at room temperature under dry nitrogen. After stirring for 4 hr the benzene was removed with a nitrogen stream. The residue was diluted with THF (50 ml), mixed with **8** (30 mmol, 6.4 g) and $Pd(PPh_3)_4$ (0.87 g) and stirred for 15 hr at room temperature under dry nitrogen. The mixture was poured into strongly stirred *n*-hexane

(300 ml), the precipitate filtered off and the solution was finally concentrated *in vacuo*. The residue was diluted with *n*-hexane. After successive washings with water and a sodium chloride solution, the *n*-hexane solution was dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The crude material was chromatographed over a silica gel column to give pure **16** (4.7 g, 59%); IR ν_{max} cm^{-1}: 3050 (m), 2980 (sh), 2960 (s), 2890 (s), 1140 (s), 1120 (s), 1080 (s), 1040 (s), 980 (s); NMR δ: 0.9 (3H, distorted t, $J=6$ Hz), 1.1 ~ 1.8 (14H, m), 1.9 ~ 2.3 (4H, m), 3.1 ~ 4.0 (4H, m), 4.5 (1H, bs), 5.2 ~ 6.2 (4H, m); GC-high MS: M^+ *m/z* 266.2252, Calcd. for $C_{17}H_{30}O_2$ 266.2245.

*(5E,7E)-5,7-Dodecadien-1-ol (***17***).* The THP protective group of **16** was removed in the usual way to give **17**, which was purified by a silica gel column impregnated with 20% $AgNO_3$. IR ν_{max} cm^{-1}: 3300 (br, s), 3050 (m), 2980 (sh), 2960 (s), 2890 (s), 1630 (w), 1470 (sh), 1460 (m), 1440 (sh), 1380 (w), 1060 (m), 1040 (sh), 980 (s); NMR δ: 0.9 (3H, distorted t, $J=6$ Hz), 1.1 ~ 1.8 (8H, m), 1.9 ~ 2.3 (4H, m), 3.5 (2H, t, $J=6$ Hz), 3.7 (1H, s), 5.2 ~ 6.2 (4H, m); GC-high MS: M^+ *m/z* 182.1675, Calcd. for $C_{12}H_{22}O$ 182.1670.

*(5E,8E)-5,8-Dodecadien-1-ol (***22***).* To a solution of the zirconocene hydride (50 mmol, 12.9 g) in dry benzene (50 ml), **2** (50 mmol, 9.1 g) was added at room temperature under dry nitrogen. After stirring for 4 hr, benzene was replaced to dry THF in the same manner as the synthesis of **16**. The THF solution was added with **19** (50 mmol, 8.2 g) and $Pd(Ph_3P)_4$ (1.5 g) and then stirred for 15 hr at room temperature under dry nitrogen. The same work up to the synthesis of **16** gave 7.2 g of (5*E*,8*E*)-5,8-dodecadien-1-ol THP ether (**21**) (54% yield). The usual acidic methanol treatment of **21** afforded the homoconjugated dienol (**22**); IR ν_{max} cm^{-1}: 3300 (br. s), 3050 (m), 2980 (sh), 2960 (s), 1650 (w), 1470 (sh), 1460 (m), 1440 (sh), 1380 (w), 1060 (m), 1040 (sh), 960 (s), 910 (m); NMR δ: 0.9 (3H, distorted t, $J=6$ Hz), 1.1 ~ 1.8 (6H, m), 1.8 ~ 2.3 (4H, m), 2.6 (2H, m), 2.8 (1H, s), 3.5 (2H, t, $J=6$ Hz), 5.3 (4H, m); GC-high NS: M^+ *m/z* 182.1671, Calcd. for $C_{12}H_{22}O$ 182.1670.

*(5Z,9Z)-5,9-Dodecadien-1-ol (***26***).* To a solution of **2** (30 mmol, 5.5 g) in dry THF (50 ml) and HMPA (10 ml), *n*-butyllithium (1.8 M *n*-hexane solution, 17 ml) was added slowly with effective stirring at −78°C under nitrogen. After additive, the reaction mixture was sitirred for 30 min at 0°C, and then added with (*Z*)-1-bromo-3-hexene (**24**) (30 mmol, 4.9 g) at the same temperature. This mixture was stirred for 15 hr at room temperature under nitrogen and then poured into ice-water (200 ml). The usual work up gave **25** (5.2 g, 66% yield) which was affected by hydrolysis followed by hydrogenation over the Lindlar catalyst to afford crude **26**. The chromatographic purification gave pure **26** (3.3 g, 60% yield from 2); IR ν_{max} cm^{-1}: 3300 (br. s), 3050 (s), 2980 (sh), 2890 (s), 1660 (w), 1460 (m), 1440 (m), 1380 (w), 1070 (s), 1040 (sh), 720 (m); NMR δ: 0.9 (3H, distorted t, $J=7$ Hz), 1.2 ~ 1.7 (4H, m), 1.8 ~ 2.3 (8H, m), 3.0 (1H, s), 3.5 (2H, t, $J=6$ Hz), 5.3 (4H, t, $J=4$ Hz); GC-high MS: M^+ *m/z* 182.1675, Calcd. for $C_{12}H_{22}O$ 182.1670.

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