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INSECT PHEROMONES AND THEIR ANALOGUES XLVIII. A CONVENIENT SYNTHESIS OF THE 10E,12Z- AND 10E,12E- ISOMERS OF HEXADECADIEN-1-OL AND OF HEXADECA-10E,12Z-DIENAL — COMPONENTS OF THE SEX PHEROMONE OF THE SILKWORM MOTH

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The 10E,12Z- and 10E,12E- isomers of hexadecadien-1-ol and of hexadeca-10E,12Z-dienal — components of the sex pheromone of the silkworm moth Bombyx mori *— have been synthesized from the readily available octa-2E,7-dien-1-ol.*

The synthesis of bombykol - a component important in the practical respect of the pheromone of the silkworm moth *Bombyx mori*, which includes hexadeca-10E,12Z- and -10E,12E-dienols (I and II, respectively) and hexadeca-10E,12Z-dienal (III) [1] — has been the subject of considerable attention [2-11]. However, the very convenient, as it has proved, and readily available [12] octa-2E,7-dien-1-ol (IV) has not hitherto been used as the starting compound. The presence in the dienol (IV) of an allylic alcohol group and a terminal vinyl group has predetermined the tactics of the synthesis of the desired compounds. In the construction of the conjugated dienic system we made use of the Wittig reaction with the aldehyde (V), smoothly obtained by the oxidation of the alcohol (IV). The olefination of the aldehyde (V) with n-butylidenetriphenylphosphorane gave dodeca-1,6E,8Z-triene (VI) containing not less than 96% of the main stereoisomer (according to capillary GLC). The hydroboration of triene (VI) took place selectively at the terminal double bond and (after the oxidation of the organoboron intermediate) led to the (E,Z)-dienic alcohol (VII), which was then converted into the key synthon 1-iodododeca-6E,8Z-diene (VIII) containing 85% of the main stereoisomer. The synthesis of the dienic iodide (VIII) from the alcohol (IV) via the intermediate iodohydrin (IX) and the iodoaldehyde (X) enabled it to be obtained with a higher stereoselectivity (about 95%). The subsequent growth of the hydrocarbon chain of the iodide (VIII) was achieved by a cross-coupling reaction with 1-(tetrahydropyran-2-yloxy)butylmagnesium bromide catalyzed by CuBr. However, in contrast to [3], in this process practically complete isomerization of the (E,Z)- to an (E,E)-conjugated dienic system took place, as a result of which the rection product proved to be the dienol (II). The overall yield of pheromone (II), calculated on the initial dienol (IV), was 14%. It is interesting to note that in the ^{13}C NMR spectrum of the reaction product after its chromatography on a column of SiO_2, together with the signals corresponding to the (E,E)-dienol (II) there were signals corresponding to the carbon skeleton of the (E,Z)- isomer (I), with the exception of the signals of the vinyl and allyl atoms, which were substantially shifted [(δ, ppm): 25.4 (C-9); 84.0 (C-10, C-13); 132.5 (C-11, C-12); 24.5 (C-14)] as compared with the diagnostic signals of compound (I) [(δ, ppm): 32.6 (C-9); 134.6 (C-10); 125.9 (C-11); 128.4 (C-12); 130.5 (C-13); 27.7 (C-14). The fusion of the signals of the vinyl C atoms and the observed shift of the signals were apparently caused by the formation of a cuprate π-complex of the (E,Z)-dienol (I), a confirmation of which is the nature of the shift, which was similar to that described for a π-complex of butadiene with zirconium [13]. The complex detected gradually decomposed with the formation, as the sole product, of the (E,E)-isomeric dienol (II). This process was accelerated on heating, and the ^{13}C NMR spectrum contained signals corresponding exclusively to the (E,E)-dienone (II).

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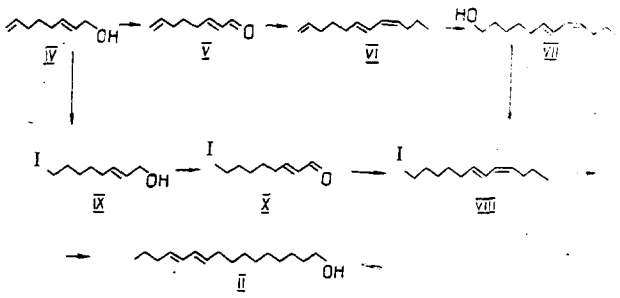
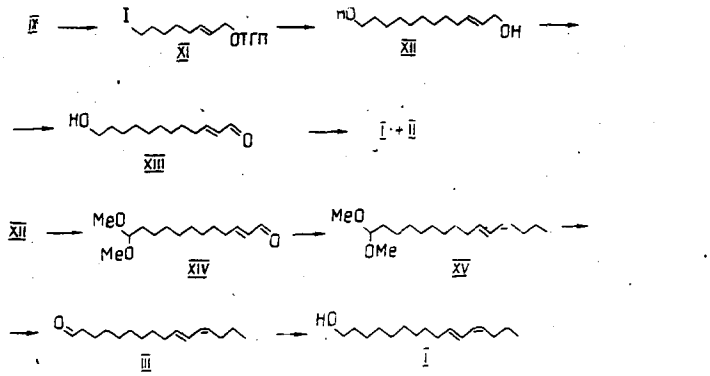


To obtain the (E,Z)-dienol (I) we changed the sequence of transformations of the iodohydrin. After its conversion into the tetrahydropyran-2-yl (THPL) ether (XI), the growth of the carbon chain was brought about by its coupling with the Grignard reagent generated from the THPL derivative of 4-bromobutan-1-ol. The diol (XII) with chemically nonequivalent hydroxy groups obtained after acid hydrolysis was converted with the aid of active MnO_2 into the hydroxyaldehyde (XIII). However, its olefination led to a mixture of the (E,Z)- and (E,E)-dienols (I and II). The diol (XII) was therefore oxidized with pyridinium chlorochromate to the corresponding dialdehyde, in which it was possible by treatment with methanol in the presence of NH_4Cl to protect one of the carbonyl groups selectively and to obtain 12,12-dimethoxydodec-2E-enal (XIV). The Wittig olefination of the latter gave the (E,Z)-dienone acetal (XV) with high stereoselectivity (not less than 98%). After the completing operations (acid hydrolysis and hydride reduction), the (E,Z)-dienic aldehyde (III) and the (E,Z)-dienic alcohol (I) were obtained successively, their overall yields being 4.1 and 3.3%, respectively, calculated on the initial dienone (IV).



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film), and the PMR spectra for compounds (V) and (VI) were recorded on a Tesla BS-467 instrument (working frequency 60 MHz), those for compounds (III), (VII-X), and (XII) on a Tesla BS-567 instrument (100 MHz), and those for compounds (I), (II), and (XV) on a Bruker AM-300 instrument (working frequency 300 MHz). The ^{13}C NMR spectra for compounds (VI-IX) were recorded on a JEOL FX-90 Q instrument (working frequency 75.47 MHz) with broad-band and off-resonance suppression of proton effects, the solvents being $CDCl_3$ and acetone-d_6, and the internal standard TMS. GLC analysis was conducted on a Chrom-5 instrument [with the stationary phase silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm), working temperature 50-300°C] or a Shimadzu instrument (for compounds (I-III, VI-VIII, and XV) (stationary phase PEG-20M, glass capillary column 0.2 mm × 20 m, working temperature 50-180°C, carrier gas helium). The elementary analyses of the compounds synthesized corresponded to the calculated figures.

Octa-2E,7-dienal (V). With stirring (20°C, Ar), 8.6 g ($68.3 \cdot 10^{-3}$ mole) of the dienol (IV) in 20 ml of CH_2H_2 was added in one portion to a suspension of 18.0 g ($83.5 \cdot 10^{-3}$ mole) of pyridinium chlorochromate in 100 ml of abs. CH_2Cl_2; the mixture was stirred for 1.5 h, and 120 ml of diethyl ether was added. The solution was decanted off, the residue was washed with diethyl ether (3 × 70 ml), the combined ethereal solutions were filtered through a layer of SiO_2 (10 cm, 50 g), the filtrate was evaporated, and the residue was chromatographed (SiO_2, pentane–diethyl ether (10:1)), to give 6.76 g (80%) of the alde-

hyde (V) n_D^{23} 1.4568 [14, 15]. IR spectrum (ν, cm^{-1}): 920, 980, 1000, 1645, 3085 (E-CH=CH, $CH=CH_2$), 1700, 2740 (CHO). PMR spectrum (60 MHz, CCl_4): 1.4-1.8 (m, 2H, H-5), 1.85-2.6 (m, 4H, H-4, H-6), 4.75-5.2 (m, 2H, H-8), 5.4-5.75 (m, 1H, H-7), 6.0 (dd, 1H, J_1 = 16 Hz, J_2 = 8 Hz, H-2), 6.8 (dt, 1H, J_1 = 16 Hz, J_2 = 7 Hz, H-3), 9.43 (d, 1H, J = 8 Hz).

Dodeca-1,6E,8Z-triene (VI). A solution of 0.92 g ($5.03 \cdot 10^{-3}$ mole) of sodium bis(trimethylsilyl)amide in 15 ml of abs. THF was treated with 2.11 g ($5.03 \cdot 10^{-3}$ mole) of n-butyltriphenylphosphonium bromide and the mixture was stirred (25°C, 30 min; boiling, 1 h), and cooled to −78°C; then a solution of 0.62 g ($5.0 \cdot 10^{-3}$ mole) of the aldehyde (V) in 5 ml of abs. THF was added dropwise, and the resulting reaction mixture was stirred at −78°C for 1 h and was then warmed to room temperature, kept for 12 h, and evaporated. The residue was treated with 50 ml of a 1:3 mixture of diethyl ether and hexane, the resulting solution was filtered, and the filtrate was washed successively with 40% $NaHSO_3$ solution and saturated solutions of $NaHCO_3$ and NaCl, and it was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, pentane), to give 0.57 g (68%) of the triene (VI) containing, according to capillary GLC, not less than 96% of the main substance., n_D^{23} 1.4768. IR spectrum (ν, cm^{-1}): 920, 955, 990, 1645, 3030, 3090 ($CH=CH_2$, E,Z-CH=CH−CH=CH). PMR spectrum (60 MHz, CCl_4): 0.88 (t, 3H, J = 6.5 Hz, H-12), 1.1-1.7 (m, 4H, H-4, H-11), 1.8-2.3 (m, 6H, H-3, H-5, H-10), 4.7-6.5 (m, 7H, H-1, H-2, H-6, H-7, H-8, H-9). C_{13} NMR spectrum (22.5 MHz, $CDCl_3$): 114.56 (t, C-1), 138.66 (d, C-2), 33.33 (t, C-3), 28.69 (t, C-4), 32.29 (t, C-5), 134.02 (d, C-6), 126.09 (d, C-7), 128.82 (d, C-8), 129.94 (d, C-9), 29.82 (t, C-10), 22.97 (t, C-11), 13.78 (q, C-12).

Dodeca-6E,8Z-dien-1-one. A solution of 0.48 g ($2.9 \cdot 10^{-3}$ mole) of the triene (VI) in 2 ml of abs. THF was added over 10 min to a suspension of 0.5 g ($4.1 \cdot 10^{-3}$ mole) of BBN in 5 ml of abs. THF at 10°C, and after 2 h the mixture was treated at 0°C with a solution of 0.83 g of AcONa in 2 ml of water and then, over 15 min, with 3 ml of 30% H_2O_2. The reaction mixture wa stirred at 25°C for 2 h and was diluted with 100 ml of diethyl ether and washed successively with saturated NaCl solution, 0.1 N $Na_2S_2O_3$, and saturated NaCl again, and was dried with Na_2SO_4 and evaporated. The residue was distilled, giving 0.38 g (72%) of the alcohol (VII) containing, according to capillary GLC, not less than 93% of the main substance, bp 108-110°C (0.5 mm). IR spectrum (ν, cm^{-1}): 995, 990, 1650, 3025 (E,Z-CH=CH−CH=CH), 1060 (C−O), 3200-3600 (OH). PMR spectrum (100 MHz acetone-d_6): 0.90 (t, 3H, J = 7.5 Hz, H-12), 1.15-1.7 (m, 8H, H-2, H-3, H-4, H-11), 1.85-2.2 (m, 4H, H-5, H-10), 2.92 (s, 1H, OH), 3.51 (t, 2H, J = 5.4 Hz, H-1), 5.02-6.42 (m, 4H, H-6, H-7, H-8, H-9). ^{13}C NMR spectrum (22.5 MHz acetone-d_6): 62.33 (t, C-1), 33.46 (t, C-2), 26.22 (t, C-3), 30.21 (t, C-4), 33.55 (t, C-5), 135.01 (d, C-6), 126.61 (d, C-7), 129.86 (d, C-8), 129.99 (d, C-9), 30.04 (t, C-10), 23.49 (t, C-11), 13.96 (q, C-12).

8-Iodooct-2E-en-1-ol (IX). To a solution of $HAlCl_2$ (0.6 mole) in 500 ml of abs. diethyl ether [obtained from 5.7 g (0.15n mole) of $LiAlH_4$ and 60 g (0.45 mole of $AlCl_3$ according to [16]] were added successively (0°C, Ar) 1.3 g ($10 \cdot 10^{-3}$ mole) of phenylboronic acid and a solution of 25.0 g (0.2 mole) of the dienol (IV) in 100 ml of abs. diethyl ether; the mixture was stirred at 25°C for 2 h and was then cooled to 0°C, and 11.6 g (0.2 mole) of abs. acetone, and 7.5 g (0.3 mole) of iodine were added successively, the reaction mxture was stirred at 25°C for 4 h and was then cooled to 0°C; 200 ml of water was added, and it was extracted with diethyl ether (3 × 500 ml), and the extract was dried with Na_2SO_4 and evaporated. After chromatography (SiO_2, pentane−diethyl ether (1:)), 25.0 g (50% of the iodohydrin (IX) was obtained. n_D^{24} 1.5144. IR spectrum (ν, cm^{-1}): 980, 1675 (E-CH=CH), 3320 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.25-1.6 (m, 4H, H-5, H-6), 1.7-1.94 (m, 2H, H-7), 1.94-2.24 (m, 2H, H-4), 2.96 (br.s, 1H, OH), 3.18 (t, 2H, J = 7 Hz, H-8), 4.05 (d, 2H, J = 3.3 Hz, H-1), 5.58-5.8 (m, 2H, H-2, J-3). ^{13}C NMR spectrum (22.5 MHz, $CDCl_3$): 62.99 (t, C-1), 131.53 (d, C-1), 131.53 (d, C-2), 129.25 (d, C-3), 33.23 (t, C-4), 29.83 (t, C-5), 27.94 (t, C-6), 31.79 (t, C-7), 6.98 (t, C-8).

8-Iodooct-2E-enal (X). With stirring (20°C, argon), 3.0 g ($11.8 \cdot 10^{-3}$ mole) of the iodohydrin (IX) in 5 ml of CH_2Cl_2 was added in one portion to a suspension of 4.24 g ($19.7 \cdot 10^{-3}$ mole) of pyridinium chlorochromate in 50 ml of abs. CH_2Cl_2, and the mixture was stirred for 0.5 h and was worked up as described for compound (V). This gave 2.7 g (91%) of the aldehyde (X), n_D^{25} 1.5052. IR spectrum (ν, cm^{-1}): 990, 1645 (E-CH=CH), 1690, 2750 (CHO). PMR spectrum (100 MHz, $CDCl_3$): 1.35-1.7 (m, 4H, H-5, H-6), 1.75-1.97 (m, 2H, H-7), 2.25-2.5 (m, 2H, H-4), 3.20 (t, 2H, J = 6.8 Hz, H-8), 6.12 (dd, 1H, J_1 = 15.5 Hz, J_2 = 7.7 Hz, H-2), 6.86 (dt, 1H, J_1 = 15.5 Hz, J_2 = 6.6 Hz, H-3), 9.50 (d, 1H, J= 7.7 Hz, H-1).

1-Iodododeca-6E,8Z-diene (VIII). a. A solution of 1.91 g ($10.4 \cdot 10^{-3}$ mole) of sodium bis(trimethylsilyl)amide in 9 ml of abs. THF (Ar, 20°C) was treated with 4.15 g ($10.4 \cdot 10^{-3}$ mole) of n-butyltriphenylphosphonium bromide, and the mixture was stirred (25°C, 30 min; boiling, 2 h) and was then cooled to −78°C, after which a solution of 1.51 g ($6.0 \cdot 10^{-3}$ mole) of the aldehyde (X) in 5 ml of abs. THF was added, and the mixture was worked up as described for the triene (VI). This gave 1.14 g (65%) of the iodide (VIII) containing, according to capillary GLC, not less than 95% of the main substance., n_D^{25} 1.4869. IR spectrum: (ν, cm^{-1}): 945, 980, 1650, 3025 (E,Z-CH=CH−CH=)> PMR spectrum (100 MHz, $CDCl_3$); 0.92

(t, 3H, J = 6.8 Hz, H-12), 1.2-1.6 (m, 6H, H-3, H-4, H-11), 1.7-1.95 (m, 2H, H-2), 1.95-2.3 (m, 4H, H-5, H-10), 3.19 (t, 2H, J = 7.1 Hz, H-1), 5.2-6.5 (m, 4H, H-6, H-7, H-8, H-9). ^{13}C spectrum (22.5 MHz, CDl_3): 6.79 (t, C-1), 33.36 (t, C-2), 28.26 (t, C-3), 30.03 (t, C-4), 32.57 (t, C-5), 133.69 (d, C-6), 125.99 (t, C-7), 128.66 (d, C-8), 129.90 (d, C-9), 29.70 (t, C-10), 22.85 (t, C-11), 13.77 (q, C-12).

b. A solution of 0.37 g ($2.03 \cdot 10^{-3}$ mole of the alcohol (VII) in 0.85 ml of dry pyridine was treated at 0°C with 0.546 g ($2.87 \cdot 10^{-3}$ mole) of TsCl in portions, and then the mixture was kept at the same temeprature for 12 h and was diluted with 30 ml of diethyl ether, washed sucessively with 10% HCl and saturated aqueous solutions of $NaHCO_3$ and NaCl, dried, and evaporated. The residue (0.65 g) was dissolved in 4.4 ml of abs. acetone, 0.505 g ($3.37 \cdot 10^{-3}$ mole of NaI was added, the mixture was boiled for 15 h and was then kept in the dark at 20°C for 24 h, and was evaporated; the new residue was diluted with 3 ml of water cooled to 0°C and was extracted with diethyl ether (3 × 10 ml), and the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, pentane), giving 0.45 g (76%) of the iodide (VIII), containing, according to the results of capillary chromatography, about 85% of the main stereoisomer, its IR, PMR, and ^{13}C NMR spectra being identical with those of the compound obtained in experiment **a**.

Hexadeca-10E,12E-dien-1-ol (II). A solution of 0.26 g ($0.89 \cdot 10^{-3}$ mole) of the iodide (VIII) in 4 ml of abs. THF (Ar) was treated with 0.05 g of CuBr, the mixture was cooled to −15°C, and a solution of the Grignard reagent prepared from 1.0 g ($4.2 \cdot 10^{-3}$ mole) of 1-bromo-4-(tetrahydropyran-2-yloxy)butane and 0.1 g ($4.2 \cdot 10^{-3}$ gram-atom) of magnesium in 30 ml of abs. THF was added dropwise. The reaction mixture was warmed to 10°C, stirred for 0.5 h, cooled to −10°C, and treated with a saturated solution of NH_4Cl, after which it was extracted with diethyl ether (3 × 50 ml), and the extract was washed with saturated NaCl solution and evaporated. A mixture of the residue with 5 ml ot MeOH and 0.005 g of TsOH was stirred at 20°C for 24 h and was then evaporated; the residue was dissolved in 50 ml of diethyl ether, and the solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl, and was dried with Na_2SO_4 and evaporated. The residue was chromatographed (SiO_2, pentane−diethyl ether (3:1)), and 0.2 g of product was obtained [^{13}C PMR spectrum (75.47 MHz, $CDCl_3$): 63.0 (t, C-1), 34.9 (t, C-2), 25.7 (t, C-3), 29.4 (t, C-4 tp C-7), 32.8 (t, C-8), 25.4 (t, C-9), 84.0 (d, C-10), 132.5 (d, C-11, C-12), 84.0 (d, C-13), 24.5 (t, C-14), 22.6 (t, C-15), 14.0 (q, C-16)]. After the product had been distilled in vacuum, 0.10 g (48%) of the (E,E)-dienol (II) was obtained, with bp 110-112°C (0.01 mm), containing 98% of the main stereoisomer according to capillary GLC. Its IR and PMR spectra were identical with those given for the (E,E)-dienol (II) [2]. ^{13}C PMR spectrum (75.47 MHz, $CDCl_3$): 63.1 (t, C-1), 34.8 (t, C-2), 25.9 (t, C-3), 29.6 (t, C-4), 29.5 (t, C-5 to C-7), 29.2 (t, C-8), 32.6 (t, C-9), 132.2 (t, C-10), 130.5 (d, C-11), 130.6 (d, C-12), 132.4 (d, C-13), 32.8 (t, C-14), 22.7 (t, C-15), 13.7 (q, C-16).

8-Iodo-1-(tetrahydropyran-2-yloxy)oct-2-ene (XI). At 10-15°C, 5.1 ml (4.6 g, $56.7 \cdot 10^{-3}$ mole of 2,3-dihydro-4H-pyran was added to a solution of 4.2 g ($16.5 \cdot 10^{-3}$ mole) of the iodohydrin (IX) and 0.1 g of TsOH in 51 ml of abs. diethyl ether, and the mixture was warmed to room temperature and stirred for 20 h, after which 100 ml of diethyl ether was added and it was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, hexane−diethyl ether (4:1)), giving 4.6 g (82.4%) of compound (XI). IR spectrum (ν, cm^{-1}): 980 and 1660 (E-CH=CH), 1040, 1080, 1110, 1140 and 1180 (C−O).

Dodec-2E-ene-1,12-diol (XII). A solution of 4.4 g ($1.30 \cdot 10^{-2}$ mole of the iodide (XI) in 65 ml of abs. THF was treated with 0.15 g of CuBr (20°C, Ar) and, after the mixture had been cooled to 0°C, a solution of the Grignard reagent prepared from 6.0 g ($25.3 \cdot 10^{-3}$ mole) of 1-bromo-4-(tetrahydropyran-2-uloxy)butane and 0.64 g ($26.0 \cdot 10^{-3}$) g-atom of magnesium in 65 ml of abs. THF was added; the resulting mixture was stirred at 10°C for 3 h, and then 50 ml of a saturated solution of NH_4Cl was added and, after another hour's stirring, the whole was exracted with diethyl ether (3 × 250 ml). The extract was evaporated, the residue was dissolved in 100 ml of MeOH containing 0.05 g of TsOH, and the solution was stirred for 24 h and was evaporated in vacuum . The new residue was dissolved in 0.5 liter of diethyl ether and the solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl and was dried and evaporated; the resulting residue was chromatographed (SiO_2, hexane−diethyl ether (1:1)) to give 1.7 g (65%) of the diol (XII), mp 35.0-35.5°C, its IR and PMR spectra being identical with those given in [17].

12-Hydroxydodec-2E-enal (XIII). To 0.7 g ($3.5 \cdot 10^{-3}$ mole) of the diol (XII) in 25 ml of abs. CCl_4 was added 5 g of freshly prepared finely ground MnO_2. The resulting suspension was stirred for 30 min and was then filtered, and the filtrate was evaporated to give 0.46 g (66.6%) of the hydroxyaldehyde (XII), the IR and PMR spectra of which were identical with those given in [17].

Mixture of Hexadeca-10E,12Z- and -10E,12E-dien-1-ols (I and II). A solution of 0.63 g ($1.6 \cdot 10^{-3}$ mole) of n-butyltriphenylphosphonium bromide in 6 ml of abs. THF was cooled to −30°C, and 0.17 g ($1.5 \cdot 10^{-3}$ mole) of tert-BuOK was added

(Ar); after 45 min stirring, a solution of 0.19 g ($1.0 \cdot 10^{-3}$ mole) of the hydroxyaldehyde (XIII) in 5 ml of abs. THF was added and the mixture was stirred at −20°C for 3.5 h, and it was then heated to 20°C and, after 15 h, it was diluted with diethyl ether (30 ml) and was filtered through a thin layer of SiO_2 (2 g, 3 cm). The filtrate was evaporated, to give 0.11 g (48%) of a product consisting, according to capillary chromatography, of a mixture (3:2) of (I) and (II).

1,1-Dimethoxyhexadeca-10E,12Z-diene (XV). With stirring (20°C, Ar), a solution of 0.4 g ($2.0 \cdot 10^{-3}$ mole) of the diol (XII) in 3 ml of CH_2Cl_2 was added to a suspension of 1.72 g ($8.0 \cdot 10^{-3}$ mole) of pyridinium chlorochromate in 12 ml of dry CH_2Cl_2, and the mixture was stirred for 1.5 h, after which 15 ml of diethyl ether was added, the solution was decanted off, the residue was was washed with diethyl ether (3 × 20 ml), and the combined ethereal solutions were fitlered through a layer of SiO_2 (8 g, 5 cm) and evaporated. The residue was dissolved in 4 ml of absolute methanol, and 0.35 g of dry NH_4Cl was added to the solution and it was stirred for 24 h and was then diluted with 100 ml of diethyl ether and was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated.

The residue was chromatographed (SiO_2, hexane−diethyl ether (4:1)), giving 0.19 g (39%) of the oxoacetal (XIV) [IR spectra (ν, cm^{-1}): 980, 1650 (CH=CH), 1050, 1090, 1140, 1190 (C−O), 1690, 2740 (C=O)], which was dissolved in 1.2 ml of abs. THF. A solution of 0.26 g ($1.41 \cdot 10^{-3}$ mole) of sodium bis(trimethylsilyl)amide in 2 ml of abs. THF (Ar, 20°C) was treated with 0.67 g ($1.41 \cdot 10^{-3}$ mole) of n-butyltriphenylphosphonium bromide, the mixture was stirred (25°C, 30 min; boiling, 2 h) and was cooled to −78°C and the solution of the oxoacetate (XIV) was added dropwise; then the whole was worked up as described for the triene (VI). This gave 0.11 g (50%) of the acetal (XV), containing about 98% of the main stereoisomer, according to capillary GLC.

PMR spectrum (300 MHz, $CDCl_3$): 0.92 (t, 3H, J = 7.6 Hz, C-16), 1.20-1.70 (m, 16H, H-2-H-8, H-15), 2.00-2.20 (m, 4H, C-9, C-14), 3.30 (s, 6H, CH_3O), 4.34 (t, 1H, J = 6.7 Hz, H-1), 5.30 (dt, 1H, J = 10.9 Hz, J = 7.6 Hz, H-13), 5.65 (dt, 1H, J = 15.0 Hz, J = 6.9 Hz, H-10), 5.94 (dd, 1H, J = 10.9 Hz, J = 10.9 Hz, H-12), 6.28 (dd, 1H, J = 15.0 Hz, J = 10.9 Hz, H-11). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$): 10.47 (d, C-1), 32.90 (t, C-2), 29.30 (t, C-8), 32.30 (t, C-9), 134.60 (d, C-10), 123.80 (d, C-11), 128.70 (d, C-12), 128.80 (d, C-13), 28.20 (t, C-14), 22.90 (t, C-15), 13.80 (q, C-16), 52.60 (q, CH_3O)

Hexadeca-10E,12Z-dienal (III). With stirring, 0.2 ml of 15% H_2SO_4 was added to a solution of 80 mg ($0.28 \cdot 10^{-3}$ mole) of the acetal (XV) in 1 ml of MeOH (20°C, Ar), and then the reaction mixture was stirred for another 5 h and was left overnight. It was evaporated, and the residue was diluted with 5 ml of water and extracted with diethyl ether (3 × 50 ml). The ethereal extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, and was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, pentane−diethyl ether (9:1)) and 54 mg (80%) of the aldehyde (III) was obtained, its IR and PMR spectra being identical with those given for the (E,Z)-dienal (III) [1].

Hexadeca-10E,12Z-dien-1-ol (I). A solution of 40 mg ($0.17 \cdot 10^{-3}$ mole) of the aldehyde (III) in 0.5 ml of abs. diethyl ether was treated (Ar, 0°C) with 11 mg of $LiAlH_4$, and the mixture was stirred for 1 h, after which 0.2 ml of H_2SO_4 was added dropwise and stirring was continued for 1 h. The mixture was extracted with diethyl ether, and the ethereal extract was dried with Na_2SO_4 and evaporated, to give 33 mg (81%) of the alcohol (I), containing not less than 93% of the main isomer according to capillary GLC. Its IR and PMR spectra wee identical with those given in the literature [2] for the (E,Z)-dienol [2]. ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$): 63.1 (t, C-1), 34.8 (t, C-2), 25.9 (t, C-3), 29.6 (t, C-4), 29.5 (t, C-5 to C-7), 29.2 (t, C-8), 32.6 (t, C-9), 134.6 (d, C-10), 125.9 (d, C-11), 128.4 (d, C-12), 130.5 (d, C-13), 27.7 (t, C-14), 22.9 (t, C-15), 136.7 (q, C-16).

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