Chemistry of Natural Compounds and Bioorganic Chemistry

Stereospecific syntheses of sex pheromones of the californian red scale and white peach scale (Homoptera: *Diaspididae*) based on 1,4-*cis*-hydrogenation of dienes

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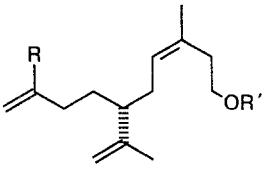
Stereospecific syntheses of (±)-3-methyl-6-isopropenyl-3(*Z*),9-decadien-1-yl acetate and (±)-3,9-dimethyl-6-isopropenyl-3(*Z*),9-decadien-1-yl propionate (the Racemoc forms of the pheromones of the scales *Aonidiella aurantii* and *Pseudaulascaspis pentagona*) with a geometrical purity of the (*Z*)-trisubstituted double bond not lower than 99 % were performed. The key step in both syntheses was the 1,4-*cis*-hydrogenation of the corresponding ethyl 3-methyl-6-(1,1-ethylenedioxyethyl)-2,4,9-decatrienoates catalyzed with chromium carbonyl complexes. These 2,4-dienes were obtained in five conventional steps including the alkylation of ethyl acetoacetate by the appropriate 1-bromo-3-butenes and the Horner—Emmons olefination of the corresponding α-branched aldehydes.

Key words: (±)-3-methyl-6-isopropenyl-3(*Z*),9-decadien-1-yl acetate, (±)-3,9-dimethyl-6-isopropenyl-3(*Z*),9-decadien-1-yl propionate, synthesis; aldehydoketals; ethyl 2,4-alkadienoates, 1,4-*cis*-hydrogenation; the Horner—Emmons olefination; ethyl acetoacetate, alkylation; arene chromium tricarbonyl complexes.

One of the two components of the sex pheromone of Californian red scale *Aonidiella aurantii* (**1a**) and the sex pheromone of white peach scale *Pseudaulascaspis pentagona* (**1b**) are the esters of two homologous alcohols (**2a, b**) having the (*Z*)-configuration of the trisubstituted double bond.[1,2] Therefore the stereocontrolled formation of the (*Z*)-configurated Δ^3-bond in the alcohol moiety is an important problem in the syntheses of **1a** and **1b**.



1a: R = H, R′ = Ac
1b: R = Me, R′ = COE
2a: R = R′ = H
2b: R = Me, R′ = H

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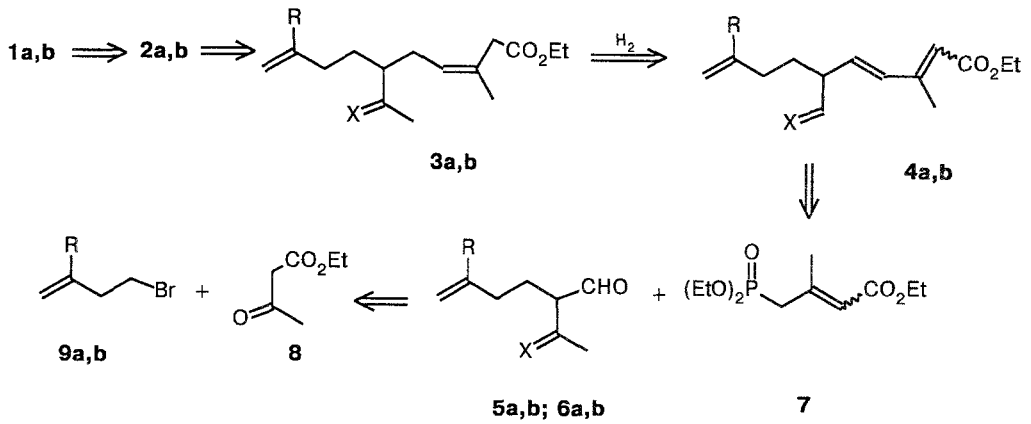
Scheme 1



R = H (**a**), Me (**b**); L = arene or $(CO)_3$

3,4,6: X = OCH_2CH_2O

5: X = CH_2

Previously, the following ways of solving this problem were elaborated: stereocontrolled [2,3]-sigmatropic rearrangement *via* the substituted allyloxy methyl carbanions,[3,4] use of "ready-made" olefinic building blocks with the required (*Z*)-configuration of the double bond,[5,6] various modifications of the Wittig reaction,[7–9] transformation of the aldehyde function of the (*E*)-2,3-disubstituted acroleins into the methyl group,[10] and complexing of an allylic carbanion with cerium(IV) and subsequent interaction of the resulting (*Z*)-configurated species with formaldehyde.[11] Nearly all of these protocols are quite strenuous and/or involve the use of rather expensive chemicals.

Here we describe a strategically new approach to the pheromones **1a** and **1b** employing the stereospecific 1,4-*cis*-hydrogenation of conjugated dienes over chromium carbonyl complexes (*cf.* Ref. 12) as the key step. On many occasions the same strategy proved to be quite rewarding in the synthesis of *Z*-disubstituted olefins when the properly substituted dienic precursors were easily accessible (for review, see Ref. 13). Recently we showed this approach to be very promising for the stereospecific synthesis of trisubstituted olefins with the homoallylic pattern of functionalization.[14,15]

Retrosynthetic analysis of structures **1** and their synthetic equivalents, ethyl 3(*Z*)-alkenoates **3** (Scheme 1), shows that the respective dienic precursors **4** can be obtained by the Horner—Emmons olefination of aldehydes **5** or **6** with the isoprenoidal allylic phosphonate **7**. However, since under the basic conditions of the Horner—Emmons reaction the pH-sensitive β,γ-alkenals **5** (X=CH_2) tend to isomerize into α,β-enals, instead of employing **5** we decided to use the aldehyde ketals **6a,b**. The removal of the ethylene ketal group of the latter at a late stage of the synthesis and subsequent the Wittig methylenation of the demasqued methyl ketone would give the propen-2-yl moiety of the target molecule. Aldehyde ketals **6** were obtained by alkylating ethyl acetoacetate **8** with available homoallylic bromides and the transformation of functional groups.

During the alkylation of keto esters **8** by homoallylic bromides **9a,b** the best yield of the desired product (55 %) was achieved in the case of the classic technique using EtONa in EtOH.* Along with keto esters **10a,b** O-alkylated products were also formed in small amounts, which, however, disappeared in the next step upon introduction of the ketal protective group (Scheme 2). As a result, practically pure "vinyl" homolog **11a** was obtained in a yield of 78 %.

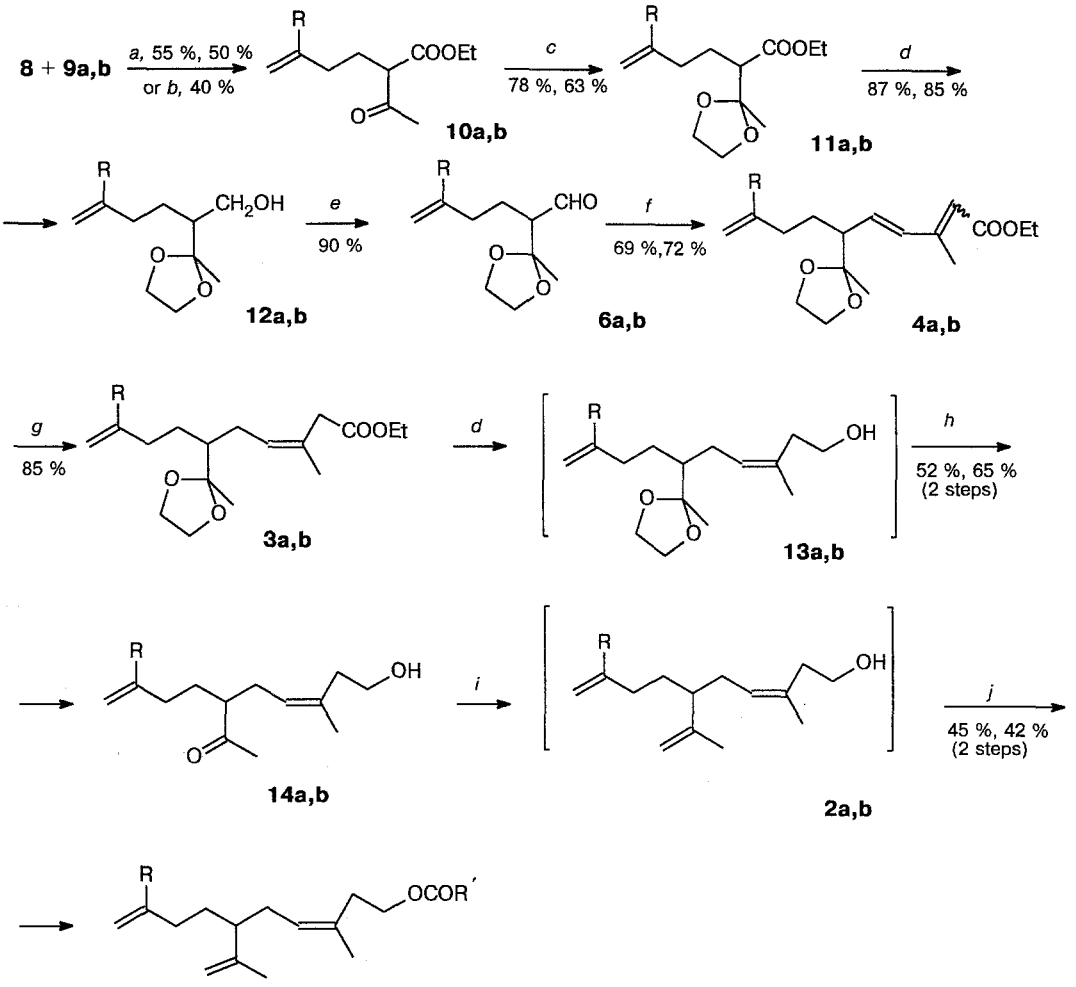
Unfortunately, during the ketalization of the "isopropenyl" homolog **10b** in the presence of TsOH there occurs partial isomerization of the readily protonated isopropenyl group into the isopropylidene group (at the extent of *ca.* 5 %). The corresponding minor isomers accompany all subsequent intermediates in the series **b**, although their portion in the target product somewhat decreases to the end of the synthesis.

The conversion of keto esters **11a,b** into aldehydes **6a,b** was not difficult. Olefination of aldehydes **6a,b** by the Horner—Emmons reaction was carried out according to the earlier developed procedure[16] under conditions of the phase transfer catalysis (KOH/18-C-6/benzene). This led to ethyl dienoates **4a,b** in *ca.* 70 % yield; the ratio of 2(*E*),4(*E*)- and 2(*Z*),4(*E*)-isomers was 65 : 35.

1,4-*cis*-Hydrogenation of dienoates **4a,b** as the key step was performed in acetone with the use of $(PhCO_2Me)Cr(CO)_3$ as the catalyst (120 °C, 80 atm

* The use of K_2CO_3 as the deprotonating reagent in acetone, DMSO, or dioxane in combination with 18-C-6 (*cf.* Ref. 17) gave lower yields of products **10a,b**.

Scheme 2*



R = H (**a**), Me (**b**)

1a: R = H, R'= Me (Σ 4.3 %)

1b: R = H, R' = Et (Σ 4.0 %)

Reagents and conditions: *a*. EtONa/EtOH; *b*. K_2CO_3/dioxane/18-C-6, 70—80 °C; *c*. $HO(CH_2)_2OH$—TsOH/PhH, Δ; *d*. $LiAlH_4/Et_2O$; *e*. PCC/CH_2Cl_2; *f*. **7**, KOH/PhH/18-C-6, 20 °C; *g*. $H_2/(PhCO_2Me)Cr(CO)_3$, Me_2CO, 120 °C, 80 atm, 3.5 h; *h*. H_2O—$Me_2CO/(CO_2H)_2$, Δ; *i*. $Ph_3P{=}CH_2$/THF—DMSO, 20 °C; *j*. $(R^1CO)_2O/Na_2CO_3$, 100 °C, 1 h.

* Yields of isolated products: the first figure refers to compounds of series **a**; the second, to series **b**.

H_2, 3.5 h) (*cf.* Ref. 13,15).* Hydrogenation of both 2(*E*),4(*E*)- and 2(*Z*),4(*E*)-isomers **4** gave the 3(*Z*)-olefin **3** as the sole product, both the conversion of **4** and the geometrical purity of **5** being close to 100 % (a small remainder of the less active 2(*Z*),4(*E*)-isomers was detected in the hydrogenizate by GLC).

Conversion of the (*Z*)-configurated ketal esters **3** into the hydroxy ketals **13** and further into ketols **14** was accomplished in one synthetic operation. Transformation of the methyl ketone moiety of compounds **14** into the isopropenyl group was performed by the Wittig reaction with $Ph_3P{=}CH_2$; that led to alcohols **2** at a conversion of about 60 %. Acylation of crude alcohols **2a** and **2b** by the corresponding anhydrides followed by the separation from the ketonic impurities (the products of acylation of ketols **14**) afforded the target racemic pheromones **1a** and **1b**.

* An attempt to hydrogenate **4** using the more accessible $Cr(CO)_6$ at an elevated temperature of 180 °C resulted in a complex mixture of products, which hardly contained any of the desired diolefin **3**. Judging from the absence of signals of the vinyl (correspondingly isopropenyl) group and the high integral intensity of aliphatic protons (δ 1.2 ppm) in the ^1H NMR spectra, hydrogenation at higher temperatures competes1 with the Diels—Alder reaction, which involves the dienic system and the distant Δ^9-bond; that could lead to the formation of up to eight regio- and stereoisomers.

The total yield of these products from the limiting starting compounds **9a** and **9b** over ten synthetic steps was 4.3 % for **1a** and 4.0 % for **1b**. Obviously, this yield might be optimized by improving the alkylation of ethyl acetoacetate and methylation of the ketols **14** by the Wittig reaction as well as by recirculating the recovered compound **14**.

In comparison with the known procedures of similar synthetic efficiency,[3–11] the proposed scheme does not involve labor-consuming operations and employs more expensive chemicals.

Experimental

NMR spectra were taken in $CDCl_3$ using a Bruker AC-200 spectrometer operating at 200 MHz for ^1H and 50 MHz for ^{13}C. GLC analyses were performed on an LKhM-8MD chromatograph (column 2000×3 mm, XE-60 on Chromaton N-AW-DMCS, injector temperature 225 °C, oven temperature 100—150 °C, nitrogen flow 40 mL min^{-1}),(Methyl benzoate)tricarbonylchromium was obtained by refluxing the excess methyl benzoate with $Cr(CO)_6$ in the Bu_2O—THF system.[18] Homoallylic bromides **9a** and **9b** were prepared according to the known procedures.[19,20] Chromatographic separation was carried out on silica gel L 100/160 (Chemapol).

Ethyl alkenylacetoacetates (10a,b). Method A. Sodium metal (1.68 g, 73 mmol) was dissolved in absolute ethanol (37 mL), the solution was cooled to room temperature, and ethyl acetoacetate (10.3 g, 79 mmol) was added dropwise to the solution of NaOEt thus obtained over a period of 10 min. Then with stirring and reflux homoallylic bromide **9a** or **9b** (77 mmol) was added over 2 h, and the reflux was continued for 10 h. Glacial AcOH (~1 mL) was added to neutralize the reaction mixture, and the bulk of the ethanol was removed *in vacuo*. Water (~70 mL) was added to the residue to dissolve the NaBr formed, the mixture was extracted with ether, the combined extracts were dried with $CaCl_2$, the solvents were evaporated, and the residue was distilled *in vacuo*.

Ethyl 2-(3-butene-1-yl)acetoacetate (**10a**), yield 7.8 g (55 %), b. p. 120—125 °C (30 Torr). ^1H NMR, δ: 1.25 (t, 3 H, Me, J = 6.9 Hz); 1.92 (m, 2 H, CH_2); 2.02 (m, 2 H, $=CCH_2$); 2.20 (s, 3 H, COMe); 3.43 (t, 1 H, CH, J = 6.9 Hz); 4.27 (q, 2 H, OCH_2, J = 6.9 Hz); 5.0 (m, 2 H, $=CH_2$); 5.72 (m, 1 H, =CH).

Ethyl 2-(3-methyl-3-buten-1-yl)acetoacetate (**10b**), yield 7.6 g (55 %), b. p. 125—130 °C (25 Torr). ^1H NMR, δ: 1.27 (t, 3 H, Me, J = 6.9 Hz); 1.70 (br. s, 3 H, =CMe); 1.98 (m, 2 H, CH_2); 2.21 (s, 3 H, COMe); 3.39 (m, 1 H, CH); 4.20 (q, 2 H, OCH_2, J = 6.9 Hz); 4.68 and 4.72 (both br. s, 2 H, $=CH_2$).

Method B. A mixture of 1-bromo-3-butene **9a** (17.3 g, 130 mmol), ethyl acetoacetate (21 g, 157 mmol), dioxane (110 mL), K_2CO_3 (45 g), water (6 mL), and 18-crown-6 (0.8 g) was stirred at 70—80 °C for 3 h under GLC control. The mixture was cooled, diluted with water, extracted, and distilled *in vacuo*. This led to 9.4 g (40 %) of the compound **10a** containing about 15 % of the admixture of the O-alkylation product (the side signals in the ^1H NMR, δ: 2.47 m, 3.70 t (OCH_2)).

Ketal esters (11a,b). A mixture of acetoacetic derivatives **10a,b** (45 mmol), ethylene glycol (4 mL), benzene (40 mL), and *p*-toluenesulfonic acid (0.2 g) was refluxed for 2.5—3 h with separation of the liberated water in a Dean—Stark trap (GLC control). The mixture was cooled, dry $Na_2CO_3 \cdot 10H_2O$ (3 g) was added followed by stirring for 10 min, water (50 mL) was added, the organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic materials were dried over $CaCl_2$ with a small amount of K_2CO_3, then the solvents were evaporated, and the residue was distilled *in vacuo*.

Ethyl 2-(1,1-ethylenedioxyethyl)-5-hexenoate (**11a**), yield 8.1 g (78 %), b. p. 95—98 °C (3 Torr). ^1H NMR, δ: 1.30 (t, 3 H, Me, J = 6.9 Hz); 1.43 (s, 3 H, Me); 1.72 and 1.92 (both m, 2 H, H(3)); 2.05 (m, 2 H, H(4)); 2.70 (m, 1 H, H(2)); 3.98 (m, 4 H, $O(CH_2)_2O$); 4.2 (q, 3 H, OCH_2Me, J = 6.9 Hz); 5.02 (m, 2 H, H(6)); 5.8 (m, 1 H, H(5)).

Ethyl 2-(1,1-ethylenedioxyethyl)-5-methyl-5-hexenoate (**11b**), yield 6.8 g (63 %), b. p. 105—115 °C (3 Torr). ^1H NMR, δ: 1.25 (t, 3 H, Me, J = 6.9 Hz); 1.40 (s, 3 H, Me); 1.7 (br. s 3 H, =CMe); 1.72 and 1.88 (both m, 2 H, H(3)); 1.98 (m, (2 H, H(4)); 2.62 (m, 1 H, H(8)); 3.95 (m, 4 H, $O(CH_2)_2O$); 4.18 (q, 3 H, OCH_2Me, J = 6.9 Hz); 4.68 and 4.72 (both br. s, 2 H, $=CH_2$). Fragments of the spectrum of the minor isopropylidenic isomer (δ, ppm): 1.6 and 1.67 (both br. s, $=C(Me_2)$, 5.01 br. s, H(4)).

Hydroxy ketals 12a,b were obtained by the reduction of esters **11a,b** with $LiAlH_4$ in absolute ether according to the standard procedure, yields 87 % and 85 %, respectively.

2-(1,1-Ethylenedioxyethyl)-5-hexene-1-ol (**12a**), yield 87 %, b. p. 93—96 °C (3 Torr). ^1H NMR, δ: 1.28 (m, 1 H, CH); 1.35 (s, 3 H, Me); 1.58 and 1.81 (both m, 2 H, H(3)); 2.06 and 2.18 (both m, 2 H, H(4)); 3.12 (br. s, 1 H, OH); 3.64 (m, 2 H, OCH_2); 3.96 (m, 4 H, $O(CH_2)_2O$); 5.01 (m, 2 H, $=CH_2$); 5.78 (m, 1 H, =CH).

2-(1,1-Ethylenedioxyethyl)-5-methyl-5-hexen-1-ol (**12b**), yield 85 %, b. p. 110—115 °C (3 Torr). ^1H NMR, δ: 1.28 (m, 1 H, CH); 1.32 (s, 3 H, Me); 1.65 and 1.80 (both m, 2 H, H(3)); 1.70 (br. s, 3 H, =CMe); 2.04 and 2.12 (both m, 2 H, H(4)); 3.11 (br. s, 1 H, OH); 3.62 (m, 2 H, OCH_2); 3.98 (m, 4 H, $O(CH_2)_2O$); 4.70 (br. s, 2 H, $=CH_2$).

Ketal aldehydes (6a,b) were obtained in yields of ~90 % by the oxidation of alcohols **12a,b** with pyridinium chlorochromate in CH_2Cl_2 by the standard procedure[21] and were used in the next step without distillation *in vacuo*.

2-(1,1-Ethylenedioxyethyl)-5-hexenal (**6a**), ^1H NMR, δ: 1.28 (s, 3 H, Me); 1.62 and 1.80 (both m, 2 H, H(3)); 1.95 and 2.08 (both m, 2 H, H(4)); 2.54 (m, 1 H, CH); 3.95 (m, 4 H, $O(CH_2)_2O$); 4.96 (m, 2 H, $=CH_2$); 5.72 (m, 1 H, =CH); 9.66 (d, 1 H, CHO, J = 2.4 Hz).

2-(1,1-Ethylenedioxyethyl)-5-methyl-5-hexenal (**6b**), ^1H NMR, δ: 1.30 (s, 3 H, Me); 1.65 and 1.81 (both m, 2 H, H(3)); 1.70 (br. s, 3 H, =CMe); 2.0 (m, 2 H, $=CCH_2$); 2.55 (m, 1 H, CH); 3.98 (m, 4 H, $O(CH_2)_2O$); 4.65 and 4.73 (both br. s, 2 H, $=CH_2$); 9.70 (d, 1 H, CHO, J = 2.4 Hz).

Dienic ketal esters (4a,b). According to the procedure,[16] a mixture of triethyl 3-methyl-4-phosphonocrotonate (5.5 g, 21 mmol), ketal aldehyde **6** (21 mmol), powdered KOH (2.25 g), 18-crown-6 (0.2 g), and benzene (60 mL) was stirred vigorously at room temperature for 16 h under GLC control up to complete conversion of the phosphonate. Then saturated $NaHCO_3$ solution (50 mL) was added to the mixture, the organic layer was separated, and the aqueous layer was extracted with benzene. The extracts were dried over $CaCl_2$, and the solvents were evaporated. The residue was passed through a short column with SiO_2 (eluent — ethyl acetate—heptane, 1 : 2). After the eluate evaporation compounds **4a,b** were obtained (yield 69—72 %) and were used in the next step without additional purification.

Ethyl 3-methyl-6-(1,1-ethylenedioxyethyl)-2,4,9-decatrienoate (**4a**), a mixture of 2(*E*),4(*E*)- and 2(*Z*),4(*E*)-isomers, 65 : 35. ^{1}H NMR, δ: 2.01 (br. s, Me, 2(*Z*),4(*E*)-isomer); 2.28 (br. s, Me, 2(*E*),4(*E*)-isomer); 2.36 (m, CH(6)); 5.0 (m, 2 H, $=CH_2$); 5.61 (s, CH(2), 2(*Z*),4(*E*)-isomer); 5.71 (s, CH(2), 2(*E*),4(*E*)-isomer); 5.8 (m, =CH); 6.12 (d, C(4),2(*E*),4(*E*)-isomer, J = 15.1 Hz); 7.6 (d, H(4), 2(*Z*),4(*E*)-isomer).

Ethyl 3,9-dimethyl-6-(1,1-ethylenedioxyethyl)-2,4,9-decatrienoate (**4b**), a mixture of 2(*E*),4(*E*)- and 2(*Z*),4(*E*)-isomers, 65 : 35. ^{1}H NMR, δ: 1.65 (br. s, =CMe); 2.00 (br. s, 3-Me, 2(*Z*),4(*E*)-isomer); 2.25 (br. s, 3-Me, 2(*E*),4(*E*)-isomer); 2.36 (m, CH(6)); 4.65 (br. s, 2 H, $=CH_2$); 5.56 (s, CH(2) 2(*Z*),4(*E*)-isomer); 5.70 (s, CH(2), 2(*E*),4(*E*)-isomer); 6.08 (d, H(4), 2(*E*),4(*E*)-isomer, J = 15.1 Hz); 7.58 (d, H(4), 2(*Z*),4(*E*)-isomer, J = 15.1 Hz).

Ethyl 3-methyl-9-R-6-(1,1-ethylenedioxyethyl)-3(*Z*),9-decadienoates (3a,b). Into a stainless steel autoclave of 50 mL volume diene **4** (12 mmol), (methyl benzoate)tricarbonylchromium (0.32 g), and oxygen-free acetone (8 mL) were loaded. The autoclave was closed and blown with hydrogen 3 times up to 10 atm, and an initial pressure of 60 atm was charged. Hydrogenation was carried out at 120—125 °C for 3.5 h. The autoclave was opened, acetone was distilled off, benzene (20 mL) was added to the residue, and the mixture was filtered through silica gel. Evaporation of the solvents led to compounds **3a,b** (yield 80—85 wt. %), which were used in the next step without further purification.

Ethyl 3-methyl-6-(1,1-ethylenedioxyethyl)-3(*Z*),9-decadienoate (**3a**), ^{1}H NMR, δ: 1.78 (br. s, 3 H, =CMe); 3.02 (s, 2 H, CH_2COO); 5.32 (br. t, 1 H, =CH).

Ethyl 3,9-dimethyl-6-(1,1-ethylenedioxyethyl)-3(*Z*),9-decadienoate (**3b**), ^{1}H NMR, δ: 1.72 (br. s, 3 H, =CMe); 1.78 (br. s, 3 H, =CMe); 3.08 (s, 2 H, CH_2COO); 4.65 and 4.70 (both br. s, 2 H, $=CH_2$); 5.42 (br. t, 1 H, =CH).

Ketols (14a,b). A solution of **2** (9 mmol) in ether (10 mL) was added dropwise to a suspension of $LiAlH_4$ (0.5 g) in absolute ether (20 mL), and the mixture was stirred for 30 min. Water (30 mL) was added very carefully to the mixture; then 5 % H_2SO_4 was added to extinction of the emulsion, while the aqueous layer remained white. The ethereal layer was separated, the aqueous layer was extracted with ether, and the combined extracts were dried over $MgSO_4$. After evaporation of ether, crude hydroxy ketals **13a,b** were obtained and subjected to hydrolysis without any purification. For this purpose, they were boiled for 3 h with H_2O (5 mL) and oxalic acid (0.29 g) in acetone (20 mL) under GLC control. Acetone was distilled off, Na_2CO_3 was added to neutralize the acid, and the mixture was extracted with ether. The combined extracts were dried over $MgSO_4$ and evaporated. Distillation of the residue *in vacuo* led to ketols **14**.

3-Methyl-6-acetyl-3(*Z*),9-decadien-1-ol (**14a**), yield 1.0 g (52 %, by two steps from **13a**), b. p. 140—141 °C (3 Torr). ^{1}H NMR, δ: 1.51 and 1.70 (both m, 2 H, H(7)); 1.68 (br. s, 1 H, OH); 1.70 (br. s, 3 H, =CMe); 2.00 (m, 2 H, H(8)); 2.12 (s, 3 H, COMe); 2.15 (m, 2 H, H(5)); 2.32 (m, 2 H, H(2)); 2.57 (m, 1 H, CH); 3.65 (m, 2 H, OCH_2); 5.0 (m, 2 H, $=CH_2$); 5.19 (br. t, 1 H, H(4), J = 7.1 Hz); 5.75 (m, 1 H, =CH). ^{13}C NMR, δ: 213.1 (C=O); 137.7 (CH); 133.73 (C(3)); 123.7 (C(4)); 115.0 (CH_2); 60.2 (OCH_2); 52.1 (CH); 34.9 (C(2)); 31.3 (C(8)); 30.1 (C(7)); 29.7 (C(5)); 29.4 (MeCO); 23.3 (Me).

3,9-Dimethyl-6-acetyl-3(*Z*),9-decadien-1-ol (**14b**), yield 1.3 g (65 %, by two steps from **13b**), b. p. 138—139 °C (2 Torr). ^{1}H NMR, δ: 1.57 and 1.73 (both m, 2 H, H(7)); 1.70 (br. s, 6 H, CMe_2); 1.82 (br. s, 1 H, OH); 1.97 (t, 2 H, H(8), J = 7.2 Hz); 2.12 (s, 3 H, COMe); 2.15 (m, 1 H, H(5)); 2.36 (m, 3 H, H(5) and H(2)); 2.54 (m, 1 H, CH); 3.68 (t, 2 H, OCH_2, J = 6.3 Hz); 4.66 and 4.72 (both br. s, 2 H, $=CH_2$); 5.20 (br. t, 1 H, H(4), J = 6.9 Hz). ^{13}C NMR, δ: 212.6 (C=O); 145.0 (=CH); 133.8 (C(3)); 124.4 (C(4)); 110.5 (CH_2); 60.5 (OCH_2); 52.5 (CH); 35.4 (C(8)); 35.1 (C(2)); 29.9 (C(5)); 29.6 (MeCO); 29.1 (C(7)); 23.4 (Me); 22.2 (Me).

Compounds 1a,b. According to the procedures,[22,23] to a solution of ketol **13** (1 mmol) in THF (5 mL) a solution of methylenetriphenylphosphorane (1.5 mmol) in DMSO (1.5 mL) was added at room temperature over 20 min. The mixture was stirred for 4 h and left overnight. Conversion of **13** into **14** was near 60 % (GLC). The mixture was poured into water (5 mL) and extracted with hexane, and the extracts were washed successively with a mixture of water and DMSO (1 : 1), water, and saturated solution of NaCl, dried over $MgSO_4$, and evaporated. ^{1}H NMR spectra of the crude products exhibited two broad singlets at 4.67 and 4.72 ppm, which were assigned to the olefinic protons of the isopropenyl group formed. Then the product was heated with the corresponding anhydride (0.3 g) in the presence of a catalytic amount of Na_2CO_3 on a water bath for 1 h (Ac_2O in the case of **14a** and $(EtCO)_2O$ in the case of **14b**). Water (2 mL) was added to the reaction mixture followed by neutralization with Na_2CO_3, extraction with hexane, drying over $MgSO_4$, and evaporation of the solvent. Purification of the target esters **1a,b** from the attendant keto compounds was carried out by chromatography on SiO_2 (a mixture of hexane and ethyl acetate, 10 : 1, as eluent) under TLC (Silufol) control with the same eluent (R_f 0.6). Evaporation of the solvents led to compounds **1a** and **1b**, whose physicochemical constants were close to those described earlier.[3—5]

3-Methyl-6-isopropenyl-3(*Z*),9-decadien-1-yl acetate (**1a**), yield 112 mg (45 %). ^{1}H NMR, δ: 1.41 (m, 2 H, H(7)); 1.61 (br. s, 3 H, $MeC=CH_2$); 1.71 (br. s, 3 H, Me); 1.98 (m, 5 H, H(5)), H(6) and H(8)); 2.03 (s, 3 H, MeCO); 2.34 (t, 2 H, CH_2, J = 6.9 Hz); 4.08 (t, 2 H, OCH_2, J = 6.9 Hz); 4.68 and 4.75 (both br. s, 2 H, $=CH_2$); 4.95 (m, 2 H, H(10)); 5.20 (m, 1 H, H(4)); 5.80 (m, 1 H, H(9)). ^{13}C NMR, δ: 171.1 (C=O); 147.2 ($MeC=CH_2$); 139.0 (C(9)); 131.2 (C(3)); 126.5 (C(4)); 114.4 (C(10)); 111.7 ($MeC=CH_2$); 62.8 (OCH_2); 47.1 (C(6)); 32.1, 32.1, 31.7, 31.3 (C(2); C(5); C(7); C(8)); 23.6 (Me); 21.1 (MeCO); 18.6 ($MeC=CH_2$).

3,9-Dimethyl-6-isopropenyl-3(*Z*),9-decadien-1-yl propionate (**1b**), yield 117 mg (42 %). ^{1}H NMR, δ: 1.12 (t, 3 H, $MeCH_2CO$, J = 6.9 Hz); 1.49 (m, 2 H, H(8)); 1.60 (br. s, 3 H, $MeC=CH_2$); 1.70 (br. s, 6 H, 3-Me and 9-Me); 1.95 (m, 5 H, H(5), H(6) and H(8)); 2.31 (q, 2 H, CH_2CO, J = 6.8 Hz); 2.33 (t, 2 H, H(2), J = 6.8 Hz); 4.08 (t, 2 H, OCH_2, J = 6.9 Hz); 4.63 (m, 2 H, H(10)); 4.61 and 4.72 (both br. s, $MeC=CH_2$); 5.20 (m, 1 H, H(4)). ^{13}C NMR, δ: 174.5 (C=O); 147.3 ($MeC=CH_2$); 146.2 (C(9)); 131.3 (C(3)); 126.5 (C(4)); 111.7 ($MeC=CH_2$); 109.7 (C(10)); 62.7 (OCH_2); 47.3 (C(6)); 35.6 (C(8)); 32.1, 31.4, 30.9 (C(2); C(5); C(7)); 27.7 (CH_2CO); 23.7 (3-Me); 22.6 (9-Me); 18.6 ($MeC=CH_2$); 9.2 ($MeCH_2CO$).

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