# Palladium(II)-catalysed Rearrangements of Allylic Acetates in the Syntheses of Methyl (10*E*,12*Z*)-9-Hydroxyoctadeca-10,12-dienoate (α-Dimorphecolate) and (2*E*,4*Z*)-Deca-2,4-dienal

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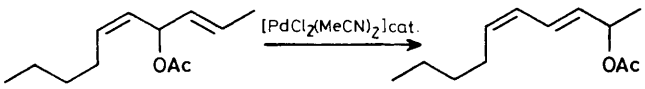
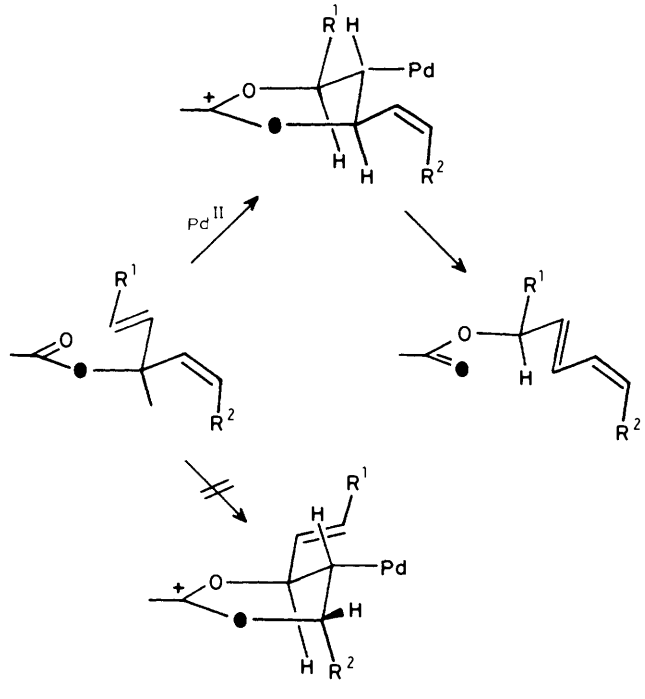
Preparatively useful examples of the kinetically controlled $Pd^{II}$-catalysed rearrangement of (1*E*,4*Z*)-3-acetoxy-1,4-dienes into (2*E*,4*Z*)-1-acetoxy-2,4-dienes are described. These include the conversion of (2*E*,5*Z*,8*Z*)-4-acetoxydeca-2,5,8-triene into (3*E*,5*Z*,8*Z*)-2-acetoxydeca-3,5,8-triene and steps in syntheses leading to the natural products 9-hydroxyoctadeca-10,12-dienoic acid (α-dimorphecolic acid, obtained as its methyl ester) and (2*E*,4*Z*)-deca-2,4-dienal. Studies of a variety of substrates show that the order of reactivity of double bonds in the $Pd^{II}$-catalysed rearrangement is *E*-disubstituted > *Z*-disubstituted ~ vinyl > α-methylvinyl. $Pd^{0}$-catalysed rearrangements of these substrates proceed, in contrast to the $Pd^{II}$-catalysed rearrangements, to thermodynamically controlled product(s), *e.g.* the above triene gives mainly (3*E*,5*E*,8*Z*)-2-acetoxydeca-3,5,8-triene.

The rearrangement of (1*E*,4*Z*)-3-acetoxy-1,4-dienes into (2*E*,4*Z*)-1-acetoxy-2,4-dienes catalysed by certain $Pd^{II}$ complexes {*e.g.* bis(acetonitrile)palladium dichloride, $[PdCl_2(MeCN)_2]$} is a rapid, efficient, stereocontrolled process for substrates substituted at the 1- and 5-positions by alkyl groups (*e.g.* Equation 1).[1]



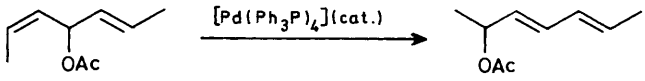

**Equation 1.**

The rearrangement of substrates (**1a**—**c**) occurs preferentially at the *E*-double bond to give mainly the products (**2a**—**c**), respectively. Using $^{17}O$ n.m.r. spectroscopy to monitor the rearrangement it was shown that [$^{17}$OCOMe]-(2*E*,5*Z*)-4-acetoxyhepta-2,5-diene is converted into [OC$^{17}$OMe](3*E*,5*Z*)-2-acetoxyhepta-3,5-diene.[2] Hence, a plausible mechanism for the rearrangement is as shown in Scheme 1, in which the formation of the *E*,*Z*-product is a kinetically controlled process favoured by a lower energy transition state leading to the intermediate drawn.[2] The alternative intermediate and corresponding transition state are destabilised by a 1,3-diaxial interaction.



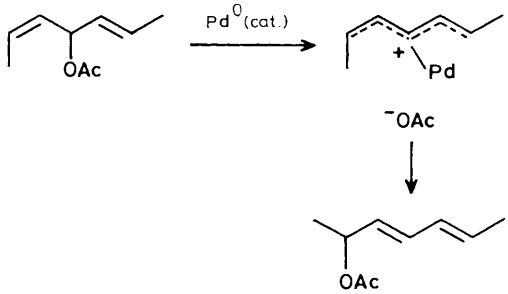

**Scheme 1.** Mechanism (ref. 2) for the $Pd^{II}$-catalysed rearrangement of dienyl acetates

In contrast, the rearrangement of substrates (**1a**—**c**) catalysed by tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] gives the thermodynamically stable *E*,*E*-products (*e.g.* Equation 2).




**Equation 2.**

The mechanism of this process, supported by a $^{17}O$-labelling study, was suggested[2] to be a $Pd^{0}$-assisted ionisation to acetate and a Pd-stabilised pentadienyl cation. These species recombine to afford the observed product (*cf.* Scheme 2).

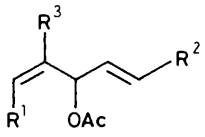



**Scheme 2.** Mechanism (ref. 2) for the $Pd^{0}$-catalysed rearrangement of dienyl acetates

We now report the application of the $Pd^{II}$-catalysed rearrangement to substrates of greater complexity and show how it can be applied to the syntheses of the natural products (10*E*,12*Z*)-9-hydroxyoctadeca-10,12-dienoic acid [α-dimorphecolic acid (**2d**); as its methyl ester, (**2e**)] and (2*E*,4*Z*)-deca-2,4-dienal (**2f**). The syntheses of compounds (**2e**) and (**2f**) also incorporate useful $Pd^{II}$-catalysed rearrangements of allylic acetates.[3] Full experimental details for all our $Pd^{0}$- and $Pd^{II}$-catalysed reactions are given herein.

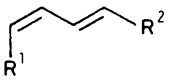
## Results and Discussion

*Further* Pd-*Catalysed Rearrangements of* 3-*Acetoxy*-1,4-*dienes*.—It was shown[1] that (*E*)-3-acetoxyhexa-1,4-diene (**1d**) undergoes $Pd^{II}$-catalysed rearrangement to give almost exclusively (*E*)-2-acetoxyhexa-3,5-diene (**2g**), whereas the $Pd^0$-assisted rearrangement yields mainly (2*E*,4*E*)-1-acetoxyhexa-2,4-diene. Treatment of (*Z*)-3-acetoxyhexa-1,4-diene with $Pd^0$ catalyst also gave mainly (2*E*,4*E*)-1-acetoxyhexa-2,4-diene, but $Pd^{II}$ catalyst gave a very slow reaction (48 h, room temperature) resulting in (*E*)-2-acetoxyhexa-3,5-diene (60%), (2*E*,4*E*)-1-acetoxyhexa-2,4-diene (30%), and (2*E*,4*Z*)-1-acetoxyhexa-2,4-diene (10%). Thus, the order of reactivity of double bonds in the $Pd^{II}$-catalysed rearrangement is *E*-disubstituted > *Z*-disubstituted ~ vinyl. It was therefore of interest to examine a substrate containing an α-methylvinyl group and either an *E*- or *Z*-disubstituted double bond. We found that $Pd^{II}$-catalysed rearrangement of (*E*)-3-acetoxy-2-methylhexa-1,4-diene (**1e**) was rapid and gave predominantly (*E*)-2-acetoxy-5-methylhexa-3,5-diene. However, (*Z*)-3-acetoxy-2-methylhexa-1,4-diene reacted very slowly (48 h, room temperature) to give the same product as the *E*-isomer. This result shows that the α-methylvinyl group does not participate readily in $Pd^{II}$-catalysed rearrangements. The examples described make easily available a range of product dienes suitable for use in the Diels–Alder reaction. This extension of the chemistry described is under investigation.



(**1**)

**a**; $R^1 = R^2 = Me$, $R^3 = H$
**b**; $R^1 = Bu$, $R^2 = Me$, $R^3 = H$
**c**; $R^1 = Me$, $R^2 = Bu$, $R^3 = H$
**d**; $R^1 = R^3 = H$, $R^2 = Me$
**e**; $R^2 = R^3 = Me$, $R^1 = H$
**f**; $R^1 = MeCH{=}CHCH_2$, $R^2 = Me$, $R^3 = H$



(**2**)

**a**; $R^1 = Me$, $R^2 = CHOAcMe$
**b**; $R^1 = Bu$, $R^2 = CHOAcMe$
**c**; $R^1 = Me$, $R^2 = CHOAcBu$
**d**; $R^1 = C_5H_{11}$, $R^2 = CHOH(CH_2)_7CO_2H$
**e**; $R^1 = C_5H_{11}$, $R^2 = CHOH(CH_2)_7CO_2Me$
**f**; $R^1 = C_5H_{11}$, $R^2 = CHO$
**g**; $R^1 = H$, $R^2 = CHOAcMe$
**h**; $R^1 = MeCH{=}CHCH_2$, $R^2 = CHOAcMe$
**i**; $R^1 = C_5H_{11}$, $R^2 = CHOAc(CH_2)_7CO_2Me$

For certain applications of the $Pd^{II}$-catalysed rearrangement in the synthesis of natural products, it was important to show that a *Z*-double bond, in 'skipped' relationship to the *Z*-double bond of a (1*E*,4*Z*)-3-acetoxyhexa-1,4-diene, does not interfere. Therefore (2*E*,5*Z*,8*Z*)-4-acetoxydeca-2,5,8-triene (**1f**) was synthesised and exposed to $Pd^{II}$-catalyst, and gave predominantly (3*E*,5*Z*,8*Z*)-2-acetoxydeca-3,5,8-triene (**2h**). In contrast, $Pd^0$-catalysed rearrangement gave >80% (3*E*,5*E*,8*Z*)-2-acetoxydeca-3,5,8-triene.

Pd-*Catalysed Allylic Rearrangements*.—For the synthesis of (2*E*,4*Z*)-deca-2,4-dienal [(**2f**), see below] we required a monoester of (*E*)-but-2-ene-1,4-diol as starting material. We originally prepared two such esters [(**3a**) and (**3b**)] by saponification of the diacetate (**3c**) and dipivalate (**3d**) of the diol. These esters were conveniently prepared in high yield by $Pd^0$-catalysed rearrangement of the corresponding diesters of (*Z*)-but-2-ene-1,4-diol, a cheap commercially available compound. The mechanisms of these reactions presumably involve an initial $Pd^0$-catalysed rearrangement to the diester of but-1-ene-3,4-diol, followed by a further $Pd^0$-catalysed rearrangement to the observed product.

$R^1OCH_2CH{=}CHCH_2OR^2$

(**3a**) $R^1 = H$, $R^2 = Ac$
(**3b**) $R^1 = H$, $R^2 = Bu^tCO$
(**3c**) $R^1 = Ac$, $R^2 = Ac$
(**3d**) $R^1 = Bu^tCO$, $R^2 = Bu^tCO$
(**3e**) $R^1 = Bu^tSiMe_2$, $R^2 = Ac$
(**3f**) $R^1 = Bu^tSiMe_2$, $R^2 = H$

$CH_2{=}CHCHOR^1CH_2OR^2$

(**4a**) $R^1 = H$, $R^2 = Bu^tSiMe_2$
(**4b**) $R^1 = Ac$, $R^2 = Bu^tSiMe_2$

$Bu^tSiMe_2OCH_2CH{=}CHCHO$

(**5**)

In a better approach, but-1-ene-3,4-diol[4] was dimethyl-t-butylsilylated[5] to give the silyl ether (**4a**) [92%], which was converted into its acetate (**4b**) [94%]. In the presence of a catalytic quantity (5 mol %) of $[PdCl_2(MeCN)_2]$ in benzene, the acetate (**4b**) gave the (*E*)-allylic acetate (**3e**) [ratio of (**3e**):(**4b**) = 1.3:1 after 2 h at room temperature]. Treatment of the mixture of acetates with lithium aluminium hydride in ether, followed by chromatography, gave the (*E*)-allylic alcohol (**3f**) (54%). Oxidation of the alcohol (**3f**) with pyridinium dichromate (1.5 mol equiv.) in dichloromethane afforded the (*E*)-aldehyde (**5**) (60%). $Pd^{II}$-Catalysed isomerisation of a (*Z*)-allylic acetate into an (*E*)-allylic acetate should be a general reaction.

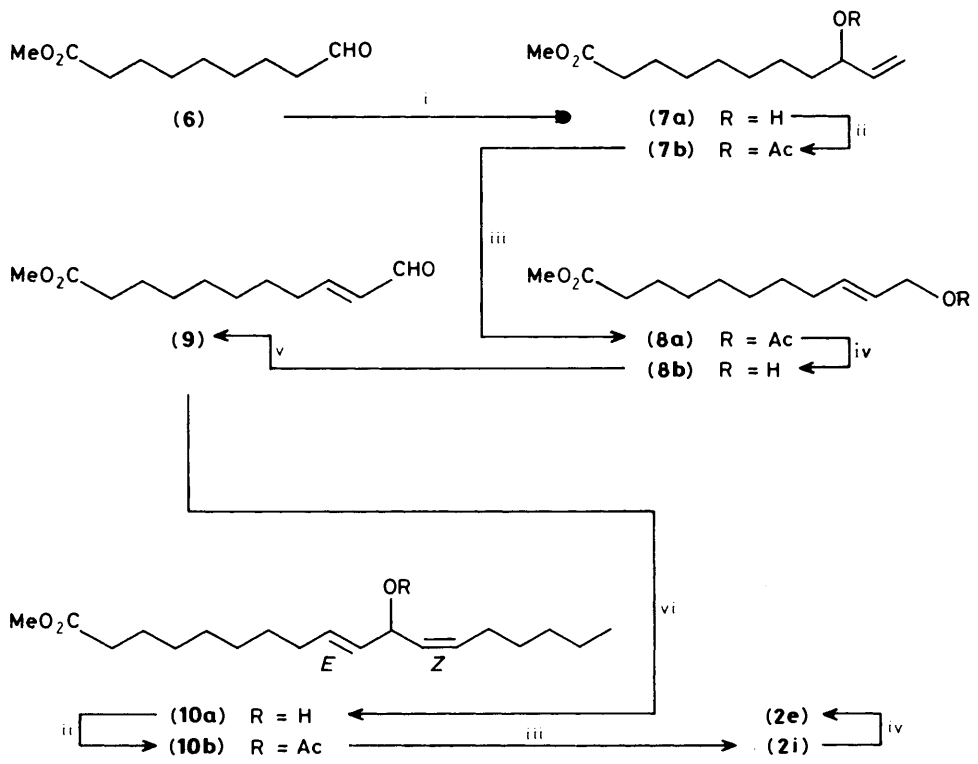
For the synthesis of methyl α-dimorphecolate (see below) we needed to convert an aldehyde into an homologous α,β-unsaturated aldehyde. Although several methods have been reported[6] for accomplishing this transformation, we have applied the $Pd^{II}$-catalysed rearrangement of allylic acetates to the solution of this problem. The protocol shown in Scheme 3 was defined using 3-chlorobenzaldehyde as starting material, which was converted into (*E*)-3-chlorocinnamaldehyde (overall yield 23%, not optimised). Although this sequence requires five steps, most, if not all of these steps are trivial, simple reactions, and it is possible to proceed quickly from start to finish with minimal purification of intermediates.

$$RCHO \xrightarrow{i\ \text{to}\ v} RCH{=}CHCHO$$

**Scheme 3.** Procedure for conversion of aldehydes into homologous α,β-unsaturated aldehydes. *Reagents*: i, $CH_2{=}CHMgBr$, THF; ii, $Ac_2O$, DMAP (cat.), py; iii, $[PdCl_2(MeCN)_2]$ (cat.), benzene; iv, NaOMe (cat.), MeOH; v, $MnO_2$, THF = tetrahydrofuran, DMAP = 4-dimethylaminopyridine, py = pyridine

*Synthesis of Methyl* α-*Dimorphecolate* (**2e**).—The acid (**2d**) was originally obtained from marigold seeds (*Calendula officinalis* L.).[7] It has been isolated as its cholesteryl ester from human atheroma plaques[8] and recently was identified as a self-defensive substance of the rice plant *Oryza sative* L.[9] A 10-step synthesis of methyl α-dimorphecolate (**2e**) from (*E*)-pent-2-en-4-yn-1-ol, using a Lindlar reduction to generate the *Z*-double bond, has been reported.[10] However, the stereochemical homogeneity of the product was not confirmed. Our synthesis of ester (**2e**), based on the $Pd^{II}$-catalysed rearrangement of acetoxydienes (*cf.* Equation 1), is summarised in Scheme 4.

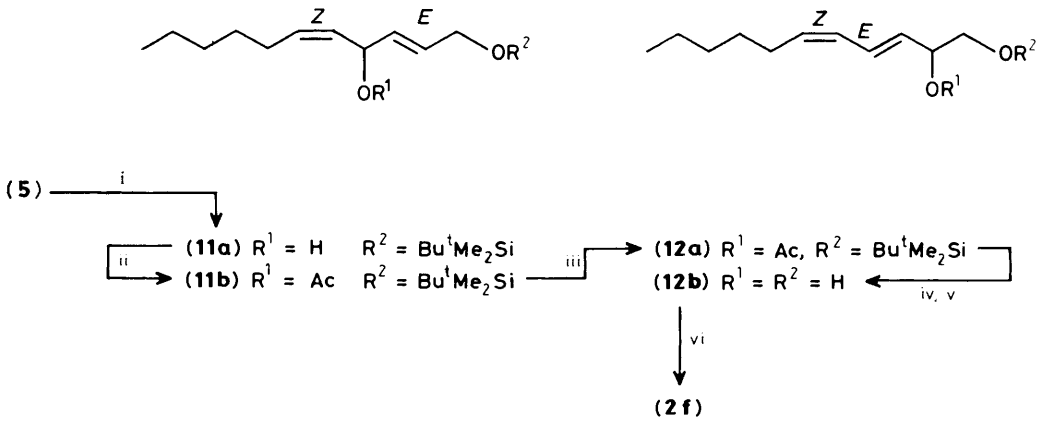
Thus, the aldehyde (**6**), prepared by ozonolysis of methyl (9*Z*) octadec-9-enoate, was treated with vinylmagnesium bromide in tetrahydrofuran to give the alcohol (**7a**) (61%), which was converted into the acetate (**7b**) (60%). In the presence of a catalytic quantity (5 mol %) of $[PdCl_2(MeCN)_2]$ the acetate (**7b**) [0.1M in benzene] was equilibrated with the (*E*)-allylic acetate (**8a**) [ratio of (**7b**):(**8a**) = 1:3 after 45 min at room temperature]. Treatment of the mixture with catalytic sodium methoxide in methanol gave the (*E*)-allylic alcohol (**8b**) (64%)




**Scheme 4.** Synthesis of (±)-methyl α-dimorphecolate. *Reagents:* i, $CH_2$=CHMgBr, THF; ii, $Ac_2O$, DMAP (catalytic), py; iii, [$(MeCN)_2PdCl_2$] (catalytic), $C_6H_6$; iv, NaOMe (catalytic), MeOH; v, $MnO_2$, petroleum; vi, $C_5H_{11}CH\overset{Z}{=}CHMgBr$, THF. THF = tetrahydrofuran; DMAP = 4-dimethylaminopyridine; py = pyridine

and the secondary alcohol (**7a**) (17%), after separation by chromatography on silica gel [elution with petroleum–diethyl ether (5:1)]. The alcohol (**8b**) in petroleum was oxidised with manganese dioxide (10 mass equiv.) to give the (*E*)-enal (**9**) (74%).

Coupling of the aldehyde (**9**) with (*Z*)-hept-1-enylmagnesium bromide [prepared from (*Z*)-1-bromoheptene, obtained from hexanal analogously to (*Z*)-1-bromohexene from pentanal [2]] gave the dienyl alcohol (**10a**) (33%) and recovered aldehyde (**9**) (36%), after chromatography on silica gel [elution with petroleum–diethyl ether (5:1)]. The alcohol (**10a**) was predominantly (>90%) the (9*E*,12*Z*)-isomer according to $^1H$ and $^{13}C$ n.m.r. spectroscopic analysis. The dienyl acetate (**10b**), prepared from the alcohol (**10a**) in 78% yield, was isomerised in the presence of $[PdCl_2(MeCN)_2]$ (5 mol %) in benzene (45 min, room temperature) preferentially at the *E*-double bond to give predominantly the (*E*,*Z*)-diene (**2i**) (total yield of conjugated dienes >95%). Methanolysis of the diene (**2i**) gave methyl 9-hydroxyoctadeca-10,12-dienoate [(**2e**) 74%], after purification by silica gel chromatography [elution with petroleum–diethyl ether (3:1)]. The $^1H$ and $^{13}C$ n.m.r. spectra of the ester obtained were in close agreement with the reported data for the (10*E*,12*Z*)-methyl ester (**2e**) prepared from natural α-dimorphecolic acid (**2d**).[11] However, minor resonances indicated the presence of *ca.* 15% *E*,*E*-isomer(s). This was expected because the $Pd^{II}$-catalysed rearrangement of (1*E*,4*Z*)-3-acetoxy-1,4-dienes is a kinetically controlled process favouring migration of the acetate *via* the *E*-double bond by a rate factor




**Scheme 5.** *Reagents:* i, $C_5H_{11}CH\overset{Z}{=}CHMgBr$, THF; ii, $Ac_2O$, DMAP (catalytic), py; iii, $[PdCl_2(MeCN)_2]$ (catalytic), benzene; iv, NaOMe (catalytic), MeOH; v, $Bu_4N^+F^-$, THF; vi, $NaIO_4$, THF–pH 7 aq. phosphate buffer

of *ca.* 5:1 over migration *via* the *Z*-double bond (but see below).[1,2]

*Synthesis of* (2*E*,4*Z*)-*Deca*-2,4-*dienal* (**2f**).—This compound is a flavour constituent of black tea.[12] It has been synthesized from prop-2-yn-1-ol using Wittig chemistry[13] and from 3-dimethylaminopropenal by an application of the Benary reaction.[14] Our synthesis is summarised in Scheme 5. Thus, coupling of the aldehyde (**5**) with (*Z*)-hept-1-enylmagnesium bromide in tetrahydrofuran gave the (*E*,*Z*)-dienyl alcohol (**11a**) (78%) that was acetylated to (**11b**) (87%). These substances were contaminated with *ca.* 10% of conjugated dienes. Isomerisation of the acetate (**11b**) occurred with catalytic (5 mol %) [$PdCl_2(MeCN)_2$] in benzene, but was significantly slower (*ca.* 6 h for completion) than normal.[1,2] The product (94%) was a 3:1 mixture of the (*E*,*Z*)-dienyl acetate (**12a**) and an *E*,*E*-isomer. We rationalise these observations as being due to the deactivation of the *E*-double bond by the neighbouring silyloxy group (either by inductive electron withdrawal or by $\pi \rightarrow \sigma^*$ hyperconjugation), making reaction at the *Z*-double bond competitive with reaction at the *E*-double bond. Methanolysis of the mixture of (**12a**) and its isomer, followed by desilylation, gave the diol (**12b**) after chromatography. Periodate cleavage[15] of the diol (**12b**) in tetrahydrofuran–pH 7 phosphate buffer gave (2*E*,4*Z*)-deca-2,4-dienal [(**2f**), 15% overall from (**12a**)], the spectroscopic properties of which were identical with those reported.[14]

The chemistry described illustrates further uses of palladium in organic synthesis (for reviews see ref. 16). Extension of this chemistry to the synthesis of leukotrienes and other hydroxy-polyunsaturated fatty acids is being investigated.

## Experimental

*Materials and Methods.*—Dry solvents referred to below were prepared as follows: pyridine was kept over potassium hydroxide, distilled and stored over molecular sieves (type 4A). Tetrahydrofuran and diethyl ether were stored over lithium aluminium hydride and immediately prior to use, distilled. Benzene was purified by successively washing with concentrated sulphuric acid, dilute sodium hydroxide, and water, followed by distillation from phosphorus pentaoxide under nitrogen. Deuteriobenzene was stored over molecular sieves (type 3A). Petroleum refers to light petroleum (b.p. 40—60 °C).

T.l.c. was performed on Schleicher and Schull plastic sheets coated with silica gel (F 1500 LS 254); the plates were initially examined under u.v. light and spots were then visualised with potassium permanganate. Column chromatography was effected under pressure, using Merck Kieselgel H (type 60).

Evaporations were carried out using a rotary evaporator. M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded using either a Nicolet 20SXB or a Perkin-Elmer 257 spectrophotometer. Either a Unicam SP 800 spectrometer or a Cecil CE505 was employed to determine u.v. spectra. $^1$H N.m.r. spectra were measured using tetramethylsilane as internal standard. The spectra were determined at 200, 220, or 300 MHz using a Bruker WP 200, Perkin-Elmer R34 or Bruker WM 300 instrument, respectively. Mass spectra were determined using either a Kratos MS 9 or a Kratos MS 80 instrument.

(*E*)- and (*Z*)-Hexa-1,4-dien-3-ol, (*E*)- and (*Z*)-2-methylhexa-1,4-dien-3-ol, and (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-hepta-2,5-dien-4-ol were prepared by a literature procedure,[2,17] and were converted into the corresponding acetates by acetic anhydride–pyridine. All of these acetates gave $^1$H n.m.r. spectral data consistent with their assigned structures.

*Example of a* $Pd^{II}$-*Catalysed Rearrangement:* (E)-2-*Acetoxyhexa*-3,5-*diene*.—To a stirred solution of (*E*)-3-acetoxyhexa-1,4-diene (0.4 g, 2.86 mmol) in dry tetrahydrofuran (5 $cm^3$) was added $PdCl_2(MeCN)_2$ (0.037 g, 5 mol %) and the reaction was allowed to proceed for 10 min. The solvent was removed and pentane was added to the residue. Filtration and evaporation gave a liquid that was distilled (Kugelrohr) to afford (*E*)-2-acetoxyhexa-3,5-diene (0.36 g, 90%), b.p. 36—38 °C at 4 mmHg: $\lambda_{max.}$(EtOH) 221 nm (ε 26 000 $dm^3$ $mol^{-1}$ $cm^{-1}$); $\delta_H$(220 MHz; $CCl_4$) 1.30 (3 H, d, *J* 6.5 Hz, 1-Me), 1.98 (3 H, s, COMe), 5.08 (1 H, d, *J* 10.5 Hz, 6-H), 5.20 (1 H, d, *J* 17 Hz, 6-H), 5.30 (1 H, m, 2-H), 5.61 (1 H, dd, *J* 6.5 and 15 Hz, 3-H), and 6.21 (2 H, m, 4- and 5-H); *m*/*z* 140 ($M^+$), 98 ($M^+ - 42$), and 43 (base peak).

(E)-2-*Acetoxy*-5-*methylhexa*-3,5-*diene*.—A solution of the (*E*)-3-acetoxy-2-methylhexa-1,4-diene was treated as described above to give, after distillation (*E*)-2-acetoxy-5-methylhexa-3,5-diene (93%), b.p. 95—100 °C at 20 mmHg: $\delta_H$(220 MHz, $CDCl_3$) 1.34 (3 H, d, *J* 6.5 Hz, 1-Me), 1.84 (3 H, s, 5-Me), 2.05 (3 H, s, COMe), 5.00 (2 H, s, 6-$H_2$), 5.43 (1 H, pentuplet, 2-H), 5.63 (1 H, dd, *J* 6.6 and 16 Hz, 3-H), and 6.32 (1 H, d, *J* 16 Hz, 4-H); *m*/*z* 154 ($M^+$), 112 ($M^+ - 42$), 111 ($M^+ - 43$), 79 ($M^+ - 75$), and 43 (base peak).

(3E,5Z,8Z)-2-*Acetoxydeca*-3,5,8-*triene*.—A solution of (2*E*,-5*Z*,8*Z*)-4-acetoxydeca-2,5,8-triene (0.3 g, 1.55 mmol) was treated as described above to give after distillation (3*E*,5*Z*,8*Z*)-2-acetoxydeca-3,5,8-triene (0.279 g, 93%), b.p. 96—98 °C at 0.05 mmHg: $\lambda_{max.}$ 235 nm (ε 19 400 $dm^3$ $mol^{-1}$ $cm^{-1}$); $\delta_H$(220 MHz, $CCl_4$) 1.32 (3 H, d, *J* 6.6 Hz, 1-Me), 1.66 (3 H, d, *J* 6.6 Hz, 10-Me), 2.04 (3 H, s, COMe), 2.94 (2 H, t, 7-$CH_2$), 5.3–5.6 (3 H, m, 2-, 8-, and 9-H), 5.66 (1 H, dd, *J* 7 and 15 Hz, 3-H), 5.97 (1 H, t, *J* 10 Hz, 5-H), and 6.55 (1 H, dd, *J* 11 and 15 Hz, 4-H); *m*/*z* 194 ($M^+$), 79 ($M^+ - 115$), and 43 (base peak).

(E)-1,4-*Dipivaloyloxybut*-2-*ene* (**3d**).—To an ice-cooled solution of (*Z*)-but-2-ene-1,4-diol (26.4 g, 0.3 mol) in dry pyridine (200 $cm^3$) was added trimethylacetyl chloride (81 $cm^3$, 0.66 mol). After 3 h the solution was extracted with diethyl ether, and the extract washed with 5M hydrochloric acid and aqueous sodium hydrogen carbonate, dried, and evaporated to give (*Z*)-1,4-dipivaloyloxybut-2-ene (74 g, 96%). The crude dipivalate (12 g, 0.047 mol) in dry benzene (50 $cm^3$) was treated with [$Pd(Ph_3P)_4$] (1.1 g, 2 mol %) under nitrogen. The reaction was allowed to proceed for 4 h at room temperature. The solvent was removed and the residue was washed with petroleum through Celite. The combined filtrates were washed with 2% aqueous sodium cyanide and water, and the solvent was removed to give the title compound (11.8 g, 98%); $\nu_{max.}$(liq. film) 2 974 and 1 733 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 1.39 (18 H, s, $Me_3C$), 4.58 (4 H, dd, *J* 1.5 and 4 Hz, 2 × $CH_2$), and 5.79 (2 H, m, CH:CH); *m*/*z* 256 ($M^+$), 241 ($M^+ - CH_3$), 155 ($M - C_5H_9O_2$), 85 ($C_5H_9O$), and 57 (base peak, $C_4H_9^+$).

(E)-1,4-*Diacetoxybut*-2-*ene* (**3c**).—To an ice-cooled solution of (*Z*)-but-2-ene-1,4-diol (17.8 g, 0.2 mol) in dry pyridine (100 $cm^3$) was added acetic anhydride (42 $cm^3$, 0.44 mol). After 6 h the solution was extracted with diethyl ether, and the extract washed with 5M hydrochloric acid and aqueous sodium hydrogen carbonate, dried, and evaporated to give (*Z*)-1,4-diacetoxybut-2-ene (28.8 g, 84%). To a stirred solution of the crude diacetate (17.2 g, 0.1 mol) in dry benzene (75 $cm^3$) was added [$Pd(Ph_3P)_4$] (2.3 g, 2 mol %). The reaction was allowed to proceed for 5 h at room temperature after which the solvent was removed and the residue washed with petroleum through Celite. The combined filtrates were washed with 2% aqueous sodium cyanide, dried, and evaporated to give the title compound (17 g, 98%); $\delta_H$(200 MHz, $C_6D_6$) 1.89 (6 H, s, 2 × $COCH_3$), 4.58 (4 H, dd, *J* 1.5 and 4.4 Hz, 2 × $CH_2$), and 5.77—5.82 (2 H, m, CH:CH).

3-*Acetoxy*-4-*dimethyl*-t-*butylsilyloxybut*-1-*ene* (**4b**).—A solution of but-1-ene-3,4-diol[4] (4.4 g, 50 mmol) in dry *N*,*N*-dimethylformamide (30 $cm^3$) was treated with imidazole (4.93 g, 72.5 mmol) followed by dimethyl-t-butylsilyl chloride (7.6 g, 50 mmol) for 4 h at room temperature. The solution was poured into brine and extracted with diethyl ether. The extract was washed with dilute hydrochloric acid, dried, and evaporated to give the crude product (**4a**) (9.3 g, 92%). This was dissolved in dry pyridine (30 $cm^3$) and treated with acetic anhydride (5.6 $cm^3$, 60 mmol) followed by 4-dimethylaminopyridine (0.28 g, 5 mol %) for 1 h at room temperature. The solution was washed with 5M hydrochloric acid and extracted with diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to provide a residue which by chromatography on silica gel with petroleum–diethyl ether (9:1) as eluant yielded the title compound (**4b**) (11.43 g, 94%); $\nu_{max.}$($CHCl_3$) 2 930 and 1 750 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.06 (6 H, s, $SiMe_2$), 0.89 (9 H, s, $CMe_3$), 2.09 (3 H, s, COMe), 3.67 (2 H, d, *J* 5 Hz, 4-$CH_2$), 5.19—5.35 (3 H, m, 2 × 1- and 3-H), and 5.82 (1 H, ddd, *J* 6, 11 and 15 Hz, 2-H); *m*/*z* 187 ($M^+ - 57$) and 43 (base peak) (Found: $M^+ - 57$, 187.0795. $C_8H_{15}O_3Si$ requires 187.0795).

(E)-1-*Dimethyl*-t-*butylsilyloxybut*-2-*en*-4-*ol* (**3f**).—A stirred solution of the acetate (**4b**) (11.39 g, 46.6 mmol) in dry benzene (70 $cm^3$) was treated with [$PdCl_2$(MeCN)] (0.543 g, 5 mol %). The reaction was allowed to proceed for 2 h at room temperature after which the solvent was removed and the residue extracted with petroleum and the extract filtered through Celite. The combined filtrates were washed with 2% aqueous sodium cyanide and water, dried, and evaporated to give a *ca.* 1.3:1 mixture of acetates (**3e**) and (**4b**) (10.95 g, 96%). To a cooled solution of the crude mixture (7.5 g, 31 mmol) in dry diethyl ether (180 $cm^3$) was added lithium aluminium hydride (0.582 g, 15 mmol). After 2 h at room temperature, the mixture was cautiously added to ice-cooled 5M hydrochloric acid and extracted into diethyl ether. The extract was washed with water, dried, and evaporated to provide a residue which by chromatography on silica gel with petroleum–diethyl ether (5:1) as eluant gave two products. The faster-running component was the acetate (**4b**) (1.34 g, 18%). The slower-running component was the alcohol (**3f**) (3.4 g, 54%); $\nu_{max.}$($CHCl_3$) 3 350, 2 930, and 2 858 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.036 (6 H, s, $SiMe_2$), 0.86 (9 H, s, $CMe_3$), 3.72 (1 H, br s, OH), 4.04—4.09 (2 H, m, 1-$CH_2$), 4.13—4.15 (2 H, m, 4-$CH_2$), and 5.76—5.79 (2 H, m, 2- and 3-H) (addition of $D_2O$ caused the signal at δ 3.72 to disappear); *m*/*z* 202 ($M^+$), 171 ($M^+ - 31$), 145 ($M^+ - 57$), and 127 ($M^+ - 75$) (Found: $M^+$, 202.1381. $C_{10}H_{22}O_2Si$ requires 202.1389).

(E)-4-*Dimethyl*-t-*butylsilyloxybut*-2-*enal* (**5**).—A vigorously stirred solution of the alcohol (**3f**) (4.5 g, 22 mmol) in dry dichloromethane (35 $cm^3$) was oxidised with pyridinium dichromate (12.4 g, 33 mmol) for 5 h at room temperature. The mixture was filtered through silica gel and the silica was washed with diethyl ether. The combined extracts were washed with dilute hydrochloric acid, dried, and evaporated to afford a residue which by chromatography on silica gel with petroleum–diethyl ether (5:1) as eluant gave the aldehyde (**5**) (2.62 g, 60%); $\nu_{max.}$($CHCl_3$) 2 960, 2 930, and 2 860, and 1 690 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.095 (6 H, s, $SiMe_2$), 0.93 (9 H, s, $CMe_3$), 4.45 (2 H, dd, *J* 2 and 4 Hz, 4-$CH_2$), 6.44 (1 H, d, *J* 8 and 16 Hz, 2-H), 6.89 (1 H, dt, *J* 4 and 16 Hz, 3-H), and 9.60 (1 H, d, *J* 8 Hz, CHO); $\delta_C$ 193.0, 156.2, 130.8, 62.4, 25.9, 25.7, and 5.32; *m*/*z* 200 ($M^+$) and 143 ($M^+ - 57$) (Found: $M^+$, 200.1219. $C_{10}H_{20}O_2Si$ requires 200.1233).

(E)-3-*Chlorocinnamaldehyde*.—A solution of 3-chlorobenzaldehyde (1.40 g, 0.01 mol) in dry tetrahydrofuran (10 $cm^3$) was treated with vinylmagnesium bromide (0.011 mol) in dry tetrahydrofuran (10 $cm^3$). After 40 min at room temperature the solution was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether (2 × 20 $cm^3$). The combined extracts were washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give the crude alcohol (0.942 g, 56%). A solution of the alcohol (0.942 g) in pyridine (4 $cm^3$) was treated with acetic anhydride (0.635 $cm^3$, 6.7 mmol) followed by 4-dimethylaminopyridine (0.032 g, 5 mol %). After 1 h at room temperature the mixture was poured into dilute hydrochloric acid and extracted into diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give the acetate (0.968 g, 82%). The acetate (0.768 g) was treated with [$PdCl_2$(MeCN)$_2$] (40 mg, 5 mol %) in benzene (6 $cm^3$) and the resulting mixture was heated at 80 °C for 1 h. After cooling, the solvent was removed and the residue extracted with petroleum. After filtration through Celite the petroleum extract was washed with 2% aqueous sodium cyanide, dried, and evaporated to give 3-acetoxy-1-*m*-chlorophenylpropene (0.76 g). The crude acetate (0.6 g, 2.84 mmol) in dry methanol (2 $cm^3$) was treated with sodium methoxide in methanol (0.042 $cm^3$, 5 mol % NaOMe) under nitrogen for 1 h at room temperature. The mixture was treated with IR-120$H^+$ resin until neutral, filtered, and the filtrate evaporated. Chromatography of the residue on silica gel with petroleum–diethyl ether (2:1) as eluant gave (*E*)-3-chlorocinnamyl alcohol (0.4 g, 83%). To a vigorously stirred solution of the (*E*)-alcohol (0.168 g, 0.1 mmol) in petroleum (10 $cm^3$) was added manganese dioxide (1.68 g, 10 mass equiv.). After 3 h at room temperature the mixture was filtered through Celite and the filter pad was washed with diethyl ether. The combined filtrates were concentrated to give a crude product which was recrystallised from ethanol to afford (*E*)-3-chlorocinnamaldehyde (0.1 g, 61%), m.p. 71—73 °C; $\nu_{max.}$(KBr) 1 677 and 1 690 $cm^{-1}$; $\delta_H$(300 MHz, $CDCl_3$) 6.46 (1 H, d, *J* 16 Hz, 3-H), 6.73 (1 H, dd, *J* 8 and 16 Hz, 2-H), 7.32—7.75 (4 H, m, ArH), and 9.72 (1 H, d, *J* 8 Hz, CHO); *m*/*z* 166 ($M^+$) and 137 ($M^+$ − CHO) (Found: $M^+$, 166.0178. $C_9H_7{}^{35}ClO$ requires 166.0185).

*Methyl* 9-*Hydroxyundec*-10-*enoate* (**7a**).—To a stirred ice-cooled solution of the aldehyde (**6**)[18] (8.113 g, 44 mmol) in dry THF (50 $cm^3$) was added vinylmagnesium bromide (6.84 g, 52 mmol) in dry THF (30 $cm^3$). After 20 min at 0 °C, the solution was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give the title compound (**7a**) as a syrup (5.69 g, 61%); $\nu_{max.}$($CHCl_3$) 3 500, 2 931, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 1.21—1.73 (12 H, m, 6 × $CH_2$), 1.81 (1 H, br s, OH), 2.31 (2 H, t, *J* 7 Hz, 2-$H_2$), 3.67 (3 H, s, $CO_2Me$), 4.08 (1 H, dt, *J* 6 and 6 Hz, 9-H), 5.12 (1 H, dt, *J* 1, 1, and 10 Hz, 11-H), 5.26 (1 H, dt, *J* 1, 1, and 17 Hz, 11-H), and 5.82 (1 H, ddd, *J* 6, 10, and 17 Hz, 10-H) (addition of $D_2O$ caused the signal at δ 1.81 to disappear); *m*/*z* 187 ($M^+ - 27$) and 155 ($M^+ - 59$).

*Methyl* 9-*Acetoxyundec*-10-*enoate* (**7b**).—To a solution of the alcohol (**7a**) (4.28 g, 20 mmol) in pyridine (25 $cm^3$) was added acetic anhydride (2.2 $cm^3$, 24 mmol) followed by 4-dimethylaminopyridine (0.112 g, 5 mol %). After 1 h at room temperature the solution was poured into dilute hydrochloric acid and extracted with diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to afford a residue which by chromatography on silica gel with petroleum–diethyl ether (2:1) as eluant gave the title compound (**7b**) as a syrup (2.99 g, 60%); $\nu_{max.}$($CHCl_3$) 2 930, 2 860, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 1.26—1.50 (8 H, m, 4 × $CH_2$), 1.61—1.73 (4 H, m, 2 × $CH_2$), 2.06 (3 H, s, COMe),

2.30 (2 H, t, *J* 7 Hz, 2-$CH_2$), 3.67 (3 H, s, $CO_2Me$), 5.13—5.23 (3 H, m, 2 × 11- and 9-H), and 5.77 (1 H, ddd, *J* 6, 10, and 17 Hz, 10-H); *m/z* 214 ($M^+ - 42$) and 43 (base peak, $C_2H_3O^+$).

*Methyl* (E)-11-*Hydroxyundec*-9-*enoate* (**8b**).—To a stirred solution of the acetate (**7b**) (2.72 g, 11 mmol) in dry benzene (15 $cm^3$) was added [$PdCl_2(MeCN)_2$] (0.12 g, 5 mol %). The reaction was allowed to proceed for 45 min at room temperature after which the solvent was removed and the residue extracted with petroleum and the extract filtered through Celite. The filtrate was washed with 2% aqueous sodium cyanide (× 3), dried, and evaporated to give a 1:3 mixture of the acetates (**7b**) and (**8a**). The syrup (2.5 g, 11.7 mmol) in dry methanol (18 $cm^3$) was treated with sodium methoxide (0.257 g, 5 mol % NaOMe) under nitrogen for 6 h at room temperature. The solution was treated with IR-120$H^+$ until neutral, filtered, and the filtrate evaporated to afford a residue which by chromatography on silica gel with petroleum–diethyl ether (5:1) as eluant gave two fractions. The fast-running component was the alcohol (**7a**) (0.394 g, 17%). The slower-running component was methyl (9*E*)-11-hydroxyundec-9-enoate (**8b**) (1.6 g, 64%); $\nu_{max.}(CHCl_3)$ 3 500, 2 930, 2 860, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 1.31—1.47 (8 H, m, 4 × $CH_2$), 1.49 (1 H, br s, OH), 1.54—1.65 (2 H, m, $CH_2$), 2.05 (2 H, m, 8-$CH_2$), 2.31 (2 H, t, *J* 7 Hz, 2-$CH_2$), 3.67 (3 H, s, $CO_2Me$), 4.09 (2 H, dd, *J* 1 and 5 Hz, 11-H), and 5.55—5.69 (2 H, m, 9- and 10-H) (addition of $D_2O$ caused the signal at δ1.49 to disappear); *m/z* 196 ($M^+ - 18$).

*Methyl* (9E)-11-*Oxoundec*-9-*enoate* (**9**).—To a rapidly stirred solution of the alcohol (**8b**) (1.6 g, 7.5 mmol) in petroleum (40 $cm^3$) was added manganese dioxide (16 g, 10 mass equiv.). After 18 h at room temperature the mixture was filtered through Celite and the filter pad was washed with diethyl ether (× 2). The combined eluants were evaporated to afford a residue, chromatography of which on silica gel with petroleum–diethyl ether (2:1) as eluant gave the aldehyde (**9**) (1.17 g, 74%): $\nu_{max.}(CHCl_3)$ 2 930, 1 738, and 1 695 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 1.33—1.66 (12 H, m, 6 × $CH_2$), 2.31 (2 H, t, *J* 8 Hz, 2-$CH_2$), 3.67 (3 H, s, $CO_2Me$), 6.17 (1 H, dd, *J* 8 and 16 Hz, 10-H), 6.86 (1 H, dt, *J* 7 and 16 Hz, 9-H), and 9.51 (1 H, d, *J* 8 Hz, CHO); *m/z* 212 ($M^+$), 181 ($M^+ - 31$), 152 ($M^+ - 60$), and 55 (base peak) (Found: $M^+$, 212.1406. $C_{12}H_{20}O_3$ requires 212.1412).

*Methyl* (9E,12Z)-11-*Hydroxyoctadeca*-9,12-*dienoate* (**10a**).—To a flame-dried flask under argon containing magnesium (0.108 g, 4.5 mmol) in dry tetrahydrofuran (8 $cm^3$) was added 1,2-dibromoethane (4 drops) followed by (*Z*)-1-bromoheptene (0.531 g, 3 mmol) in dry tetrahydrofuran (8 $cm^3$). The mixture was heated under reflux for 6 h. After the mixture had cooled to room temperature a solution of the aldehyde (**9**) (0.424 g, 2 mmol) in tetrahydrofuran (8 $cm^3$) was added and the mixture stirred for a further 8 h. The mixture was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was washed with brine, dried, and evaporated to afford a residue, chromatography of which on silica gel with petroleum–diethyl ether (5:1) as eluant gave successively the (*Z*)-1-bromoheptene (0.236 g), aldehyde (**9**) (0.153 g, 36%), the title compound (**10a**) (0.206 g, 33%); $\nu_{max.}(CHCl_3)$ 3 520, 2 930, 2 855, 1 740, and 1 690 $cm^{-1}$; $\delta_H$(200 MHz, $C_6D_6$) 0.96 (3 H, t, 18-Me), 1.24 (16 H, m, 8 × $CH_2$), 1.56 (3 H, m, $CH_2$ and OH), 2.02 (2 H, m, 14-$CH_2$), 2.14 (2 H, t, *J* 7 Hz, 2-$CH_2$), 3.38 (3 H, s, $CO_2Me$), 4.95 (1 H, m, 11-H), and 5.34—5.68 (4 H, m, 9-, 10-, 12-, and 13-H); $\delta_C$ 173.4, 133.0, 132.6, 131.2, 130.9, 68.9, 50.9, 34.1, 32.5, 32.4, 31.8, 29.6, 29.5, 29.4, 29.3, 28.0, 25.3, 22.9, and 14.2; *m/z* 310 ($M^+$), 292 ($M^+ - 18$), and 43 (base peak) (Found: $M^+$, 310.2493. $C_{19}H_{34}O_3$ requires 310.2508).

*Methyl* (9E,12Z)-11-*Acetoxyoctadeca*-9,12-*dienoate* (**10b**).—To a solution of the alcohol (**10a**) (0.206 g, 0.66 mmol) in pyridine (2 $cm^3$) was added acetic anhydride (0.075 $cm^3$, 0.79 mmol) followed by 4-dimethylaminopyridine (4 mg, 5 mol %). After 30 min at room temperature the mixture was washed with dilute hydrochloric acid (1M) and extracted into diethyl ether. The extract was washed with saturated aqueous sodium hydrogen carbonate and water, dried, and evaporated to afford a residue, chromatography of which on silica gel with petroleum–diethyl ether (2:1) as eluant gave the dienyl acetate (**10b**) (0.182 g, 78%); $\nu_{max.}(CHCl_3)$ 2 930, 2 860, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.96 (3 H, t, 18-Me), 1.38 (16 H, m, 8 × $CH_2$), 1.62 (2 H, m, $CH_2$), 2.09 (3 H, s, COMe), 2.14 (2 H, m, 14-$CH_2$), 2.29 (2 H, t, *J* 7 Hz, 2-$CH_2$), 3.67 (3 H, s, $CO_2Me$), 5.30—5.78 (4 H, m), and 5.96 (1 H, dd, *J* 7 and 15 Hz, 10-H) (Found: $M^+$, 352.2602. $C_{21}H_{36}O_4$ requires 352.2613).

$Pd^{II}$-*Catalysed Rearrangement of Methyl* (9E,12Z)-11-*Acetoxyoctadeca*-9,12-*dienoate* (**10b**)—A solution of the dienyl acetate (**10b**) (0.150 g, 0.43 mmol) in dry benzene (2 $cm^3$) was treated with [$PdCl_2(MeCN)_2$] (5 mg, 5 mol %). The reaction was allowed to proceed for 45 min at room temperature after which the solvent was removed and the residue extracted with petroleum. The extract was filtered through Celite and the combined filtrates were washed with 2% aqueous sodium cyanide, dried, and evaporated to give predominantly methyl (10*E*,12*Z*)-9-acetoxyoctadeca-10,12-dienoate (**2i**) (0.145 g, 97%); $\nu_{max.}(CHCl_3)$ 2 930, 2 860, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.85 (3 H, t, 18-Me), 1.03—1.43 (14 H, m, 7 × $CH_2$), 1.57—1.90 (4 H, m, 2 × $CH_2$), 2.05 (3 H, s, COMe), 2.18 (2 H, d, *J* 7 Hz, 14-$CH_2$), 2.29 (2 H, t, *J* 8 Hz, 2-$CH_2$), 3.63 (3 H, s, $CO_2Me$), 5.23 (1 H, m, 9- or 13-H), 5.31 (1 H, m, 9- or 13-H), 5.51 (1 H, dd, *J* 7 and 15 Hz, 10-H), 5.94 (1 H, t, *J* 11 Hz, 12-H), and 6.50 (1 H, dd, *J* 11 and 15 Hz, 11-H); *m/z* 352 ($M^+$) 310 ($M^+ - 42$) and 292 ($M^+ - 60$) (Found: $M^+$, 352.2602. $C_{21}H_{36}O_4$ requires $M^+$, 352.2613).

*Methyl* (10E,12Z)-9-*Hydroxyoctadeca*-10,12-*dienoate* (**2e**).—A solution of the dienoate (**2i**) (0.145 g, 0.41 mmol) in dry methanol (1 $cm^3$) was treated with sodium methoxide (5 mol % NaOMe) under nitrogen for 5 h at room temperature. The mixture was treated with IR-120$H^+$ resin until neutral, filtered, and the filtrate evaporated to afford a residue, chromatography of which on silica gel with petroleum–diethyl ether (3:1) (containing 1% triethylamine) as eluant gave the title compound (**2e**) (0.094 g, 74%); $\lambda_{max.}$(EtOH) 233 (ε 23 480 $dm^3$ $mol^{-1}$ $cm^{-1}$) and 244sh nm (14 490); $\nu_{max.}(CHCl_3)$ 3 430, 2 930, 2 860, and 1 740 $cm^{-1}$; $\delta_H$(200 MHz, $CDCl_3$) 0.88 (3 H, t, 18-Me), 0.92–1.47 (14 H, m, 7 × $CH_2$), 1.55—1.65 (3 H, m, $CH_2$ and OH), 2.18 (2 H, q, *J* 7 Hz, 14-$CH_2$), 2.30 (2 H, t, *J* 7 Hz, 2-$CH_2$), 3.67 (3 H, s, $CO_2Me$), 4.14 (1 H, dd, *J* 6 and 13 Hz, 9-H), 5.46 (1 H, dt, *J* 7 and 11 Hz, 13-H), 5.65 (1 H, dd, *J* 7 and 15 Hz, 10-H), 5.97 (1 H, t, *J* 11 Hz, 12-H), and 6.48 (1 H, dd, *J* 11 and 15 Hz, 11-H); $\delta_C$ 174.2, 135.8, 133.0, 127.8, 125.9, 72.9, 51.4, 37.4, 34.1, 31.5, 29.3, 29.2, 29.1, 27.8, 25.4, 24.9, 22.6, and 14.0; *m/z* 310 ($M^+$), 292 ($M^+ - 18$), and 279 ($M^+ - 31$) (Found: $M^+$, 310.2487. $C_{19}H_{34}O_3$ requires $M^+$, 310.2508).

(2E,5Z)-1-*Dimethyl*-*t*-*butylsilyloxyundeca*-2,5-*dien*-4-*ol* (**11a**).—A suspension of magnesium (0.432 g, 18 mmol) in dry tetrahydrofuran (30 $cm^3$) under argon was treated with 1,2-dibromoethane (4 drops). The mixture was heated under reflux for 10 min after which (*Z*)-1-bromoheptene (3.19 g, 18 mmol) in tetrahydrofuran (10 $cm^3$) was added and heating under reflux continued for 3.5 h. The mixture was cooled and a solution of the aldehyde (**5**) (2.1 g, 11 mmol) in tetrahydrofuran (10 $cm^3$) was added. After the mixture had been stirred for a further 1 h at room temperature, the reaction was quenched with saturated

aqueous ammonium chloride. The resulting mixture was extracted wiith diethyl ether and the combined extracts were dried and evaporated to provide, by chromatography on silica gel with petroleum–diethyl ether (5:1) as eluant, the (*E,Z*)-dienyl alcohol (**11a**) (2.56 g, 78%); $\nu_{max.}$(CHCl$_3$) 3 355, 2 957, 2 929, and 2 858 cm$^{-1}$; $\delta_H$(200 MHz, CDCl$_3$) 0.067 (6 H, s, SiMe$_2$), 0.91—0.99 (12 H, m, CMe$_3$ and 11-Me), 1.22—1.50 (6 H, m, 3 × CH$_2$), 1.73 (1 H, br s, OH), 2.04—2.11 (2 H, m, 7-CH$_2$), 4.17 (2 H, m, 1-CH$_2$), 4.97 (1 H, m, 4-H), and 5.34—5.84 (4 H, m, 2-, 3-, 5-, and 6-H); $\delta_C$ 132.6, 131.7, 130.9, 130.2, 68.4, 63.3, 31.6, 29.4, 27.8, 26.1, 25.8, 22.6, 18.5, 18.1, 14.1, −3.4, and −5.1; *m/z* 298 ($M^+$), 280 ($M^+$ − 18), and 241 ($M^+$ − 57) (Found: $M^+$, 298.2323. $C_{17}H_{34}O_2Si$ requires $M^+$, 298.2328).

(2E,5Z)-4-*Acetoxy*-1-*dimethyl-t-butylsilyloxyundeca*-2,5-*diene* (**11b**).—A solution of the dienol (**11a**) (2.4 g, 8 mmol) in dry pyridine (15 cm$^3$) was treated with acetic anhydride (0.91 cm$^3$, 9.7 mmol) followed by 4-dimethylaminopyridine (0.045 g, 5 mol %) for 1 h at room temperature. The solution was poured into 5M hydrochloric acid and extracted into diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and the solvent removed to give the compound (**11b**) (2.36 g, 87%); $\nu_{max.}$(CHCl$_3$) 2 930 and 1 740 cm$^{-1}$; $\delta_H$(200 MHz, CDCl$_3$) 0.061 (6 H, s, SiMe$_2$), 0.85—0.94 (12 H, m, CMe$_3$ and 11-Me), 1.22—1.64 (6 H, m, 3 × CH$_2$), 2.05 (3 H, s, COMe), 2.09 (2 H, m, 7-CH$_2$), 4.17 (2 H, m, 1-CH$_2$), 5.38 (1 H, m), 5.52—5.85 (3 H, m), and 6.02 (1 H, m); *m/z* 283 ($M^+$ − 57), 281 ($M^+$ − 59), and 43 (base peak) (Found: $M^+$ − 57, 283.1732. $C_{15}H_{27}O_3Si$ requires 283.1729).

(3E,5Z)-2-*Acetoxy*-1-*dimethyl-t-butylsilyloxyundeca*-3,5-*diene* (**12a**).—A stirred solution of the diene (**11b**) (2.3 g, 6.9 mmol) in dry benzene (5 cm$^3$) was treated with [PdCl$_2$(MeCN)$_2$] (0.087 g, 0.34 mmol). The reaction was allowed to proceed for 2 h at room temperature after which the solvent was removed and the residue extracted with petroleum. The extract was filtered through Celite and the combined filtrates were washed with 2% aqueous sodium cyanide, dried, and evaporated to give predominantly the diene (**12a**) (2.16 g, 94%); $\delta_H$(200 MHz, CDCl$_3$) *inter alia* 0.06 (6 H, s, SiMe$_2$), 0.89 (12 H, m, CMe$_3$ and 11-Me), 1.25 (6 H, m, 3 × CH$_2$), 2.05 (3 H, s, COMe), 2.11 (2 H, m, 7-CH$_2$), 3.68 (2 H, m, 1-CH$_2$), 5.36—5.89 (4 H, m, 2-, 3-, 5-, and 6-H), and 6.58 (1 H, dd, *J* 11 and 15 Hz, 4-H).

(3E,5Z)-*Undeca*-3,5-*diene*-1,2-*diol* (**12b**).—A solution of the diene (**12a**) (2.16 g, 6.3 mmol) in dry methanol (10 cm$^3$) was treated with sodium methoxide in methanol (0.082 cm$^3$, 5 mol % NaOMe) under nitrogen for 12 h at room temperature. The mixture was treated with IR-120H$^+$ resin until neutral, filtered, and evaporated. The crude product (1.48 g) was dissolved in tetrahydrofuran (20 cm$^3$) and treated with tetrabutylammonium fluoride in tetrahydrofuran (5.95 cm$^3$, 5.95 mmol F$^-$) for 1 h at room temperature. The solution was poured into water, extracted with diethyl ether, and the extract dried and evaporated to afford a residue, chromatography of which on silica gel with petroleum–diethyl ether (5:1) (containing 1% triethylamine) as eluant gave the diol (**12b**) (0.155 g, 17%); $\nu_{max.}$(CHCl$_3$) 3 380 and 2 930 cm$^{-1}$; $\delta_H$(200 MHz, CDCl$_3$), 0.89 (3 H, t, 11-Me), 1.89 (6 H, m, 3 × CH$_2$), 2.13 (2 H, m, 7-CH$_2$), 2.41 (2 H, br s, OH), 3.49 (1 H, dd, *J* 7.5 and 15 Hz, 1-H), 3.66 (1 H, dd, *J* 3.5 and 15 Hz, 1-H), 4.24 (1 H, m, 2-H), 5.45 (1 H, dt, *J* 7.5 and 16 Hz, 3-H), 5.58 (1 H, dt, *J* 6.5 and 11 Hz, 6-H), 5.98 (1 H, t, *J* 11 Hz, 5-H), and 6.60 (1 H, dd, *J* 11 and 16 Hz, 4-H) (addition of $D_2O$ caused the signal at δ 2.41 to disappear); *m/z* 185 ($MH^+$) and 167 ($MH^+$ − 18) (Found: $M^+$, 184.1471. $C_{11}H_{20}O_2$ requires $M^+$, 184.1463).

(2E,4Z)-*Deca*-2,4-*dienal* (**2f**).—A solution of the diol (**12b**) (0.059 g, 0.32 mmol) in tetrahydrofuran (0.7 cm$^3$) was treated with a solution of sodium periodate (0.075 g, 0.35 mmol) in pH 7 phosphate buffer (0.5 cm$^3$) for 1 h at room temperature. The suspension was filtered, washed with water, and extracted with diethyl ether and the extract dried and evaporated. Chromatography of the residue on silica gel with petroleum–diethyl ether (5:1) as eluant gave predominantly (2*E*,4*Z*)-deca-2,4-dienal (**2f**) (0.045 g, 82%); $\nu_{max.}$(CHCl$_3$) 1 680 and 1 630 cm$^{-1}$; $\delta_H$(200 MHz, CDCl$_3$) *inter alia* 0.91 (3 H, m, 10-Me), 1.11—1.66 (6 H, m, 3 × CH$_2$), 2.35 (2 H, m, 6-CH$_2$), 6.04 (1 H, dt, *J* 8 and 11 Hz, 5-H), 6.14 (1 H, dd, *J* 8 and 15 Hz, 2-H), 6.36 (1 H, dd, *J* 11 Hz, 4-H), 7.44 (1 H, dd, *J* 11 and 15 Hz, 3-H), and 9.63 (1 H, d, *J* 8 Hz, CHO); *m/z* 152 ($M^+$), 123 ($M^+$ − 29), 95 ($M$ − 57), and 81 (base peak) (Found: $M^+$, 152.1204. $C_{10}H_{16}O$ requires *M*, 152.1201).

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## References

1 B. T. Golding, C. Pierpoint, and R. Aneja, *J. Chem. Soc., Chem. Commun.*, 1981, 1030.
2 E. H. Curzon, B. T. Golding, C. Pierpoint, and B. W. Waters, *J. Organomet. Chem.*, 1984, **262**, 263.
3 P. M. Henry, *J. Am. Chem. Soc.*, 1972, **92**, 5200.
4 D. A. Howes, M. H. Brookes, D. Coates, B. T. Golding, and A. T. Hudson, *J. Chem. Res.*, 1983, (*S*), 9; (*M*), 217.
5 E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, 1972, **94**, 6190.
6 M. Julia and C. Lefebvre, *Tetrahedron Lett.*, 1984, 189.
7 R. C. Badami and L. J. Morris, *J. Am. Oil Chem. Soc.*, 1965, **42**, 1119.
8 C. J. W. Brooks, W. A. Harland, G. Steel, and J. D. Gilbert, *Biochim. Biophys. Acta*, 1970, **202**, 563.
9 T. Kato, Y. Yamaguchi, T. Hirano, T. Yokoyama, T. Uyehara, T. Namai, S. Yamanaka, and N. Harada, *Chem. Lett.*, 1984, 409.
10 A. V. Rama Rao, E. Rajarathnam Reddy, G. V. M. Sharma, P. Yadagiri, and J. S. Yadav, *Tetrahedron Lett.*, 1985, 465.
11 L. Crombie and S. J. Holloway, *J. Chem. Soc., Chem. Commun.*, 1984, 953.
12 W. Renold, R. Naf-Muller, U. Keller, B. Willhalm, and G. Oholff, *Helv. Chim. Acta*, 1974, **57**, 1301.
13 G. Rickards and L. Weiler, *J. Org. Chem.*, 1978, **43**, 3607.
14 F. Naf and R. Decorzant, *Helv. Chim. Acta*, 1974, **57**, 1309.
15 E. L. Jackson, in 'Organic Reactions,' ed. R. Adams, Wiley, New York, vol. II, p. 341.
16 B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; E. I. Negishi, *ibid.*, 1982, **15**, 340; R. F. Heck, 'Palladium Reagents in Organic Synthesis,' Academic Press, London, 1985.
17 E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1951, 2078 and 2085.
18 *cf.* B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchell, 'Vogel's Textbook of Practical Organic Chemistry,' Longman, London, 1978, p. 419.

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