Acetylcyclopropane as a Five-Carbon Building Block in the Synthesis of some Acetogenin Insect Pheromones†

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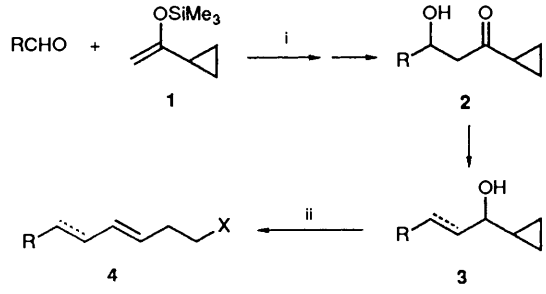
Interaction of deprotonated acetylcyclopropane cyclohexylimine with several aliphatic alkyl halides, epoxides, and aldehydes efficiently gave the corresponding cyclopropyl ketones. Some of the respective alcohols were rearranged in a highly stereoselective manner under the action of trimethylsilyl bromide in the presence of zinc bromide into the corresponding linear (*E*)-homoallyl bromides. The latter were used, in turn, as key intermediates in concise syntheses of thirteen terminally functionalized straight-chain oligoolefins which are known to constitute acetogenin pheromonal components for more than 65 species of lepidopteran insects.

Most of the known acetogenin-type sex pheromones and attractants produced by moth and butterfly species (Lepidoptera) belong to a series of terminally functionalized, straight-chain linear oligoolefins with a fixed stereochemistry of internal, disubstituted C=C bond(s).[1,2] Conventional methods for their synthesis are based now mainly on the transformation of appropriate acetylene and/or olefination of suitable aldehyde precursors.[1,3] Our own interest in the transoid mono- and 1,3-di-enic representatives of these compounds as well as related semiochemicals has recently led to elaboration of an effective approach based on transformation of zinc chloride-catalysed coupling products of aliphatic aldehydes with acetylcyclopropane as its trimethylsilyl enolate **1** (Scheme 1).[4,5] Further



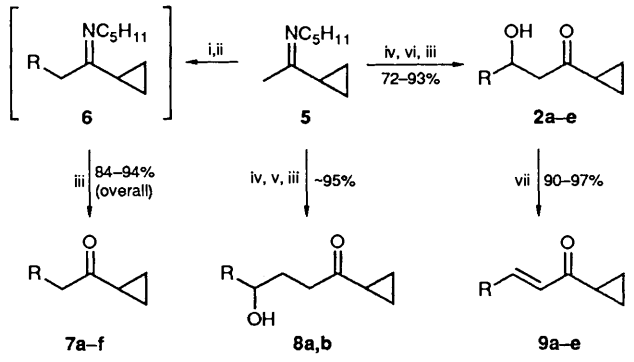
Scheme 1 *Reagents:* i, $ZnCl_2$; ii, Me_3SiX, ZnX_2

steps in this sequence involve simple conversion of intermediate aldol **2** into synthetically useful[6–9] (un)saturated cyclopropyl ketones and their respective secondary alcohols **3** which were found readily to undergo trimethylsilyl halide–zinc halide-induced, highly stereoselective rearrangement into the corresponding linear homoallyl halides **4**. We have considerably extended the developed methodology, introducing into the above sequence the cyclohexylimino derivative of acetylcyclopropane, which is more reactive than the silyl enol ether **1**. As a result, coupling of this five-carbon building block with a series of alkyl halides, epoxides, or aldehydes opened up an easy access to compounds of types **3** and **4**; some of them were further used as key intermediates in short syntheses of several acetogenin sex pheromones and attractants, which are described below.[10]

Results and Discussion

Interaction of the organolithium derivative of the above

† Submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.



a, R = Me
b, R = Pr
c, R = n-C_7H_{15}
d, R = n-C_9H_{19}
e, R = (*E*)-BuCH=CH[CH_2]$_3$
f, R = (*Z*)-BuCH=CH[CH_2]$_7$

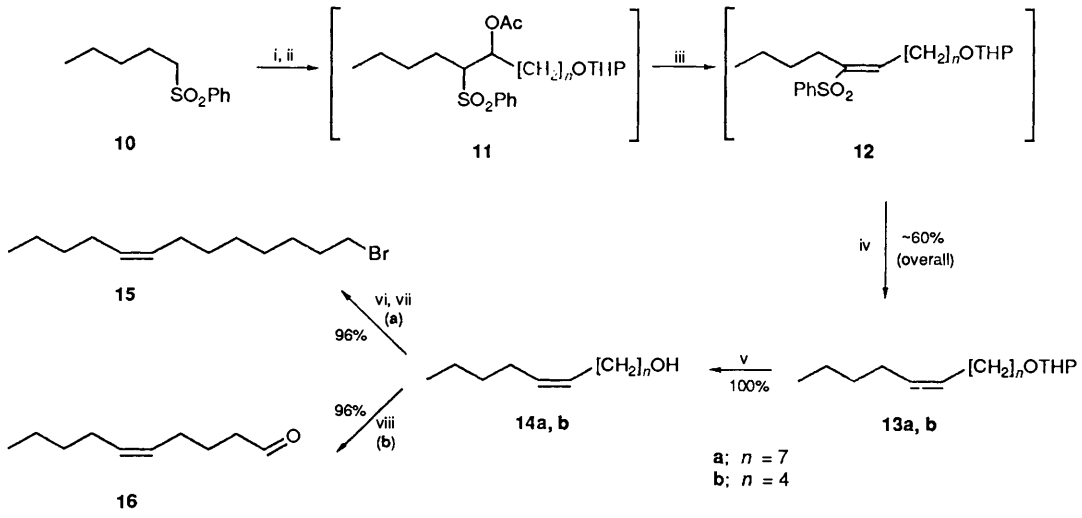
a, R = H
b, R = Me

a, R = Et
b, R = Bu
c, R = n-C_6H_{13}
d, R = n-C_8H_{17}
e, R = (*Z*)-BuCH=CH-[CH_2]$_3$

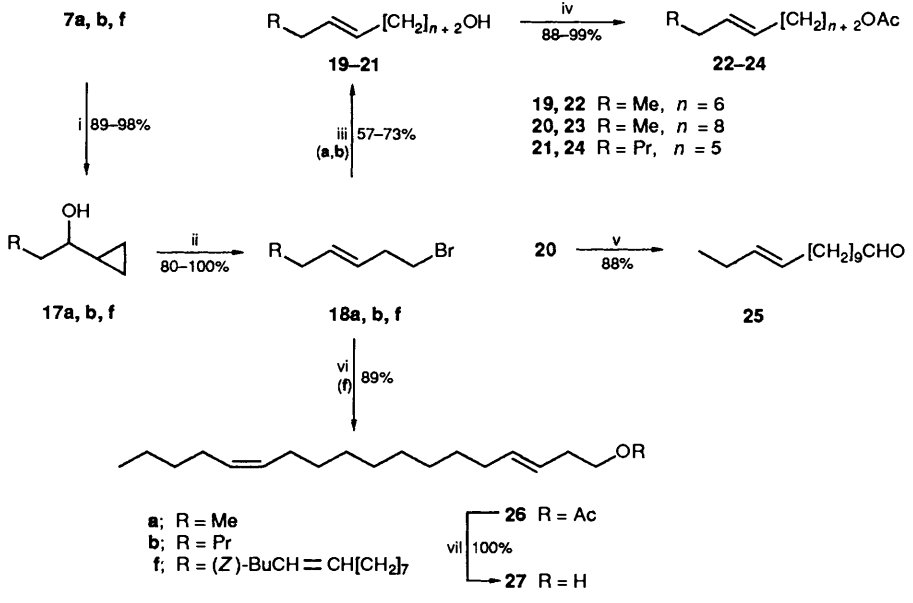
Scheme 2 *Reagents and conditions:* i, BuLi, THF HMPA hexane, −70 to 0 °C, 1 h; ii, RX (**a**, X = I, **b**–**f**, X = Br), THF, −70 to 25 °C, 2 h; iii, silica gel, without solvent, 25 °C, 15 min; iv, LDA, THF HMPA–hexane, −30 to 0 °C, 1 h; v, RCHCH$_2$O, THF, −70 to 0 °C, 40 min; vi, RCHO, THF, −70 to 5 °C, 20 min; vii, TsOH (cat.), C_6H_6, 80 °C, 20 min

mentioned imine **5** prepared in tetrahydrofuran (THF), in the presence of hexamethylphosphoramide (HMPA) as a co-solvent, with alkyl and alkenyl halides furnished intermediate ketimines **6** (Scheme 2). Their standard hydrolytic cleavage in the presence of proton or Lewis acids[11] proceeded slowly, however (for *ca.* 24 h), to give the respective cyclopropyl ketones **7a–f** in less than 50% yield. This could markedly be increased, up to 95%, on brief (*ca.* 15 min) exposure of the crude imines **6** to a 3–4-fold amount (w/w) of silica gel under 'dry state' conditions.[12]

Metallation of the imine **5** with lithium diisopropylamide (LDA) and interaction with ethylene and propylene oxides, followed by hydrolytic cleavage of intermediate products on silica gel, led to the γ-hydroxy ketones **8a**, **b** in high overall yield. A similar reaction sequence with the participation of imine **5** and several aldehydes smoothly afforded the β-hydroxy ketones **2a–e**. Their toluene-*p*-sulphonic acid (TsOH)-catalysed dehydration gave almost quantitatively the conjugated ketones **9a–e**. It is noteworthy that the lithiated imine **5** interacts with the above electrophiles regiospecifically at the methyl group in all cases.



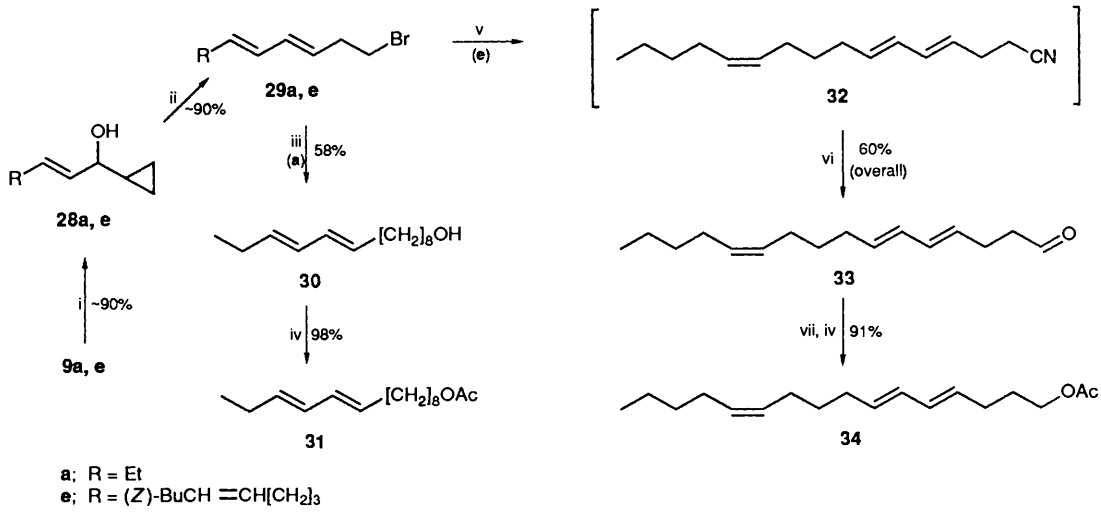
Scheme 3 *Reagents and conditions:* i, BuLi, THF–HMPA–hexane, −70 to −15 °C, 30 min; then $THPO[CH_2]_nCHO$, THF, −70 to −10 °C, 30 min; ii, Ac_2O, DMAP (cat.), −10 to 25 °C, 50 min; iii, NaOH, Et_2O, MeOH (cat.), 25 °C, 20 min; iv, $Na_2S_2O_4$, $NaHCO_3$, aq. EtOH, 80 °C, 7 h; v, PPTS (cat.), MeOH, 50 °C, 2 h; vi, BuLi, Et_2O–HMPA–hexane, −30 °C; then toluene-*p*-sulphonyl chloride (TsCl), −30 to 25 °C, 15 min; vii, NaBr, DMF, 50 °C, 1 h; viii, $(COCl)_2$, Me_2SO, Et_3N, CH_2Cl_2, −60 to −15 °C, 2 h



Scheme 4 *Reagents and conditions:* i, $LiAlH_4$, Et_2O, 0 °C, 20 min; ii, Me_3SiBr, $ZnBr_2$ (cat.), CH_2Cl_2, −10 to 0 °C, 30 min; iii, $BrMg[CH_2]_nOMgBr$, Li_2CuCl_4 (cat.), THF–HMPA, −70 to 0 °C, 1 h; iv, Ac_2O, C_5H_5N, DMAP (cat.), 25 °C, 30 min; v, PCC, CH_2Cl_2, 25 °C, 2 h; vi, AcOK, DB-18-C-6 (cat.), MeCN, 80 °C, 15 h; vii, NaOH, aq. MeOH, 25 °C, 15 min

Necessary for the preparation of previously unknown ketones **7f** and **9e**, (*Z*)-bromide **15** and (*Z*)-aldehyde **16** were synthesized according to the method of Julia[13] from the corresponding tetrahydropyranyl (THP) ethers of ω-hydroxy aldehydes and lithiated sulphone **10** *via* crude acetate **11** obtained, in turn, from the intermediate alcohols in the presence of 4-(dimethylamino)pyridine (DMAP) as catalyst (Scheme 3). It should be noted that the next step in the sequence, leading to vinyl sulphones of type **12**, is normally effected by prolonged (for *ca.* 24 h) treatment of the precursors indicated with powdered alkali in dry diethyl ether. We have found that employment in this case of a catalytic amount of methanol greatly accelerates the reaction, thus securing full conversion of the starting material **11** within *ca.* 20 min only. Further treatment of the crude vinyl sulphones **12** with sodium dithionite smoothly gave the ethers **13a**, **b**, which were first quantitatively deprotected using pyridinium toluene-*p*-sulphonate (PPTS) to give the known (*Z*)-alcohols **14a**, **b**, which were then converted by standard methods into the desired bromide **15** and aldehyde **16**. According to NMR and capillary GLC data, stereochemical purity of the olefins **13**–**16** was greater than 95%.

We have recently demonstrated the applicability of the cyclopropyl building blocks **7b**–**e** and **9a**–**d** for the construction of a variety of Lepidoptera sex pheromones and attractants.[4,5] The former series of the precursors **7** now became particularly available from the acetylcyclopropane derivative **5**. Following the elaborated approach, and starting from some of the cyclopropyl ketones **7**–**9** prepared as mentioned above, total syntheses of several mono-, di- and tri-ene representatives of the insect behaviour regulators were performed. Starting from the cyclopropyl ketones **7a**, **b**, **f** the (*E*)-monoolefinic alcohols **19**–**21**, their acetates **22**–**24**, and aldehyde **25** as well as octadeca-3*E*,13*Z*-dienyl acetate **26** and respective alcohol **27** were obtained (Scheme 4). For this purpose, the ketones **7a**, **b**, **f** were first reduced to the corresponding cyclopropyl alcohols **17a**, **b**, **f**, which were then treated with trimethylsilyl bromide and a catalytic amount of zinc bromide following the procedure reported by us,[4] to give the rearranged (*E*)-homoallyl bromides



Scheme 5 *Reagents and conditions:* i, $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, −50 °C, 15 min; ii, Me_3SiBr, $ZnBr_2$ (cat.), CH_2Cl_2, −20 °C, 15 min; iii, $BrMg[CH_2]_6OMgBr$, Li_2CuCl_4 (cat.), THF–HMPA, −70 to 0 °C, 1 h; iv, Ac_2O, C_5H_5N, DMAP (cat.), 25 °C, 30 min; v, KCN, DB-18-C-6 (cat.), MeCN, 80 °C, 12 h; vi, DIBAL, PhMe–hexane, −70 °C, 40 min; vii, $LiAlH_4$, Et_2O, 0 °C, 15 min

18a, **b**, **f** in 80–100% yield and of more than 95% stereochemical purity (NMR and GLC data). Subsequent dilithium tetrachlorocuprate[14]-catalysed coupling of the bromides **18a**, **b**, **f** with the Grignard reagents prepared, under the conditions recommended,[15] from the α,ω-bromoalkanols $Br[CH_2]_nOH$ led smoothly to the primary alcohols **19**–**21**, which were readily convertible into their respective acetates **22**–**24**. Finally, pyridinium chlorochromate (PCC) oxidation of the alcohol **20** gave the aldehyde **25**, while treatment of the bromide **18f** with potassium acetate in the presence of dibenzo-18-crown-6 (DB-18-C-6) furnished the acetate **26**, which was further hydrolysed to the alcohol **27**.

Among the compounds thus synthesized the dienes **26** and **27** are known to be sex pheromones of the female lesser peachtree borer (*Synanthedon pictipes*)[16] and the poplar twig clearwing moth (*Paran-threne tabaniformis*),[17] respectively, while their mixture attracts the strawberry crown moth (*Synanthedon bibionipennis*)[18] and the raspberry clearwing moth (*Pennisetia hylaeformis*).[19] According to earlier data,[1] the alcohols **19** and **20** and the aldehyde **25** are the components of sex pheromones and attractants for six Lepidoptera species, while the acetates **22** and **23** display the same biological functions for 18 and 30 species, respectively.

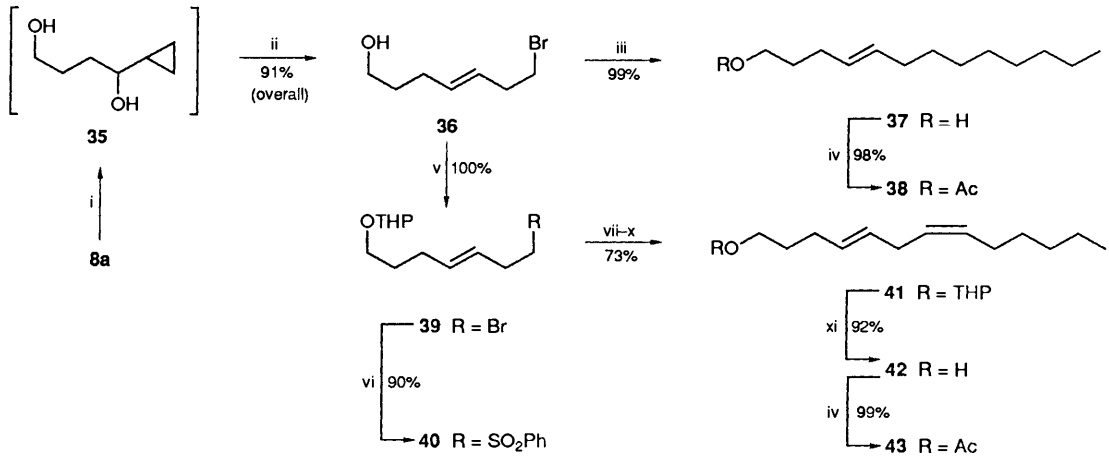
In addition, compounds **19**, **20**, **22**, **23** and **25**, either singly or in combinations, have been recently shown to constitute pheromonal components for more than 15 species of Lepidoptera insects.[20–34] For example, the alcohol **19** and its corresponding acetate **22** were identified as the major components of the sex attractant for the male pine shootmoth (*Rhyacionia buoliana*).[20] On the other hand, the acetate **22** serves itself as sex attractant for the male purple striped shootworm (*Zeiraphera unfortunana*).[25] The same role was revealed for the acetate **23** isolated from the female leafroller moth (*Syndemis musculana*),[26] sunflower moth (*Cochylis hospes*),[27] and lima-bean pod borer (*Etiella zinckenella*).[28] Finally, the aldehyde **25** is known as a pheromonal component emitted by the female eastern spruce budworm (*Choristoneura fumiferana*).[30]

Based on our developed approach the unsaturated cyclopropyl ketones **9a**, **e** were transformed into the target tetradeca-9*E*,11*E*-dienyl acetate **31**, hexadeca-4*E*,6*E*,11*Z*-trienal **33**, and the related acetate **34** (Scheme 5). Among these compounds, the former diene **31**, along with the respective 14-carbon (*E*)-olefin **23**, were recently identified as the major sex pheromone components of the female light brown applemoth (*Epiphyas postvittana*)[35] while the two latter trienes, **33** and **34**, demonstrated the same function for the erisilkworm moth (*Samia cynthia ricini*).[36] Their synthesis was performed by cerium(III) chloride-induced sodium borohydride reduction[37] of the precursors **9a**, **e**, followed by isomerization of the intermediate cyclopropylallyl alcohols **28a**, **e** to the key homoallyl bromides **29a**, **e**. Subsequent six-carbon homologation of the bromide **29a** led, as in the above cases, to the dienol **30**, and then to its corresponding acetate **31** in good overall yield. On the other hand, intermediate cyanide **32**, readily available from the bromide **29e**, was reduced with diisobutylaluminium hydride (DIBAL) to the aldehyde **33**, which was converted, in turn, into the acetate **34**.

The strategy developed was finally applied to the total synthesis of tridec-4*E*-enyl acetate **38** and trideca-4*E*,7*Z*-dienyl acetate **43** which are known to be sex pheromone components of the female tomato pinworm moth (*Keiferia lycopersicella*)[38] and the potato tuberworm moth (*Phtorimaea operculella*),[39] respectively (Scheme 6). Hence, the starting γ-hydroxy ketone **8a** was first transformed stereospecifically, *via* intermediate cyclopropyl derivative **35**, to the previously unknown homoallylic bromide **36** containing an (*E*)-hydroxypentenyl fragment characteristic of both the above pheromonal molecules. Würtz-type six-carbon elongation of the bromide **36** with an appropriate Grignard reagent furnished the alcohol **37** and, subsequently, its corresponding acetate **38** in 88% overall yield. On the other hand, the bromo alcohol **36** was also transformed to the THP ether **39** and then to the sulphone **40**. Employment of the latter for Julia olefination of hexanal gave the ether **41**, which was further hydrolysed to the alcohol **42**, which was then converted, in turn, into the target acetate **43** in good overall yield.

The structures of all the compounds under consideration were confirmed by spectral methods as well as by comparison of their physicochemical properties with those available for the known products. Purity of the hitherto unknown compounds was additionally checked by their microanalysis data. According to ^1H and ^{13}C NMR and capillary GLC data, stereochemical purity of the olefins prepared is greater than 95% in all cases.

The data presented above illustrate that readily available acetylcyclopropane is a versatile five-carbon building block for the preparation of various alkyl- and alkenyl-cyclopropyl ketones which, in turn, serve as valuable intermediates for effective regio- and stereo-controlled synthesis of a number of linear olefins, including some acetogenin-type insect pheromones.



Scheme 6 *Reagents and conditions:* i, $LiAlH_4$, Et_2O, 0 °C, 25 min; ii, Me_3SiBr, $ZnBr_2$ (cat.), CH_2Cl_2, −10 °C, 30 min; iii, n-$C_6H_{13}MgBr$, Li_2CuCl_4 (cat.), THF, −60 to 25 °C, 1 h; iv, Ac_2O, C_5H_5N, DMAP (cat.), 25 °C, 30 min; v, 3,4-dihydro-2*H*-pyran, PPTS (cat.), CH_2Cl_2, 25 °C, 2 h; vi, $PhSO_2Na$, DMF, 60 °C, 3 h; vii, BuLi, THF–HMPA–hexane, −70 to −15 °C, 30 min; then hexanal, THF, −70 to −10 °C, 30 min; viii, Ac_2O, DMAP (cat.), −10 to 25 °C, 50 min; ix, NaOH, Et_2O, MeOH (cat.), 25 °C, 20 min; x, $Na_2S_2O_4$, $NaHCO_3$, aq. EtOH, 80 °C, 7 h; xi, PPTS (cat.), MeOH, 50 °C, 2 h

Experimental

B.p.s are uncorrected. IR spectra were recorded for solutions in chloroform, by using a Perkin-Elmer 577 instrument. UV spectra were measured for solutions in ethanol on a Specord UV-VIS Zeiss Jena spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded in deuteriochloroform (tetramethylsilane as internal standard) on a Bruker WM-250 (250 MHz) and a Bruker AM-300 (75 MHz) spectrometer, respectively. *J*-Values are given in Hz. Mass spectra were obtained with a Varian MAT CH-6 instrument at 70 eV. GLC analyses were performed using a Biochrom gas chromatograph equipped with a 50 m × 0.2 mm capillary column coated with OV-275; a flame ionization detector was used. Column chromatography was carried out on silica gel (Chemapol Silicagel L 40/100 for flash chromatography, Czechoslovakia).

1-*Cyclopropylpropan*-1-*one* **7a**.—To a stirred solution of the imine **5**[40] (3 g, 18.2 mmol) in THF (5 cm^3) and HMPA (1 cm^3) under argon at −70 °C was added dropwise a solution of butyllithium (1.4 mol dm^{-3}; 13.6 cm^3, 19.04 mmol) in hexane. The mixture was warmed during 15 min to 0 °C, kept at this temperature for 45 min, and then treated at −70 °C with a solution of methyl iodide (2.71 g, 19.1 mmol) in THF (5 cm^3) for 5 min. The reaction mixture was warmed for 10 min to 25 °C, stirred at this temperature for 2 h, then poured into water (30 cm^3) and extracted with diethyl ether (3 × 15 cm^3). The extract was washed with brine (2 × 10 cm^3) and evaporated. The residue (3.5 g) was absorbed onto silica gel (12 g) and after 15 min at 25 °C the product was eluted with pentane (80 cm^3), the eluate was concentrated at atmospheric pressure, and the residue was distilled to give the ketone **7a**[9] (1.55 g, 87%) as a liquid, b.p. 127–128 °C; n_D^{21} 1.4306; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 1.08 (3 H, t, *J* 7, Me), 1.92 (1 H, m, CH) and 2.58 (2 H, q, *J* 7, 2-H_2).

1-*Cyclopropylpentan*-1-*one* **7b**.—Similarly, starting from the imine **5** (4.5 g, 27.3 mmol), butyllithium (1.4 mol dm^{-3}; 21.4 cm^3, 29.96 mmol), and propyl bromide (4.03 g, 32.8 mmol) in THF (18 cm^3)–HMPA (1.5 cm^3) the crude product (6.2 g) was obtained and was adsorbed onto silica gel (16 g). After 15 min at 25 °C the whole mixture was applied to a column of silica gel (100 g) and eluted with hexane–diethyl ether (97:3) to afford the title compound **7b**[9] (2.87 g, 84%) as a liquid, b.p. 57–58 °C at 9 mmHg; n_D^{23} 1.4352; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.93 (3 H, t, *J* 7, Me), 1.3–1.7 (4 H, m, CH_2), 1.94 (1 H, m, CH) and 2.55 (2 H, t, *J* 7, 2-H_2).

1-*Cyclopropylnonan*-1-*one* **7c**.—As described above, starting from the imine **5** (2.85 g, 17.3 mmol) and heptyl bromide (3.08 g, 17.2 mmol) and following chromatography on silica gel, the ketone **7c**[8] (2.8 g, 89%) was obtained as a liquid, b.p. 73–74 °C at 1 mmHg; n_D^{20} 1.4470; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.89 (3 H, t, *J* 7, Me), 1.2–1.7 (12 H, m, CH_2), 1.93 (1 H, m, CH) and 2.53 (2 H, t, *J* 7, 2-H_2).

1-*Cyclopropylundecan*-1-*one* **7d**.—In the same way, starting from the imine **5** (0.5 g, 3.0 mmol) and nonyl bromide (0.66 g, 3.2 mmol), the *title product* **7d** (0.56 g, 88%) was obtained as a liquid, b.p. 90–91 °C at 1 mmHg; n_D^{25} 1.4488 (Found: C, 79.6; H, 12.35. $C_{14}H_{26}O$ requires C, 79.94; H, 12.46%); ν_{max}/cm^{-1} 820, 910, 1030, 1070, 1090, 1140, 1200, 1210, 1240, 1395, 1470, 1700, 2865, 2940, 3020 and 3100; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.88 (3 H, t, *J* 7, Me), 1.2–1.7 (16 H, m, CH_2), 1.93 (1 H, m, CH) and 2.53 (2 H, t, *J* 7, 2-H_2); *m/z* 210 (M^+, 4%), 97 (14), 85 (13), 84 (100), 83 (12), 69 (71) and 41 (29).

(E)-1-*Cyclopropylundec*-6-*en*-1-*one* **7e**.—Similarly, starting from the imine **5** (2.08 g, 12.6 mmol) and (*E*)-non-4-enyl bromide[41] (2.58 g, 12.6 mmol), the *ketone* **7e** (2.33 g, 89%) was obtained as a liquid, b.p. 80–81 °C at 0.04 mmHg; n_D^{23} 1.4608 (Found: C, 80.8; H, 11.5. $C_{14}H_{24}O$ requires C, 80.71; H, 11.61%); ν_{max}/cm^{-1} 730, 820, 900, 970, 1020, 1050, 1085, 1190, 1220, 1390, 1450, 1695, 2860, 2930, 2960, 3000 and 3090; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.89 (3 H, t, *J* 7, Me), 1.2–1.7 (8 H, m, CH_2), 1.93 (1 H, m, CH), 1.9–2.1 (4 H, m, 5- and 8-H_2), 2.53 (2 H, t, *J* 7, 2-H_2) and 5.39 (2 H, m, 6- and 7-H); *m/z* 208 (M^+, 4%), 123 (16), 97 (48), 84 (55), 69 (100), 67 (22), 55 (44) and 41 (74).

(Z)-1-*Cyclopropylpentadec*-10-*en*-1-*one* **7f**.—As in the above case, starting from the imine **5** (1.51 g, 9.15 mmol) and the bromide **15** described below (2.17 g, 8.31 mmol), the *title product* **7f** (2.06 g, 94%) was obtained as an oil, n_D^{21} 1.4642 (Found: C, 81.9; H, 12.5. $C_{18}H_{32}O$ requires C, 81.75; H, 12.20%); ν_{max}/cm^{-1} 665, 725, 880, 905, 970, 1060, 1205, 1390, 1455, 1685, 2860, 2930, 3000 and 3090; δ_H 0.8–1.1 (7 H, m, Me, CH_2 of cyclopropane), 1.2–1.6 (16 H, m, CH_2), 1.9–2.1 (5 H, m, CH, 9- and 12-H_2), 2.53 (2 H, t, *J* 7, 2-H_2) and 5.30–5.45 (2 H, m,

10- and 11-H); *m/z* 264 (M^+, 6%), 178 (10), 151 (11), 97 (45), 84 (79), 69 (100), 55 (98) and 41 (72).

1-*Cyclopropyl*-4-*hydroxybutan*-1-*one* **8a**.—To a stirred solution of LDA [from diisopropylamine (6.06 g, 60.0 mmol) and butyllithium in hexane (1.58 mol dm^{-3}; 36.2 cm^3, 57.2 mmol)] in THF (20 cm^3) at −30 °C under argon was added dropwise a solution of the imine **5** (9 g, 54.5 mmol) in THF (20 cm^3)–HMPA (3 cm^3). The mixture was warmed during 15 min to 0 °C, kept at this temperature for 45 min, and then treated at −70 °C with a solution of ethylene oxide (4 cm^3, 80.6 mmol) in THF (10 cm^3) for 5 min. The reaction mixture was warmed during 40 min to 0 °C, then was poured into water (90 cm^3) and extracted with diethyl ether (3 × 45 cm^3). The extract was washed with brine (3 × 10 cm^3), then evaporated, and the residue (13.1 g) was adsorbed onto silica gel (22 g). After 15 min at 25 °C the whole mixture was applied to a column of silica gel (300 g) and chromatographed by using gradient elution from hexane to hexane–diethyl ether (1:9) to give the ketol **8a** [42] (6.77 g, 97%) as a liquid, b.p. 94–95 °C at 2 mmHg; n_D^{22} 1.4674; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.7–2.1 (3 H, m, CH, 3-H_2), 2.71 (2 H, t, *J* 7, 2-H_2) and 3.63 (2 H, t, *J* 7, 4-H_2).

1-*Cyclopropyl*-4-*hydroxypentan*-1-*one* **8b**.—Similarly, a solution of the imine **5** (1.5 g, 9.1 mmol) in THF (5 cm^3)–HMPA (0.5 cm^3) was treated with a solution of LDA (9.5 mmol) in hexane (6 cm^3)–THF (5 cm^3), followed by the addition of a solution of propylene oxide (1.05 g, 18.1 mmol) in THF (2 cm^3) to give the crude product (2.38 g), which was adsorbed onto silica gel (6 g). The whole mixture was then chromatographed on silica gel (50 g) with gradient elution from hexane to hexane–diethyl ether (2:3) to afford the *title compound* **8b** (1.2 g, 93%) as a liquid; b.p. 75–76 °C at 1 mmHg; n_D^{22} 1.4650 (Found: C, 67.8; H, 9.9. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%); ν_{max}/cm^{-1} 815, 870, 900, 950, 1020, 1070, 1120, 1220, 1390, 1450, 1695, 2980, 3020, 3460 and 3620; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 1.20 (3 H, d, *J* 6.5, Me), 1.6–2.0 (3 H, m, 3-H_2 and CH), 2.73 (2 H, t, *J* 7, 2-H_2) and 3.8 (1 H, m, 4-H); *m/z* 127 (M^+ − 15, 4%), 125 (10), 124 (3), 99 (8), 84 (30), 69 (100), 55 (15), 43 (17) and 41 (37).

1-*Cyclopropyl*-3-*hydroxypentan*-1-*one* **2a**.—To a stirred solution of LDA [from diisopropylamine (3.7 g, 36.6 mmol) and butyllithium in hexane (1.59 mol dm^{-3}; 22.0 cm^3, 35.0 mmol)] in THF (10 cm^3) at −30 °C under argon was added dropwise a solution of the imine **5** (5.5 g, 33.3 mmol) in THF (10 cm^3)–HMPA (2 cm^3). The mixture was warmed for 15 min to 0 °C, kept at this temperature for 45 min, and then treated at −70 °C with a solution of propanal (2.03 g, 35.0 mmol) in THF (10 cm^3) during 10 min. The reaction mixture was then warmed during 20 min to 5 °C, poured into water (50 cm^3), and extracted with diethyl ether (3 × 30 cm^3). The extract was washed with brine (2 × 10 cm^3), then evaporated, and the residue (7.5 g) was adsorbed onto silica gel (15 g). After 15 min at 25 °C the whole mixture was applied to a column of silica gel (150 g) and eluted with hexane–diethyl ether (9:1) to afford the *hydroxy ketone* **2a** (3.41 g, 72%) as a liquid, b.p. 97–98 °C at 10 mmHg; n_D^{20} 1.4604 (Found: C, 67.6; H, 9.9. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%); ν_{max}(cm^{-1} 900, 960, 1060, 1140, 1195, 1210, 1240, 1310, 1395, 1470, 1690, 2940, 2980, 3020, 3100, 3510 and 3680; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.96 (3 H, t, *J* 7, Me), 1.4–1.6 (2 H, m, 4-H_2), 1.93 (1 H, m, CH), 2.71 (2 H, AB-part of ABX spectrum, δ_A 2.64, δ_B 2.78, J_{AB} 18, J_{AX} 9, J_{BX} 3, 2-H_2) and 3.97 (1 H, m, 3-H); *m/z* 124 (M^+ − 18, 8%), 111 (12), 87 (8), 84 (8), 83 (9), 69 (100), 57 (11), 43 (22) and 41 (36).

1 *Cyclopropyl*-3-*hydroxyheptan*-1-*one* **2b**.—Similarly, a solution of the imine **5** (1.5 g, 9.1 mmol) in THF (4 cm^3)–HMPA (1 cm^3) was treated with a solution of LDA (9.5 mmol) in hexane (6 cm^3)–THF (4 cm^3) followed by a solution of pentanal (0.82 g, 9.5 mmol) in THF (4 cm^3) to give the crude product (2.6 g), which was adsorbed onto silica gel (6.5 g). The whole mixture was then chromatographed on silica gel (60 g) to furnish the *title compound* **2b** (1.18 g, 76%) as a liquid, b.p. 97–98 °C at 1 mmHg; n_D^{22} 1.4593 (Found: C, 70.7; H, 10.7. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.66%); ν_{max}/cm^{-1} 900, 1020, 1050, 1135, 1190, 1235, 1310, 1390, 1470, 1690, 2930, 2960, 3005, 3090 and 3530; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.91 (3 H, t, *J* 7, Me), 1.2–1.6 (6 H, m, CH_2), 1.93 (1 H, m, CH), 2.72 (2 H, AB-part of ABX spectrum, δ_A 2.65, δ_B 2.79, J_{AB} 18, J_{AX} 9, J_{BX} 3, 2-H_2) and 4.03 (1 H, m, 3-H); *m/z* 152 (M^+ − 18, 7%), 113 (34), 87 (8), 84 (16), 69 (100), 57 (14), 55 (12), 43 (47) and 41 (62).

1-*Cyclopropyl*-3-*hydroxynonan*-1-*one* **2c**.—As described above, starting from the imine **5** (3.5 g, 21.2 mmol), LDA (22.3 mmol), and heptanal (2.54 g, 22.3 mmol) in a mixture of hexane (15.1 cm^3), HMPA (1.5 cm^3), and THF (21 cm^3) and after chromatography on silica gel, the *ketol* **2c** (3.19 g, 76%) was obtained as a liquid, b.p. 89–90 °C at 0.07 mmHg; n_D^{19} 1.4602 (Found: C, 72.65; H, 11.1. $C_{12}H_{22}O_2$ requires C, 72.68; H, 11.18%); ν_{max}/cm^{-1} 910, 1030, 1080, 1135, 1200, 1250, 1300, 1390, 1460, 1690, 2940, 2960 and 3550; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.88 (3 H, t, *J* 7, Me), 1.2–1.6 (10 H, m, CH_2), 1.93 (1 H, m, CH), 2.72 (2 H, AB-part of ABX spectrum, δ_A 2.65, δ_B 2.79, J_{AB} 18, J_{AX} 9, J_{BX} 3, 2-H_2) and 4.03 (1 H, m, 3-H); *m/z* 180 (M^+ − 18, 0.5%), 113 (92), 84 (35), 71 (19), 70 (35), 69 (59), 57 (20), 55 (49), 43 (66) and 41 (100).

1-*Cyclopropyl*-3-*hydroxyundecan*-1-*one* **2d**.—In the same way, starting from the imine **5** (1.5 g, 9.1 mmol) and nonanal (1.36 g, 9.6 mmol), the *title compound* **2d** (1.68 g, 82%) was obtained as a liquid, b.p. 100–101 °C at 0.03 mmHg; n_D^{22} 1.4608 (Found: C, 74.0; H, 11.3. $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%); ν_{max}/cm^{-1} 900, 1025, 1080, 1130, 1240, 1300, 1395, 1470, 1690, 2930, 3000 and 3540; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.88 (3 H, t, *J* 7, Me), 1.2–1.7 (14 H, m, CH_2), 1.93 (1 H, m, CH), 2.72 (2 H, AB-part of ABX spectrum, δ_A 2.65, δ_B 2.79, J_{AB} 18, J_{AX} 9, J_{BX} 3, 2-H_2) and 4.03 (1 H, m, 3-H); *m/z* 208 (M^+ − 18, 3%), 113 (53), 84 (20), 71 (14), 69 (100), 57 (25), 55 (23), 43 (36) and 41 (50).

(Z)-1-*Cyclopropyl*-3-*hydroxydodec*-7-*en*-1-*one* **2e**.—As in the above case, starting from the imine **5** (1.41 g, 8.55 mmol) and the dec-5*Z*-enal **16** described below (1.2 g, 7.79 mmol), the *title ketol* **2e** (1.72 g, 93%) was obtained as an oil, b.p. 106.5–108 °C at 0.02 mmHg; n_D^{20} 1.4748 (Found: C, 75.45; H, 11.1. $C_{15}H_{26}O_2$ requires C, 75.58; H, 10.99%); ν_{max}/cm^{-1} 660, 700, 840, 905, 1025, 1110, 1195, 1310, 1395, 1460, 1690, 2960, 3010, 3100 and 3670; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.88 (3 H, t, *J* 7, Me), 1.2–1.6 (8 H, m, CH_2), 1.92 (1 H, m, CH), 1.9–2.1 (4 H, m, 6- and 9-H_2), 2.71 (2 H, AB-part of ABX spectrum, δ_A 2.66, δ_B 2.76, J_{AB} 18, J_{AX} 9, J_{BX} 3, 2-H_2), 4.02 (1 H, m, 3-H) and 5.25–5.45 (2 H, m, 7- and 8-H); *m/z* 238 (M^+, 1%), 220 (4), 136 (17), 126 (19), 110 (39), 95 (25), 84 (23), 81 (53), 69 (100), 55 (51), 43 (46) and 41 (94).

(E)-1-*Cyclopropylpent*-2-*en*-1-*one* **9a**.—A solution of the ketol **2a** (2.6 g, 18.3 mmol) and TsOH monohydrate (0.1 g) in benzene (60 cm^3) was refluxed with azeotropic removal of water (Dean–Stark water separator) for *ca.* 20 min (GLC monitoring). The reaction mixture was washed successively with saturated aq. sodium hydrogen carbonate (2 × 10 cm^3) and brine (3 × 15 cm^3), dried ($MgSO_4$), evaporated, and distilled to give the unsaturated ketone **9a** [4] (2.05 g, 90%) as a liquid, b.p. 96–97 °C

at 35 mmHg; n_D^{21} 1.4762; δ_H 0.8–1.2 (4 H, m, CH_2 of cyclopropane), 1.11 (3 H, t, *J* 7, Me), 2.13 (1 H, m, CH), 2.28 (2 H, br quint, *J* 7, 4-H_2), 6.23 (1 H, br d, *J* 16, 2-H) and 6.97 (1 H, dt, *J* 16 and 7, 3-H).

(E)-1-*Cyclopropylhept*-2-*en*-1-*one* **9b**.—As described above, starting from the ketol **2b** (0.7 g) and TsOH monohydrate (25 mg) in benzene (35 cm^3), the title product **9b**[4] (0.57 g, 91%) was obtained as a liquid, b.p. 75–76 °C at 2 mmHg; n_D^{20} 1.4747; δ_H 0.8–1.2 (4 H, m, CH_2 of cyclopropane), 0.92 (3 H, t, *J* 7, Me), 1.3–1.5 (4 H, m, CH_2), 2.13 (1 H, m, CH), 2.24 (2 H, br q, *J* 7, 4-H_2), 6.22 (1 H, dt, *J* 16 and 1.5, 2-H) and 6.91 (1 H, dt, *J* 16 and 7, 3-H).

(E)-1-*Cyclopropylnon*-2-*en*-1-*one* **9c**.—In the same way, starting from the ketol **2c** (2.75 g), the unsaturated ketone **9c**[4] (2.27 g, 91%) was obtained as a liquid, b.p. 100–101 °C at 1 mmHg; n_D^{21} 1.4741; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.89 (3 H, t, *J* 7, Me), 1.2–1.5 (8 H, m, CH_2), 2.13 (1 H, m, CH), 2.23 (2 H, br q, *J* 7, 4-H_2), 6.22 (1 H, dt, *J* 16 and 1.5, 2-H) and 6.91 (1 H, dt, *J* 16 and 7, 3-H).

(E)-1-*Cyclopropylundec*-2-*en*-1-*one* **9d**.—As above, starting from the hydroxy ketone **2d** (0.7 g), the title compound **9d**[4] (0.59 g, 92%) was obtained as a liquid, b.p. 89–90 °C at 0.03 mmHg; n_D^{20} 1.4733; δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.89 (3 H, t, *J* 7, Me), 1.2–1.5 (12 H, m, CH_2), 2.13 (1 H, m, CH), 2.24 (2 H, br q, *J* 7, 4-H_2), 6.22 (1 H, dt, *J* 16 and 1.5, 2-H) and 6.91 (1 H, dt, *J* 16 and 7, 3-H).

(2E,7Z)-1-*Cyclopropyldodeca*-2,7-*dien*-1-*one* **9e**.—Similarly, starting from the ketol **2e** (1.48 g), the *title unsaturated ketone* **9e** (1.33 g, 97%) was obtained as a liquid, b.p. 133–135 °C at 0.03 mmHg; n_D^{20} 1.4865 (Found: C, 81.5; H, 11.1. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%); ν_{max}/cm^{-1} 685, 890, 975, 1060, 1190, 1235, 1280, 1390, 1440, 1625, 1660, 1680, 2960, 3000 and 3095; λ_{max}/nm 228 (ε 18 200); δ_H 0.8–1.1 (4 H, m, CH_2 of cyclopropane), 0.89 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 10- and 11-H_2), 1.55 (2 H, quint, *J* 7, 5-H_2), 1.9–2.3 (7 H, m, CH, 4-, 6- and 9-H_2), 5.3–5.5 (2 H, m, 7- and 8-H), 6.23 (1 H, br d, *J* 16, 2-H) and 6.92 (1 H, dt, *J* 16 and 7, 3-H); *m*/*z* 220 (M^+, 2%), 177 (7), 163 (10), 152 (12), 136 (44), 123 (42), 95 (65), 81 (69), 69 (61), 67 (61), 55 (100), 43 (37) and 41 (28).

(Z)-1-(*Tetrahydropyran*-2-*yloxy*)*tridec*-8-*ene* **13a**.—To a stirred solution of the sulphone **10**[43] (1.8 g, 8.5 mmol) in THF (30 cm^3)–HMPA (2 cm^3) at −70 °C under argon was added dropwise a solution of butyllithium (1.81 mol dm^{-3}; 4.7 cm^3, 8.51 mmol) in hexane. The mixture was warmed for 5 min at −15 °C, kept at this temperature for 25 min, and then treated at −70 °C with a solution of 8-(tetrahydropyran-2-yloxy)-octanal[44] (1.94 g, 8.51 mmol) in THF (10 cm^3) during 5 min. The reaction mixture was warmed during 5 min to −10 °C, stirred at this temperature for 25 min, and then treated dropwise with a solution of DMAP (0.1 g, 0.82 mmol) in acetic anhydride (1.3 g, 12.74 mmol). The mixture was then warmed during 50 min to 25 °C, poured into water (50 cm^3), and extracted with diethyl ether (4 × 35 cm^3). The extract was washed with brine (2 × 30 cm^3), dried ($MgSO_4$), and evaporated.

A solution of the residue (4.4 g) in diethyl ether (60 cm^3)–methanol (0.6 cm^3) was vigorously stirred at 25 °C with freshly ground sodium hydroxide (0.68 g, 17.0 mmol) for 20 min. The suspension was then passed through a short pad of silica gel and the filtrate was evaporated.

A mixture of the residue (3.4 g), sodium dithionite (4.44 g, 25.52 mmol), sodium hydrogen carbonate (4.29 g, 51.07 mmol), ethanol (50 cm^3), and water (50 cm^3) was vigorously stirred at 80 °C for 7 h, then extracted with diethyl ether (4 × 50 cm^3). The extract was washed successively with water (2 × 25 cm^3) and brine (2 × 25 cm^3), dried ($MgSO_4$), then evaporated, and the residue (2.5 g) was chromatographed on silica gel (70 g) in hexane–diethyl ether (95:5) to yield the *olefin* **13a** (1.44 g, 60%) as an oil, n_D^{24} 1.4589 (Found: C, 76.1; H, 12.1. $C_{18}H_{34}O_2$ requires C, 76.54; H, 12.13%); ν_{max}/cm^{-1} 790, 905, 970, 1075, 1135, 1255, 1350, 1450, 2915 and 3000; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.9 (20 H, m, CH_2), 1.9–2.1 (4 H, m, 7- and 10-H_2), 3.3–3.9 (4 H, m, OCH_2), 4.58 (1 H, br t, *J* 4, OCHO) and 5.25–5.45 (2 H, m, 8- and 9-H); *m*/*z* 209 (2%), 180 (2), 178 (2), 97 (11), 96 (13), 95 (9), 85 (100), 84 (10), 82 (13), 81 (14), 69 (25), 67 (25), 55 (45), 43 (23) and 41 (37).

(Z)-1-(*Tetrahydropyran*-2-*yloxy*)*dec*-5-*ene* **13b**.—In the same way a solution of the sulphone **10** (8.5 g, 40.1 mmol) in THF (50 cm^3)–HMPA (5 cm^3) was treated with butyllithium (1.8 mol dm^{-3}; 22.2 cm^3, 40.0 mmol) in hexane, followed by 5-(tetrahydropyran-2-yloxy)pentanal[45] (7.25 g, 39.0 mmol) in THF (20 cm^3) to give, after treatment of the reaction mixture with acetic anhydride (5.96 g, 58.4 mmol) and DMAP (0.48 g, 3.9 mmol), the crude product (21.0 g), which was treated further with sodium hydroxide (3.12 g, 78.0 mmol) in diethyl ether (100 cm^3) containing methanol (1 cm^3). The resulting mixture (15 g) was then treated with sodium dithionite (20.35 g, 117 mmol) and sodium hydrogen carbonate (19.65 g, 234 mmol) in aq. ethanol (1:1; 400 cm^3) and the final crude product (9.51 g) was chromatographed on silica gel (200 g) to afford the *title olefin* **13b** (5.23 g, 56%) as an oil; n_D^{22} 1.4581 (Found: C, 74.7; H, 11.5. $C_{15}H_{28}O_2$ requires C, 74.95; H, 11.74%); ν_{max}/cm^{-1} 795, 905, 970, 1075, 1135, 1255, 1350, 1440, 2920 and 3000; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.9 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 4- and 7-H_2), 3.3–3.9 (4 H, m, OCH_2), 4.58 (1 H, br t, *J* 4, OCHO) and 5.35–5.45 (2 H, m, 5- and 6-H); *m*/*z* 167 (2%), 138 (3), 136 (6), 97 (15), 95 (17), 85 (100), 84 (28), 83 (31), 81 (25), 69 (45), 67 (59), 57 (54), 55 (100), 45 (86), 43 (59) and 41 (27).

(Z)-*Tridec*-8-*en*-1-*ol* **14a**.—A solution of the ether **13a** (3.36 g, 1.91 mmol) and PPTS[46] (0.3 g, 1.2 mmol) in methanol (50 cm^3) was kept at 50 °C for 2 h, then evaporated, and the residue (3 g) was chromatographed on silica gel (60 g) in hexane–diethyl ether (93:7) to give the alcohol **14a**[47] (2.36 g, ~100%) as a liquid, b.p. 90–91 °C at 0.02 mmHg; n_D^{23} 1.4539; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.6 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 7- and 10-H_2), 3.65 (2 H, t, *J* 7, 1-H_2) and 5.25–5.45 (2 H, m, 8- and 9-H); δ_C 13.92 (C-13), 22.29 (C-12), 25.67 (C-3), 26.87 and 27.11 (C-7 and -10), 29.27 and 29.64 (C-4, -5 and -6), 31.92 (C-11), 32.73 (C-2), 62.99 (C-1) and 129.79 and 129.94 (C-8 and -9).

(Z)-*Dec*-5-*en*-1-*ol* **14b**.—Similarly, starting from the ether **13b** (2.46 g, 10.25 mmol) and PPTS (0.26 g, 1.04 mmol) in methanol (40 cm^3), the title compound **14b**[48] (1.6 g, ~100%) was obtained as a liquid, b.p. 91–92 °C at 1 mmHg; n_D^{21} 1.4515; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.7 (8 H, m, CH_2), 1.9–2.1 (4 H, m, 4- and 7-H_2), 3.65 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 5- and 6-H); δ_C 13.86 (C-10), 22.26 (C-9), 25.65 (C-3), 26.87 (C-4 and -7), 31.86 (C-8), 32.23 (C-2), 62.47 (C-1) and 129.37 and 130.22 (C-5 and -6).

(Z)-*Tridec*-8-*enyl Bromide* **15**.—To a stirred solution of the alcohol **14a** (1.93 g, 9.75 mmol) in diethyl ether (40 cm^3)–HMPA (3 cm^3) at −30 °C under argon was added dropwise a solution of butyllithium (1.5 mol dm^{-3}; 6.55 cm^3, 9.83 mmol) in hexane, and then TsCl (2.0 g, 10.5 mmol) was added during 5 min. The reaction mixture was warmed during 15 min to 25 °C and was then diluted with water (30 cm^3). The aq. phase was separated and extracted with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with brine (3 × 15 cm^3), dried ($MgSO_4$), and evaporated.

A solution of the residue (3.5 g) in dimethylformamide (DMF) (40 cm^3) was vigorously stirred at 50 °C with sodium bromide (4.0 g, 38.8 mmol) for 1 h. The reaction mixture was then diluted with water (30 cm^3) and extracted with hexane (4 × 40 cm^3). The extract was washed with brine (2 × 20 cm^3), dried (Na_2SO_4), and concentrated under reduced pressure, and the residue was distilled to give the *bromide* **15** (2.43 g, 96%) as a liquid, b.p. 92–93 °C at 0.02 mmHg; n_D^{22} 1.4702 (Found: C, 60.1; H, 9.7; Br, 30.2. $C_{13}H_{25}Br$ requires C, 59.77; H, 9.65; Br, 30.58%); ν_{max}/cm^{-1} 560, 645, 710, 970, 1245, 1375, 1435, 1460 and 2930; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.5 (12 H, m, CH_2), 1.86 (2 H, quint, *J* 7, 2-H_2), 1.9–2.1 (4 H, m, 7- and 10-H_2), 3.41 (2 H, t, *J* 7, 1-H_2) and 5.30–5.45 (2 H, m, 8- and 9-H); *m/z* 262 (M^+, 32%), 260 (M^+, 30), 150 (40), 148 (40), 97 (74), 83 (74), 70 (94), 69 (98), 67 (100), 56 (55) and 41 (68).

(Z)-*Dec*-5-*enal* **16**.—To a stirred solution of oxalyl dichloride (2.57 g, 20.24 mmol) in methylene dichloride (35 cm^3) at −60 °C under argon was added dropwise a solution of dimethyl sulphoxide (2.33 g, 29.87 mmol) in methylene dichloride (15 cm^3). The mixture was kept at this temperature for 10 min and was then treated with a solution of the alcohol **14b** (1.37 g, 8.78 mmol) in methylene dichloride (40 cm^3) during 10 min. The reaction mixture was stirred at −60 °C for 40 min, then treated with triethylamine (7.14 g, 70.69 mmol) for 10 min, and warmed during 15 min to −15 °C. After an additional 45 min the mixture was quenched with hydrochloric acid (1 mol dm^{-3}; 30.2 cm^3) and extracted into diethyl ether (3 × 30 cm^3). The extracts were washed successively with water (3 × 15 cm^3), saturated aq. sodium hydrogen carbonate (2 × 15 cm^3), and brine (2 × 15 cm^3), dried (Na_2SO_4), and evaporated. The residue (2.0 g) was chromatographed on silica gel (40 g) in hexane–diethyl ether (99:1) to yield the title aldehyde **16** [49] (1.3 g, 96%) as a liquid, b.p. 51–52 °C at 1 mmHg; n_D^{20} 1.4442; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 8- and 9-H_2), 1.70 (2 H, quint, *J* 7, 3-H_2), 1.9–2.1 (4 H, m, 4- and 7-H_2), 2.45 (2 H, td, *J* 7 and 2, 2-H_2), 5.25–5.50 (2 H, m, 5- and 6-H) and 9.77 (1 H, t, *J* 2, 1-H).

1-*Cyclopropylpropan*-1-*ol* **17a**.—To a stirred solution of the ketone **7a** (3.87 g, 39.5 mmol) in diethyl ether (50 cm^3) at 0 °C under argon was added lithium aluminium hydride (1.5 g, 39.5 mmol) during 10 min. The reaction mixture was stirred for a further 10 min and then was treated, at 0 °C, successively with water (1.5 cm^3), aq. potassium hydroxide (3 mol dm^{-3}; 1.5 cm^3), and water (4.5 cm^3), and dried ($MgSO_4$). The solid thus formed was filtered off and washed with dry diethyl ether (70 cm^3). The filtrate was concentrated at atmospheric pressure and the residue was then distilled to afford the alcohol **17a** [9] (3.53 g, 89%) as a liquid, b.p. 132–133 °C; n_D^{20} 1.4365; δ_H 0.2–0.6 (4 H, m, CH_2 of cyclopropane), 0.8–1.0 (1 H, m, CH), 0.99 (3 H, t, *J* 7, Me), 1.5–1.7 (2 H, m, 2-H_2) and 2.80 (1 H, br q, *J* 7, 1-H).

1-*Cyclopropylpentan*-1-*ol* **17b**.—In the same way, starting from the ketone **7b** (3.61 g, 28.65 mmol) and lithium aluminium hydride (1.09 g, 28.7 mmol) in diethyl ether (50 cm^3), after concentration of the final filtrate under reduced pressure the title compound **17b** [4] (3.43 g, 94%) was obtained as a liquid, b.p. 82–83 °C at 17 mmHg; n_D^{23} 1.4400; δ_H 0.2–0.6 (4 H, m, CH_2 of cyclopropane), 0.8–1.0 (1 H, m, CH), 0.91 (3 H, t, *J* 7, Me), 1.2–1.7 (6 H, m, CH_2) and 2.84 (1 H, br q, *J* 7, 1-H).

(Z)-1-*Cyclopropylpentadec*-10-*en*-1-*ol* **17f**.—Similarly, starting from the ketone **7f** (1.71 g, 6.48 mmol) and lithium aluminium hydride (0.24 g, 6.3 mmol) in diethyl ether (25 cm^3), the *title alcohol* **17f** (1.69 g, 98%) was obtained as an oil; n_D^{22} 1.4661 (Found: C, 81.5; H, 12.8. $C_{18}H_{34}O$ requires C, 81.13; H, 12.86%); ν_{max}/cm^{-1} 725, 825, 920, 1050, 1205, 1380, 1460, 2930, 3080 and 3600; δ_H 0.2–0.6 (4 H, m, CH_2 of cyclopropane), 0.8–1.0 (4 H, m, Me, CH), 1.2–1.7 (18 H, m, CH_2), 1.9–2.1 (4 H, m, 9- and 12-H_2), 2.86 (1 H, br q, *J* 7, 1-H) and 5.30–5.45 (2 H, m, 10- and 11-H); *m/z* 248 (M^+ − 18, 6%), 204 (6), 121 (6), 81 (14), 71 (100), 55 (33), 43 (38) and 41 (41).

(E)-1-*Hex*-3-*enyl Bromide* **18a**—To a vigorously stirred suspension of the alcohol **17a** (1.2 g, 12.0 mmol) and zinc bromide (0.59 g, 2.6 mmol) in methylene dichloride (20 cm^3) at −10 °C under argon was added dropwise a solution of trimethylsilyl bromide (4.04 g, 26.4 mmol) in methylene dichloride (5 cm^3). The reaction mixture was warmed during 10 min to 0 °C, kept at this temperature for 20 min (GLC monitoring), and then was quenched with saturated aq. sodium hydrogen carbonate (15 cm^3) and extracted into diethyl ether (3 × 20 cm^3). The combined extracts were washed with brine (3 × 15 cm^3), dried ($MgSO_4$), and concentrated at atmospheric pressure, and the residue was distilled to give the bromide **18a** [50] (1.57 g, 80%) as a liquid, b.p. 89–90 °C at 110 mmHg; n_D^{22} 1.4679; δ_H 1.00 (3 H, t, *J* 7, Me), 2.04 (2 H, br quint, *J* 7, 5-H_2), 2.55 (2 H, br q, *J* 7, 2-H_2), 3.38 (2 H, t, *J* 7, 1-H_2), 5.38 (1 H, br dt, *J* 15 and 7, 3-H) and 5.59 (1 H, br dt, *J* 15 and 7, 4-H).

(E)-1-*Oct*-3-*enyl Bromide* **18b**.—In the same way, starting from the alcohol **17b** (3.43 g, 26.7 mmol), zinc bromide (1.33 g, 5.9 mmol), and trimethylsilyl bromide (9.02 g, 59.0 mmol) in methylene dichloride (100 cm^3), the title compound **18b** [4] (4.61 g, 90%) was obtained as a liquid, b.p. 85–86 °C at 16 mmHg; n_D^{20} 1.4695; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 6- and 7-H_2), 2.03 (2 H, br q, *J* 7, 5-H_2), 2.55 (2 H, br q, *J* 7, 2-H_2), 3.38 (2 H, t, *J* 7, 1-H_2), 5.39 (1 H, br dt, *J* 15 and 7, 3-H) and 5.56 (1 H, br dt, *J* 15 and 7, 4-H).

(3E,13Z)-*Octadeca*-3,13-*dienyl Bromide* **18f**.—Similarly, starting from the alcohol **17f** (1.59 g, 5.98 mmol), trimethylsilyl bromide (2.01 g, 13.14 mmol), and zinc bromide (0.3 g, 1.33 mmol) in methylene dichloride (35 cm^3), a crude product (2 g) was obtained, which was chromatographed on silica gel (30 g) in pentane to give the *title bromide* **18f** (1.95 g, ~100%) as an oil; n_D^{22} 1.4790 (Found: C, 65.45; H, 10.4; Br, 24.6. $C_{18}H_{33}Br$ requires C, 65.64; H, 10.10; Br, 24.26%); ν_{max}/cm^{-1} 565, 645, 670, 730, 880, 970, 1050, 1255, 1380, 1460 and 2930; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (16 H, m, CH_2), 1.9–2.1 (6 H, m, 5-, 12- and 15-H_2), 2.55 (2 H, br q, *J* 7, 2-H_2), 3.37 (2 H, t, *J* 7, 1-H_2), 5.30–5.45 (3 H, m, 3-, 13- and 14-H) and 5.55 (1 H, br dt, *J* 15 and 7, 4-H); *m/z* 330 (M^+, 41%), 328 (M^+, 38), 191 (23), 160 (25), 107 (36), 94 (58), 81 (66), 80 (66), 79 (83), 65 (83), 55 (100) and 41 (62).

(E)-*Dodec*-9-*en*-1-*ol* **19**.—To vigorously stirred, preactivated magnesium powder (1.29 g, 53.7 mmol) was added a solution of the *O*-magnesium derivative [from 6-bromohexan-1-ol [51] (3.89 g, 21.5 mmol) and ethylmagnesium bromide in THF (1.5 mol dm^{-3}; 15.7 cm^3, 23.6 mmol)] in THF (15 cm^3) under argon during *ca.* 20 min; the temperature was raised to 45–50 °C to initiate and maintain the reaction. The mixture was then cooled to 25 °C and filtered. The filtrate, cooled to −70 °C, was treated successively with HMPA (8 cm^3), a solution of the bromide **18a** (0.7 g, 4.3 mmol) in THF (12 cm^3), and a solution of dilithium tetrachlorocuprate [14] in THF (0.1 mol dm^{-3}; 7 cm^3, 0.7 mmol) during 5 min. The reaction mixture was warmed during 1 h to 0 °C, then quenched with saturated aq. copper(II) sulphate (30 cm^3), and extracted into diethyl ether (3 × 25 cm^3). The organic extracts were washed with brine (2 × 15 cm^3), dried ($MgSO_4$), evaporated, and distilled to afford the olefin **19** [52] (0.45 g, 57%) as a liquid, b.p. 81–82 °C at 0.03 mmHg; n_D^{21} 1.4534; δ_H 0.97 (3 H, t, *J* 7, Me), 1.2–1.6 (12 H,

m, CH_2), 1.9–2.1 (4 H, m, 8- and 11-H_2), 3.65 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 9- and 10-H).

(E)-*Tetradec*-11-*en*-1-*ol* **20**.—In the same way, starting from 8-bromooctan-1-ol[51] (4.49 g, 21.5 mmol) in THF (15 cm^3), ethylmagnesium bromide in THF (1.5 mol dm^{-3}; 15.8 cm^3, 23.7 mmol), magnesium powder (1.29 g, 53.7 mmol), the bromide **18a** (0.7 g, 4.3 mmol) in THF (10 cm^3)–HMPA (8 cm^3), and dilithium tetrachlorocuprate in THF (0.1 mol dm^{-3}; 7 cm^3, 0.7 mmol), the title alcohol **20**[52,53] (0.66 g, 73%) was obtained as a liquid, b.p. 93–94 °C at 0.03 mmHg; n_D^{21} 1.4554; δ_H 0.98 (3 H, t, *J* 7, Me), 1.2–1.7 (16 H, m, CH_2), 1.9–2.1 (4 H, 10- and 13-H_2), 3.65 (2 H, t, *J*, 1-H_2) and 5.3–5.5 (2 H, m, 11- and 12-H).

(E)-*Tridec*-8-*en*-1-*ol* **21**.—Similarly, starting from 5-bromopentan-1-ol[51] (2.27 g, 13.6 mmol) in THF (9 cm^3), ethylmagnesium bromide in THF (1.5 mol dm^{-3}; 10 cm^3, 15 mmol), magnesium powder (0.82 g, 34.2 mmol), the bromide **18b** (0.52 g, 2.7 mmol) in THF (7 cm^3)–HMPA (5 cm^3), and dilithium tetrachlorocuprate in THF (0.1 mol dm^{-3}; 4 cm^3, 0.4 mmol), the *title compound* **21** (0.36 g, 67%) was obtained as a liquid, b.p. 110–111 °C at 1 mmHg; n_D^{23} 1.4539 (Found: C, 78.95; H, 13.2. $C_{13}H_{26}O$ requires C, 78.72; H, 13.21%); ν_{max}/cm^{-1} 925, 980, 1060, 1245, 1385, 1470, 2970, 3020 and 3630; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.6 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 7- and 10-H_2), 3.64 (2 H, t, *J* 7, 1-H_2), 5.32 (1 H, br dt, *J* 15 and 5.5, 8-H) and 5.43 (1 H, br dt, *J* 15 and 5.5, 9-H); *m/z* 180 (M^+ − 18, 6%), 124 (8), 123 (7), 109 (15), 96 (37), 95 (39), 82 (57), 81 (61), 69 (37), 67 (69), 55 (100) and 41 (59).

(E)-*Dodec*-9-*enyl Acetate* **22**.—A solution of the alcohol **19** (0.2 g, 1.09 mmol) and DMAP (10 mg) in acetic anhydride (0.22 g, 2.16 mmol)–pyridine (1 cm^3) was kept at 25 °C for 30 min. The reaction mixture was then treated at 0 °C with hydrochloric acid (1 mol dm^{-3}; 12.5 cm^3) and extracted into diethyl ether (3 × 10 cm^3). The extracts were washed successively with saturated aq. sodium hydrogen carbonate (3 cm^3) and brine (3 × 5 cm^3), dried ($MgSO_4$), and evaporated, and the residue was distilled to yield the acetate **22**[52] (0.24 g, 98%) as a liquid, b.p. 57–58 °C at 0.01 mmHg; n_D^{21} 1.4443; δ_H 0.97 (3 H, t, *J* 7, Me), 1.2–1.7 (12 H, m, CH_2), 1.9–2.1 (4 H, m, 8- and 11-H_2), 2.06 (3 H, s, CH_3CO), 4.05 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 9- and 10-H).

(E)-*Tetradec*-11-*enyl Acetate* **23**.—In the same way, starting from the alcohol **20** (0.2 g, 0.94 mmol), acetic anhydride (0.19 g, 1.86 mmol), DMAP (10 mg), and pyridine (1 cm^3), the title acetate **23**[52,53] (0.21 g, 88%) was obtained as a liquid, b.p. 85–86 °C at 0.04 mmHg; n_D^{21} 1.4458; δ_H 0.97 (3 H, t, *J* 7, Me), 1.2–1.7 (16 H, m, CH_2), 1.9–2.1 (4 H, m, 10- and 13-H_2), 2.07 (3 H, s, CH_3CO), 4.07 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 11- and 12-H).

(E)-*Tridec*-8-*enyl Acetate* **24**.—Similarly, starting from the alcohol **21** (0.2 g, 1.0 mmol), the *title compound* **24** (0.24 g, 99%) was obtained as a liquid, b.p. 97–98 °C at 0.015 mmHg; n_D^{23} 1.4440 (Found: C, 75.1; H, 11.8. $C_{15}H_{28}O_2$ requires C, 74.95; H, 11.74%); ν_{max}/cm^{-1} 970, 1040, 1260, 1390, 1470, 1735, 2940 and 3010; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.7 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 7- and 10-H_2), 2.05 (3 H, s, CH_3CO), 4.05 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 8- and 9-H); *m/z* 180 (M^+ − 60, 23%), 124 (17), 123 (15), 96 (83), 82 (66), 81 (76), 67 (88), 55 (100), 43 (72) and 41 (47).

(E)-*Tetradec*-11-*enal* **25**.—To a stirred solution of the alcohol **20** (0.32 g, 1.5 mmol) in methylene dichloride (4 cm^3) under argon at 25 C was added PCC[54] (0.49 g, 2.3 mmol) in one portion. After 2 h the mixture was diluted with diethyl ether (10 cm^3) and passed through a short pad of silica gel. The filtrate was evaporated and the residue was distilled to give the aldehyde **25**[53] (0.28 g, 88%) as a liquid, b.p. 67–68 °C at 0.025 mmHg; n_D^{21} 1.4483; δ_H 0.97 (3 H, t, *J* 7, Me), 1.2–1.7 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 10- and 13-H_2), 2.42 (2 H, td, *J* 7 and 2, 2-H_2), 5.3–5.5 (2 H, m, 11- and 12-H) and 9.78 (1 H, t, *J* 2, 1-H).

(3E,13Z)-*Octadeca*-3,13-*dienyl Acetate* **26**.—A suspension of the bromide **18f** (1.05 g, 3.19 mmol), potassium acetate (1.56 g, 15.9 mmol), and DB-18-C-6 (20 mg) in acetonitrile (60 cm^3) was refluxed for 15 h. The reaction mixture was then passed through a short pad of silica gel, the filtrate was evaporated, and the residue (~1 g) was chromatographed on silica gel (20 g) in hexane–diethyl ether (97:3) to give the acetate **26**[55] (0.87 g, 89%) as an oil, n_D^{23} 1.4570; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (16 H, m, CH_2), 1.9–2.1 (6 H, m, 5-, 12- and 15-H_2), 2.06 (3 H, s, CH_3CO), 2.32 (2 H, br q, *J* 7, 2-H_2), 4.07 (2 H, t, *J* 7, 1-H_2), 5.28–5.33 (3 H, m, 3-, 13- and 14-H) and 5.52 (1 H, br dt, *J* 15 and 7, 4-H).

(3E,13Z)-*Octadeca*-3,13-*dien*-1-*ol* **27**.—A solution of the acetate **26** (0.45 g, 1.46 mmol) in methanol (4 cm^3) was stirred with aq. sodium hydroxide (1.5 mol dm^{-3}; 3 cm^3) at 25 °C for 15 min. The reaction mixture was then concentrated under reduced pressure and extracted with diethyl ether (4 × 10 cm^3). The extract was washed with brine (2 × 5 cm^3), dried ($MgSO_4$), and evaporated to afford the alcohol **27**[55] (0.39 g, ~100%) as an oil; n_D^{23} 1.4670; δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (16 H, m, CH_2), 1.9–2.1 (6 H, m, 5-, 12- and 15-H), 2.27 (2 H, br q, *J* 7, 2-H_2), 3.62 (2 H, br t, *J* 7, 1-H_2), 5.30–5.45 (3 H, m, 3-, 13- and 14-H) and 5.56 (1 H, br dt, *J* 15 and 7, 4-H).

(E)-1-*Cyclopropylpent*-2-*en*-1-*ol* **28a**.—To a stirred solution of the ketone **9a** (2.05 g, 16.5 mmol) in methanol (45 cm^3) at −50 °C under argon was added cerium trichloride heptahydrate (6.15 g, 16.5 mmol), followed by sodium borohydride (0.62 g, 16.5 mmol). The reaction mixture was kept at −50 °C for 15 min and then was diluted with water (30 cm^3) and extracted with hexane–diethyl ether (1:1; 4 × 40 cm^3). The extract was washed with brine (3 × 10 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure, and the residue was distilled to give the title compound **28a**[56] (1.74 g, 84%) as a liquid, b.p. 69–70 °C at 10 mmHg; n_D^{23} 1.4594; δ_H 0.2–0.6 (4 H, m, CH_2 of cyclopropane), 0.9–1.1 (1 H, m, CH), 1.00 (3 H, t, *J* 7, Me), 2.08 (2 H, br quint, *J* 7, 4-H_2), 3.43 (1 H, br t, *J* 7, 1-H), 5.55 (1 H, ddt, *J* 16, 7 and 1.5, 2-H) and 5.72 (1 H, dt, *J* 16 and 7, 3-H).

(2E,7Z)-1-*Cyclopropyldodeca*-2,7-*dien*-1-*ol* **28e**.—Similarly, starting from the ketone **9e** (1.3 g, 5.9 mmol), cerium trichloride heptahydrate (2.2 g, 5.9 mmol), and sodium borohydride (0.22 g, 5.8 mmol) in methanol (20 cm^3), the *alcohol* **28e** (1.27 g, 97%) was obtained as an oil; b.p. 109–110 °C at 0.015 mmHg; n_D^{20} 1.4765 (Found: C, 80.7; H, 11.7. $C_{15}H_{26}O$ requires C, 81.02; H, 11.79%); ν_{max}/cm^{-1} 690, 795, 920, 970, 1050, 1235, 1380, 1460, 2930, 3010, 3080 and 3600; δ_H 0.2–0.6 (4 H, m, CH_2 of cyclopropane), 0.90 (3 H, t, *J* 7, Me), 0.9–1.1 (1 H, m, CH), 1.2–1.4 (4 H, m, 10- and 11-H_2), 1.46 (2 H, quint, *J* 7, 5-H_2), 1.9–2.1 (6 H, m, 4-, 6- and 9-H_2), 3.45 (1 H, br t, *J* 7, 1-H), 5.25–5.45 (2 H, m, 7- and 8-H), 5.55 (1 H, ddd, *J* 16, 7 and 3, 2-H) and 5.66 (1 H, dtd, *J* 16, 7 and 3, 3-H); *m/z* 204 (M^+ − 18, 3%), 136 (19), 123 (21), 97 (28), 95 (46), 81 (62), 79 (80), 69 (100), 67 (80), 55 (97), 43 (73) and 41 (58).

(E,E)-*Octa*-3,5-*dienyl Bromide* **29a**.—As described above for the bromides **18**, treatment of the alcohol **28a** (0.4 g, 3.17 mmol)

with trimethylsilyl bromide (1.07 g, 7.0 mmol) and zinc bromide (0.16 g, 0.7 mmol) in methylene dichloride (15 cm^3) gave, at −20 °C for 15 min, the title compound **29a**[56] (0.51 g, 85%) as a liquid, b.p. 54–55 °C at 2 mmHg; n_D^{23} 1.5150; δ_H 1.02 (3 H, t, *J* 7, Me), 2.10 (2 H, br quint, *J* 7, 7-H_2), 2.63 (2 H, br q, *J* 7, 2-H_2), 3.39 (2 H, t, *J* 7, 1-H_2), 5.53 (1 H, dt, *J* 15 and 7, 3-H), 5.70 (1 H, dt, *J* 15 and 7 Hz, 6-H) and 5.9–6.2 (2 H, m, 4- and 5-H).

(3E,5E,10Z)-*Pentadeca*-3,5,10-*trienyl Bromide* **29e**.—Similarly, starting from the alcohol **28e** (0.4 g, 1.8 mmol), trimethylsilyl bromide (0.61 g, 4.0 mmol), and zinc bromide (90 mg, 0.4 mmol) in methylene dichloride (15 cm^3), a crude product (0.51 g) was obtained, which was chromatographed on silica gel (10 g) in pentane to give the *bromide* **29e** (0.49 g, 95%) as an oil, n_D^{21} 1.5102 (Found: C, 62.8; H, 8.9; Br, 28.3. $C_{15}H_{25}Br$ requires C, 63.16; H, 8.83; Br, 28.01%); ν_{max}/cm^{-1} 640, 685, 960, 985, 1040, 1260, 1370, 1450, 1650, 2950 and 3070; λ_{max}/nm 233 (ε 23 300); δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 13- and 14-H_2), 1.45 (2 H, quint, *J* 7, 8-H_2), 1.9–2.2 (6H m, 7-, 9- and 12-H_2), 2.63 (2 H, br q, *J* 7, 2-H_2), 3.40 (2 H, t, *J* 7, 1-H_2), 5.25–5.45 (2 H, m, 10- and 11-H), 5.53 (1 H, dt, *J* 15 and 7, 3-H), 5.66 (1 H, dt, *J* 15 and 7, 6-H) and 5.9–6.2 (2 H, m, 4- and 5-H); *m/z* 286 (M^+, 1.5%), 284 (M^+, 1.2), 121 (8), 107 (12), 105 (12), 91 (27), 81 (37), 79 (46), 67 (51), 55 (63) and 44 (100).

(E,E)-*Tetradeca*-9,11-*dien*-1-*ol* **30**.—As described above for the alcohol **19**, starting from 6-bromohexan-1-ol (2.25 g, 12.4 mmol) in THF (10 cm^3), ethylmagnesium bromide in THF (1.5 mol dm^{-3}; 9.1 cm^3, 13.6 mmol), magnesium powder (0.75 g, 31.2 mmol), the bromide **29a** (0.47 g, 2.5 mmol) in THF (8 cm^3)–HMPA (4 cm^3) and dilithium tetrachlorocuprate in THF (0.1 mol dm^{-3}; 8 cm^3, 0.8 mmol), the title alcohol **30**[57] (0.3 g, 58%) was obtained as a liquid, b.p. 106–107 °C at 0.05 mmHg; n_D^{23} 1.4828; δ_H 1.00 (3 H, t, *J* 7, Me), 1.2–1.7 (12 H, m, CH_2), 2.0–2.2 (4 H, m, 8- and 13-H_2), 3.64 (2 H, t, *J* 7, 1-H_2), 5.5–5.7 (2 H, m, 9- and 12-H) and 5.9–6.1 (2 H, m, 10- and 11-H).

(E,E)-*Tetradeca*-9,11-*dienyl Acetate* **31**.—As described above for the acetate **22**, starting from the alcohol **30** (0.29 g, 1.38 mmol), acetic anhydride (0.28 g, 2.75 mmol), DMAP (10 mg), and pyridine (1.5 cm^3), the acetate **31**[57] (0.34 g, 98%) was obtained as a liquid, b.p. 99–100 °C at 0.03 mmHg; n_D^{23} 1.4698; δ_H 1.00 (3 H, t, *J* 7, Me), 1.2–1.7 (12 H, m, CH_2), 2.0–2.2 (4 H, m, 8- and 13-H_2), 2.07 (3 H, s, CH_3CO), 4.07 (2 H, t, *J* 7, 1-H_2), 5.5–5.7 (2 H, m, 9- and 12-H) and 5.9–6.1 (2 H, m, 10- and 11-H).

(4E,6E,11Z)-*Hexadeca*-4,6,11-*trienal* **33**.—A suspension of the bromide **29e** (0.49 g, 1.72 mmol), potassium cyanide (0.44 g, 6.77 mmol), and DB-18-C-6 (60 mg) in acetonitrile (7 cm^3) was refluxed for 12 h. The reaction mixture was then filtered and the filtrate was evaporated. To a stirred solution of the residue (0.39 g) in hexane (14 cm^3) under argon at −70 °C was added dropwise a solution of DIBAL in toluene (1 mol dm^{-3}; 3.5 cm^3, 3.5 mmol). The reaction mixture was kept at this temperature for 40 min and then was quenched with hydrochloric acid (1 mol dm^{-3}; 1.8 cm^3) and extracted into diethyl ether (3 × 10 cm^3). The extracts were washed successively with water (2 × 10 cm^3) and brine (3 × 5 cm^3), dried (Na_2SO_4), and evaporated. The residue (0.3 g) was chromatographed on silica gel (10 g) in hexane–diethyl ether (99:1) to yield the *aldehyde* **33** (0.24 g, 60%) as an oil, n_D^{20} 1.4931 (Found: C, 81.7; H, 11.0. $C_{16}H_{26}O$ requires C, 81.99; H, 11.18%); ν_{max}/cm^{-1} 660, 695, 865, 975, 1055, 1260, 1360, 1440, 1460, 1580, 1625, 1660, 1730, 2940 and 3020; λ_{max}/nm 232 (ε 22 000); δ_H 0.90 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 14- and 15-H_2), 1.43 (2 H, quint, *J* 7, 9-H_2), 1.9–2.2 (6 H, m, 8-, 10- and 13-H_2), 2.40 (2 H, br q, *J* 7, 3-H_2), 2.56 (2 H, td, *J* 7 and 2, 2-H_2), 5.25–5.45 (2 H, m, 11- and 12-H), 5.55 (1 H, dt, *J* 15 and 7, 4-H), 5.61 (1 H, dt, *J* 15 and 7, 7-H), 5.9–6.1 (2 H, m, 5- and 6-H) and 9.79 (1 H, t, *J* 2, 1-H); *m/z* 234 (M^+, 1%), 190 (2), 150 (24), 134 (28), 121 (34), 119 (40), 107 (25), 95 (66), 93 (52), 91 (45), 82 (49), 81 (100), 80 (48), 79 (96), 69 (32), 67 (92), 55 (67) and 41 (70).

(4E,6E,11Z)-*Hexadeca*-4,6,11-*trienyl Acetate* **34**.—To a stirred solution of the aldehyde **33** (0.13 g, 0.56 mmol) in diethyl ether (5 cm^3) at 0 °C under argon was added lithium aluminium hydride (10 mg, 0.26 mmol) in one portion. The reaction mixture was stirred for 15 min and was then treated at 0 °C successively with water (0.01 cm^3), aq. potassium hydroxide (3 mol dm^{-3}; 0.01 cm^3) and water (0.03 cm^3) and dried ($MgSO_4$). The solid formed was filtered off and washed with dry diethyl ether (15 cm^3) and the filtrate was evaporated. A solution of the residue (0.13 g) and DMAP (10 mg) in acetic anhydride (0.1 g, 0.98 mmol)–pyridine (1 cm^3) was kept at 25 °C for 30 min. The reaction mixture was then treated at 0 °C with hydrochloric acid (1 mol dm^{-3}; 12.5 cm^3) and extracted into diethyl ether (3 × 10 cm^3). The extracts were washed successively with saturated aq. sodium hydrogen carbonate (3 cm^3) and brine (3 × 5 cm^3), dried ($MgSO_4$), and evaporated. The residue (0.15 g) was chromatographed on silica gel (6 g) in hexane–diethyl ether (99:1) to afford the *acetate* **34** (0.14 g, 91%) as an oil, n_D^{20} 1.4833 (Found: C, 78.0; H, 10.7. $C_{18}H_{30}O_2$ requires C, 77.65; H, 10.86%); ν_{max}/cm^{-1} 635, 880, 965, 1040, 1255, 1370, 1435, 1735, 2940 and 3010; ν_{max}/nm 232 (ε 30 500); δ_H 0.91 (3 H, t, *J* 7, Me), 1.2–1.4 (4 H, m, 14- and 15-H), 1.45 (2 H, quint, *J* 7, 9-H_2), 1.74 (2 H, quint, *J* 7, 2-H_2), 1.9–2.2 (8 H, m, 3-, 8-, 10- and 13-H_2), 2.08 (3 H, s, CH_3CO), 4.09 (2 H, t, *J* 7, 1-H_2), 5.25–5.45 (2 H, m, 11- and 12-H), 5.55 (1 H, dt, *J* 15 and 7, 4-H), 5.60 (1 H, dt, *J* 15 and 7, 7-H) and 5.9–6.1 (2 H, m, 5- and 6-H); *m/z* 278 (M^+, 11%), 161 (25), 147 (26), 121 (29), 120 (28), 119 (38), 107 (31), 105 (48), 95 (35), 94 (31), 93 (54), 91 (58), 81 (61), 80 (60), 79 (100), 67 (60), 55 (51), 43 (65) and 41 (41).

(E)-7-*Bromohept*-4-*en*-1-*ol* **36**.—To a stirred solution of the ketone **8a** (1.67 g, 13.0 mmol) in diethyl ether (30 cm^3) at 0 °C under argon was added lithium aluminium hydride (0.5 g, 13.2 mmol) during 5 min. The reaction mixture was stirred for a further 20 min and then was treated at 0 °C successively with water (0.5 cm^3), aq. potassium hydroxide (3 mol dm^{-3}; 0.5 cm^3), and water (1.5 cm^3), and dried ($MgSO_4$). The solid that formed was filtered off and washed with dry diethyl ether (35 cm^3) and the filtrate was evaporated. To a vigorously stirred suspension of the residue (1.58 g) and zinc bromide (1.2 g, 5.3 mmol) in methylene dichloride (30 cm^3) at −10 °C was added a solution of trimethylsilyl bromide (6.59 g, 43.1 mmol) in methylene dichloride (10 cm^3) during 10 min. The reaction mixture was kept at −10 °C for 30 min and then quenched with saturated aq. sodium hydrogen carbonate (20 cm^3) and extracted with diethyl ether (3 × 25 cm^3). The extract was washed with brine (3 × 15 cm^3), dried ($MgSO_4$), and evaporated. The residue (2.35 g) was chromatographed on silica gel (50 g) with gradient elution from hexane to hexane–diethyl ether (82:18) to give the *title compound* **36** (2.29 g, 91%) as a liquid, b.p. 82–83 °C at 1 mmHg; n_D^{19} 1.5014 (Found: C, 43.3; H, 6.55. $C_7H_{13}BrO$ requires C, 43.54; H, 6.79%); ν_{max}/cm^{-1} 565, 645, 730, 920, 975, 1060, 1210, 1265, 1390, 1440, 2950, 3000 and 3610; δ_H 1.66 (2 H, quint, *J* 7, 2-H_2), 2.12 (2 H, br q, *J* 7, 3-H_2), 2.56 (2 H, br q, *J* 7, 6-H_2), 3.39 (2 H, t, *J* 7, 7-H_2), 3.68 (2 H, t, *J* 7, 1-H_2), 5.45 (1 H, dt, *J* 15 and 7, 5-H) and 5.57 (1 H, dt, *J* 15 and 7, 4-H); *m/z* 176 (M^+ − 18, 9%), 174 (M^+ − 18, 9), 120 (10), 95 (100), 81 (52), 71 (31), 67 (58), 55 (37), 45 (36) and 41 (65).

(E)-*Tridec*-4-*en*-1-*ol* **37**.—To a stirred solution of the Grignard reagent obtained from hexyl bromide (1.28 g, 7.76 mmol) and magnesium powder (0.19 g, 7.9 mmol) in THF (5 cm^3) at −60 °C under argon were added solutions of the bromide **36** (0.3 g, 1.55 mmol) in THF (5 cm^3) and dilithium tetrachlorocuprate in THF (0.1 mol dm^{-3}; 4 cm^3, 0.4 mmol) successively during 5 min. The reaction mixture was warmed during 30 min to 25 °C, kept at this temperature for 30 min, and was then quenched with saturated aq. copper(II) sulphate (10 cm^3) and extracted into diethyl ether (3 × 8 cm^3). The extracts were washed with brine (2 × 7 cm^3), dried ($MgSO_4$), and evaporated. The residue (0.55 g) was chromatographed on silica gel (15 g) with gradient elution from hexane to hexane–diethyl ether (88:12) to yield the alcohol **37**[58] (305 mg, 99%) as a liquid, b.p. 106–107 °C at 1 mmHg; n_D^{21} 1.4550; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.4 (12 H, m, CH_2), 1.65 (2 H, quint, *J* 7, 2-H), 1.98 (2 H, br q, *J* 7, 6-H_2), 2.09 (2 H, br q, *J* 7, 3-H_2), 3.67 (2 H, t, *J* 7, 1-H_2) and 5.35–5.55 (2 H, m, 4- and 5-H).

(E)-*Tridec*-4-*enyl Acetate* **38**.—As described above for the acetate **22**, starting from the alcohol **37** (0.16 g, 0.8 mmol), acetic anhydride (0.16 g, 1.6 mmol), DMAP (10 mg), and pyridine (0.5 cm^3), a crude product (0.22 g) was obtained, which was chromatographed on silica gel (5 g) with gradient elution from hexane to hexane–diethyl ether (92:8) to afford the title compound **38**[59] (0.19 g, 98%) as a liquid, b.p. 107–108 °C at 1 mmHg; n_D^{21} 1.4445; δ_H 0.98 (3 H, t, *J* 7, Me), 1.2–1.4 (12 H, m, CH_2), 1.69 (2 H, quint, *J* 7, 2-H_2), 1.98 (2 H, br q, *J* 7, 6-H_2), 2.05 (3 H, s, CH_3CO), 2.07 (2 H, br q, *J* 7, 3-H_2), 4.07 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (2 H, m, 4- and 5-H).

(E)-(7-*Tetrahydropyran*-2-*yloxy*)*hept*-3-*enyl Bromide* **39**.—A solution of the alcohol **36** (1.67, g, 8.65 mmol), 3,4-dihydro-2*H*-pyran (0.8 g, 9.5 mmol), and PPTS (0.17 g, 0.68 mmol) in methylene dichloride (30 cm^3) was kept at 25 °C for 2 h and was then evaporated, and the residue (2.65 g) was chromatographed on silica gel (50 g) in hexane–diethyl ether (97:3) to give the *ether* **39** (2.39 g, ~100%) as an oil; n_D^{20} 1.4915 (Found: C, 51.75; H, 7.7; Br, 29.1. $C_{12}H_{21}BrO_2$ requires C, 52.00; H, 7.64; Br, 28.82%); ν_{max}/cm^{-1} 570, 645, 730, 815, 870, 910, 975, 1030, 1080, 1130, 1200, 1260, 1305, 1440, 1465, 2940 and 3000; δ_H 1.4–1.9 (8 H, m, CH_2), 2.11 (2 H, br q, *J* 7, 5-H_2), 2.55 (2 H, br q, *J* 7, 2-H_2), 3.37 (2 H, t, *J* 7, 1-H_2), 3.3–3.9 (4 H, m, OCH_2), 4.57 (1 H, br t, *J* 4, OCHO), 5.42 (1 H, br dt, *J* 15 and 7, 3-H) and 5.56 (1 H, br dt, *J* 15 and 7, 4-H); *m*/*z* 278 (M^+, 0.3%), 276 (M^+, 0.3), 176 (4), 174 (4), 95 (21), 85 (100), 84 (17), 67 (15), 55 (17), 45 (10), 43 (12) and 41 (19).

(E)-1-*Phenylsulphonyl*-7-(*tetrahydropyran*-2-*yloxy*)*hept*-3-*ene* **40**.—A suspension of the bromide **39** (2.35 g, 8.5 mmol) and sodium benzenesulphinate (2.0 g, 12.2 mmol) in DMF (20 cm^3) was vigorously stirred at 60 °C for 3 h. The reaction mixture was then diluted with water (20 cm^3) and extracted with diethyl ether (4 × 20 cm^3). The extract was washed with brine (2 × 10 cm^3), dried ($MgSO_4$), and evaporated. The residue (3 g) was chromatographed on silica gel (50 g) in hexane–diethyl ether (97:3) to yield the *sulphone* **40** (2.58 g, 90%) as an oil, n_D^{20} 1.5250 (Found: C, 64.2; H, 7.8; S, 9.4. $C_{18}H_{26}O_4S$ requires C, 63.88; H, 7.74; S, 9.47%); ν_{max}/cm^{-1} 900, 1040, 1090, 1155, 1220, 1320, 1350, 1450, 2950 and 3020; λ_{max}/nm 217 (ε 11 000); δ_H 1.4–1.9 (8 H, m, CH_2), 2.02 (2 H, br q, *J* 7, 5-H_2), 2.39 (2 H, br q, *J* 7, 2-H_2), 3.12 (2 H, m, 1-H_2), 3.3–3.9 (4 H, m, OCH_2), 4.53 (1 H, br t, *J* 4, OCHO), 5.32 (1 H, br dt, *J* 15 and 7, 3-H), 5.47 (1 H, br dt, *J* 15 and 7, 4-H) and 7.5–8.0 (5 H, m, Ph); *m*/*z* 338 (M^+, 1%), 255 (11), 254 (6), 224 (6), 143 (7), 112 (7), 95 (33), 85 (100), 57 (26), 55 (33), 46 (39), 45 (80), 43 (46) and 41 (35).

(4E,7Z)-1-(*Tetrahydropyran*-2-*yloxy*)*trideca*-4,7-*diene* **41**.—As described above for the olefin **13a**, a solution of the sulphone **40** (1.03 g, 3.05 mmol) in THF (15 cm^3)–HMPA (1.5 cm^3) was treated with butyllithium (1.6 mol dm^{-3}; 2.0 cm^3, 3.2 mmol) in hexane followed by a solution of hexanal (0.34 g, 3.4 mmol) in THF (7 cm^3) to give, after treatment of the reaction mixture with acetic anhydride (0.47 g, 4.6 mmol) and DMAP (40 mg, 0.33 mmol), a crude product (1.7 g), which was treated further with sodium hydroxide (0.24 g, 6.0 mmol) in diethyl ether (30 cm^3) containing methanol (0.3 cm^3). The resulting mixture (1.4 g) was then treated with sodium dithionite (1.57 g, 9.0 mmol) and sodium hydrogen carbonate (1.51 g, 18.0 mmol) in aq. ethanol (1:1; 35 cm^3) and the final crude product (0.9 g) was chromatographed on silica gel (25 g) in hexane–diethyl ether (99:1) to afford the *title diene* **41** (0.62 g, 73%) as an oil, n_D^{22} 1.4686 (Found: C, 77.1; H, 11.8. $C_{18}H_{32}O_2$ requires C, 77.09; H, 11.50%); ν_{max}/cm^{-1} 910, 990, 1030, 1080, 1130, 1210, 1355, 1455, 2940 and 3000; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.9 (14 H, m, CH_2), 1.9–2.1 (4 H, m, 3- and 9-H_2), 2.73 (2 H, br t, *J* 7, 6-H_2), 3.3–3.9 (4 H, m, OCH_2), 4.58 (1 H, br t, *J* 4, OCHO) and 5.3–5.5 (4 H, m, HC=CH); *m*/*z* 280 (M^+, 1%), 196 (3), 178 (3), 121 (3), 95 (6), 93 (5), 85 (100), 84 (17), 79 (10), 67 (17), 57 (10), 55 (13), 43 (12) and 41 (15).

(4E,7Z)-*Trideca*-4,7-*dien*-1-*ol* **42**.—As described above for the alcohol **14a**, starting from the ether **41** (0.31 g, 1.1 mmol) and PPTS (30 mg, 0.12 mmol) in methanol (10 cm^3), the crude title product (0.3 g) was obtained, which was then chromatographed on silica gel (6 g) with gradient elution from hexane to hexane–diethyl ether (88:12) to give the alcohol **42**[60] (0.2 g, 92%) as a liquid, b.p. 94–95 °C at 0.025 mmHg; n_D^{21} 1.4690; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.5 (6 H, m, CH_2), 1.64 (2 H, quint, *J* 7, 2-H_2), 1.95–2.15 (4 H, m, 3- and 9-H_2), 2.74 (2 H, br t, *J* 7, 6-H_2), 3.67 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (4 H, m, HC=CH).

(4E,7Z)-*Trideca*-4,7-*dienyl Acetate* **43**.—As described above for the acetate **22**, starting from the alcohol **42** (0.17 g, 0.87 mmol), acetic anhydride (0.18 g, 1.76 mmol), DMAP (10 mg), and pyridine (0.5 cm^3), the crude title product (0.21 g) was obtained, which was chromatographed on silica gel (5 g) with gradient elution from hexane to hexane–diethyl ether (95:5) to yield the title compound **43**[60] (205 mg, 99%) as a liquid, b.p. 89–90 °C at 0.02 mmHg; n_D^{21} 1.4558; δ_H 0.89 (3 H, t, *J* 7, Me), 1.2–1.4 (6 H, m, CH_2), 1.69 (2 H, quint, *J* 7, 2-H_2), 1.95–2.15 (4 H, m, 3- and 9-H_2), 2.06 (3 H, s, CH_3CO), 2.73 (2 H, br t, *J* 7, 6-H_2), 4.07 (2 H, t, *J* 7, 1-H_2) and 5.3–5.5 (4 H, m, HC=CH).

References

1 H. J. Bestmann and O. Vostrowsky, in *Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel*, ed. R. Wegler, Springer-Verlag, Berlin, Heidelberg and New York, 1981, vol. 6, p. 29; R. Baker and J. W. S. Bradshaw, in *Aliphatic and Related Natural Product Chemistry*, ed. F. D. Gustone, The Royal Society of Chemistry, London, 1983, vol. 3, p. 66; R. Baker and R. H. Herbert, *Nat. Prod. Rep.*, 1984, **1**, 299.

2 T. Ando, M. Koike, M. Uchiyama and H. Kuroko, *Agric. Biol. Chem.*, 1987, **51**, 2691.

3 K. Mori, in *Total Synthesis of Natural Products*, ed. J. ApSimon, Wiley, New York, 1981, vol. 4, p. 1; P. E. Sonnet, in *Techniques in Pheromone Research*, eds. H. E. Hummel and T. A. Miller, Springer-Verlag, New York, Berlin, Heidelberg and Tokyo, 1984, p. 371.

4 A. M. Moisseenkov, B. A. Czeskis, N. M. Ivanova and O. M. Nefedov, *Org. Prep. Proced. Int.*, 1990, **22**, 215; B. A. Czeskis, N. M. Ivanova, A. M. Moiseenkov and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2025.

5 B. A. Czeskis, N. M. Ivanova, A. M. Moiseenkov and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2539; N. M. Ivanova, B. A. Czeskis, E. V. Rubanova, V. G. Yatzynin, A. M. Moiseenkov and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 640.

6 H. N. C. Wong, M.-Y. Hon, C.-W. Tse and Y.-C. Yip, *Chem. Rev.*, 1989, **89**, 165; M. C. Aploim, A. D. Morris, W. B. Motherwell and

D. M. O'Shea, *Tetrahedron Lett.*, 1988, **29**, 4173; S. Kanemoto, M. Shimizu and H. Yoshioka, *J. Chem. Soc., Chem. Commun.*, 1989, 690; S. Kanemasa, T. Otsuka, K. Doi, O. Tsuge and E. Wada, *Synthesis*, 1990, 1167; R. F. Childs, M. D. Kostyk, C. J. L. Lock and M. Makendran, *J. Am. Chem. Soc.*, 1990, **112**, 8912.
7 K. Mori, J. Fukami and T. Ohtaki, *Agric. Biol. Chem.*, 1971, **35**, 1116; K. Mori, *Tetrahedron*, 1972, **28**, 3747.
8 R. A. Myrsina and N. V. Kuznetsov, *Ukr. Khim. Zh. (Russ. Ed.)*, 1976, **42**, 407 (*Chem. Abstr.*, 1976, **85**, 20649b).
9 R. T. Hrubiec and M. B. Smith, *J. Org. Chem.*, 1984, **49**, 431.
10 Preliminary communication, A. M. Moiseenkov, B. A. Czeskis, N. M. Ivanova and O. M. Nefedov, *Mendeleev Commun.*, 1991, 13.
11 T. Mukaiyama, *Org. React.*, 1982, **28**, 203; M. Vaultier, P. H. Lambert and K. Carrié, *Bull. Soc. Chim. Fr.*, 1986, 83; P. Sulmon, N. DeKimpe and N. Schamp, *Synthesis*, 1989, 8.
12 V. V. Veselovsky, A. S. Gybin, A. V. Lozanova, A. M. Moiseenkov, V. A. Smit and R. Caple, *Tetrahedron Lett.*, 1988, **29**, 175; R. B. Mitra and G. B. Reddy, *Synthesis*, 1989, 694.
13 M. Julia, M. Launay, J.-P. Stacino and J.-N. Verpeaux, *Tetrahedron Lett.*, 1982, **23**, 2465; J. Bremmer, M. Julia, M. Launay and J.-P. Stacino, *Tetrahedron Lett.*, 1982, **23**, 3265; M. Julia and J.-P. Stacino, *Tetrahedron*, 1986, **42**, 2469.
14 M. Tamura and J. Kochi, *Synthesis*, 1971, 303.
15 M. Gardette, N. Jabri, A. Alexakis and J. F. Normant, *Tetrahedron*, 1984, **40**, 2741.
16 J. H. Tumlinson, C. E. Yonce, R. E. Doolittle, R. R. Heath, C. R. Gentry and E. R. Mitchell, *Science*, 1974, **185**, 614; M. G. Karandinos, J. H. Tumlinson and T. D. Eichlin, *J. Chem. Ecol.*, 1977, **3**, 57; D. K. Reed, T. D. Eichlin and G. L. Reed, *Environ. Entomol.*, 1981, **10**, 488.
17 S. Voerman, H. Audemard and E. Priesner, *Entomol. Exp. Appl.*, 1983, **34**, 203; X. Zhang, G. Guo, G. Lin, Y. Wu, P. Wu, Z. Li and K. Wei, J. Chem. Ecol., 1986, **12**, 1263.
18 D. G. Nielsen, F. F. Purrington, R. L. Campbell, T. R. Wilmot, J. Capizzi and J. H. Tumlinson, *Environ. Entomol.*, 1978, **7**, 544.
19 E. Priesner, P. Witzgall and S. Voerman, *J. Appl. Entomol.*, 1986, **102**, 195.
20 T. G. Gray, K. N. Slessor, R. F. Shepherd, G. G. Grant and J. F. Manville, *Can. Entomol.*, 1984, **116**, 1525.
21 C. J. H. Booij, S. Voerman and L. P. M. Willemse, *J. Appl. Entomol.*, 1986, **102**, 2539.
22 T. G. Gray, K. N. Slessor, G. G. Grant, R. F. Shepherd, E. N. Holsten and A. S. Tracey, *Can. Entomol.*, 1984, **116**, 51.
23 J. M. Vakenti, A. P. Gaunce, K. N. Slessor, G. G. S. King, S. A. Allan, H. F. Madsen and J. H. Borden, *J. Chem. Ecol.*, 1988, **14**, 605.
24 C. Loefstedt and W. M. Herrebout, *Entomol. Exp. Appl.*, 1988, **46**, 29.
25 P. J. Silk, E. W. Butterworth, L. P. S. Kuenen, C. J. Northcott and E. G. Ketela, *J. Chem. Ecol.*, 1988, **14**, 1417.
26 E. W. Underhill, A. P. Arthur and P. G. Mason, *Environ. Entomol.*, 1986, **15**, 1063.
27 M. Toth, C. Lofstedt, B. S. Hansson, G. Szocs and A. I. Farag, *Entomol. Exp. Appl.*, 1989, **51**, 107.
28 C. J. Persoons, S. Voerman, C. Van der Kraan and C. J. H. Booij, *Entomol. Exp. Appl.*, 1984, **35**, 101.
29 W. A. Wolf and W. L. Roelofs, *J. Chem. Ecol.*, 1987, **13**, 1019.
30 C. J. Sanders and E. A. Meighen, *J. Chem. Ecol.*, 1987, **13**, 1749.
31 L. P. M. Willemse, C. J. H. Booij and S. Voerman, *J. Appl. Entomol.*, 1987, **103**, 508.
32 W. Baltensweiler and E. Priesner, *J. Appl. Entomol.*, 1988, **106**, 217.
33 E. Priesner, H. Bogenschutz and C. Loefstedt, *Z. Naturforsch., Teil C*, 1988, **43**, 918.
34 G. C. Lonergan, B. M. Ponder, W. D. Seabrook and L. R. Kipp, *J. Chem. Ecol.*, 1989, **15**, 2495.
35 T. E. Bellas, R. J. Bartell and A. Hill, *J. Chem. Ecol.*, 1983, **9**, 503; S. J. Muggleston and S. P. Foster, *Physiol. Entomol.*, 1989, **14**, 443.
36 H. J. Bestmann, A. B. Attygalle, J. Schwarz, W. Carbe, O. Vostrowsky and I. Tomida, *Tetrahedron Lett.*, 1989, **30**, 2911.
37 A. L. Gemal and J.-L. Luche, *J. Am. Chem. Soc.*, 1981, **103**, 5454.
38 K. Ogawa and A. Yamamoto, G.P. 3 814 465, 1989 (*Chem. Abstr.*, 1990, **112**, 114214j); G. G. Melikyan, G. H. Aslanyan, K. A. Aganesyan and D. A. Mkrtchyan, *Khim. Prir. Soedin.*, 1990, 102.
39 W. L. Roelofs, J. P. Kochansky, R. T. Carde, G. G. Kennedy, C. A. Henrick, J. N. Labovitz and V. L. Corbin, *Life Sci.*, 1975, **17**, 699; O. G. Bacon, J. N. Seiber and G. G. Kennedy, *J. Econ. Entomol.*, 1976, **69**, 569; M. Toth, T. E. Bellas and G. H. L. Rothschild, *J. Chem. Ecol.*, 1984, **10**, 271; T. Ono and S. Orita, *Appl. Entomol. Zool.*, 1986, **21**, 632; T. Ono, R. E. Charlton and R. T. Carde, *J. Chem. Ecol.*, 1990, **16**, 531.
40 W. Coppens and N. Schamp, *Bull. Soc. Chim. Belg.*, 1972, **81**, 643.
41 A. Chattopadhyay, V. R. Mamdapur and M. S. Chadha, *Indian J. Chem., Sect. B*, 1983, **22**, 1221.
42 V. Dedek and P. Trska, *Collect. Czech. Chem. Commun.*, 1970, **35**, 651.
43 M. Julia and C. Blasioli, *Bull. Soc. Chim. Fr.*, 1976, Pt. 2, 1941.
44 P. Vinczer, Z. Juvancz, L. Novak and Cs. Czantay, *Acta Chim. Hung.*, 1987, **125**, 737; K. Nishitani, M. Isozaki and K. Yamakawa, *Chem. Pharm. Bull.*, 1990, **38**, 28.
45 P. Audin, A. Doutheau and J. Gore, *Bull. Soc. Chim. Fr.*, 1984, Pt. 2, 297.
46 M. Miyashita, A. Yoshikoshi and P. A. Grieco, *J. Org. Chem.*, 1977, **42**, 3772.
47 M. Horiike, M. Tanouchi and C. Hirano, *Agric. Biol. Chem.*, 1980, **44**, 257.
48 H. J. Bestmann, O. Vostrowsky, K. K. Koschatzky, H. Platz, T. Brosche, I. Kantardjiew, M. Rheinwald and W. Knauf, *Angew. Chem.*, 1978, **90**, 815; A. D. Buss, N. Greeves, R. Mason and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2569.
49 H. J. Bestmann, K. H. Koschatzky and O. Vostrowsky, *Liebigs Ann. Chem.*, 1982, 1478.
50 R. Rossi and A. Carpita, *Gazz. Chim. Ital.*, 1978, **108**, 709.
51 S.-K. Kang, W.-S. Kim and B.-H. Moon, *Synthesis*, 1985, 1161.
52 C. Canevet, T. Röder, O. Vostrowsky and H. J. Bestmann, *Chem. Ber.*, 1980, **113**, 1115.
53 H. C. Brown, H. D. Lee and S. U. Kulkarni, *J. Org. Chem.*, 1986, **51**, 5282.
54 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.
55 M. Uchida, K. Mori and M. Matsui, *Agric. Biol. Chem.*, 1978, **42**, 1067; A. Yamamoto, T. Ishihara and T. Fukumoto, *Agric. Biol. Chem.*, 1989, **53**, 285; M. Hoskovec, D. Saman and B. Koutek, *Collect. Czech. Chem. Commun.*, 1990, **55**, 2270.
56 C. Descoins, D. Samain, B. Lalanne-Cassou and M. Callois, *Bull. Soc. Chim. Fr.*, 1977, 941.
57 H. J. Bestmann, J. Süss and O. Vostrowsky, *Liebigs Ann. Chem.*, 1981, 2117.
58 J. W. Patterson, *Synthesis*, 1985, 337.
59 P. E. Sonnet, *Synthesis*, 1980, 828.
60 H. J. Bestmann, T. Zeibig and O. Vostrowsky, *Synthesis*, 1990, 1039.

Paper 1/02810C
Received 11*th June* 1991
Accepted 25*th June* 1991