Acyl radical-mediated polyene cyclisations directed towards steroid ring synthesis

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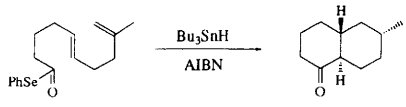
Treatment of appropriately substituted *Se*-phenyl 5,9,13-triene- and 5,9,13,17-tetraene-selenoates, *i.e* 9b, 33, 40, 47a and 47b, with Bu_3SnH–AIBN is found to lead to angular six-ring fused polycycles, *viz.* 20, 34, 50, 53 and 54 respectively, *via* consecutive 6-*endo-trig* modes of cyclisations, starting from the corresponding polyene acyl radical intermediates. The structures and stereochemistries of the polycyclic products were determined largely from detailed analysis and correlation of ^{13}C NMR spectroscopic data. The *trans-anti-trans* stereochemistry of the tricyclic ketone 50 was established from X-ray analysis of a solid solution of a 1:1 mixture of ring C methyl epimers of the corresponding 2,4-dinitrophenylhydrazone derivative.

In the preceding paper we summarised the outcome of our studies of a new and direct synthetic approach to decalone and to perhydrophenanthrone ring constructions, based on serial 6-*endo-trig* radical cyclisations initiated from 5,9-diene acyl radical intermediates, *viz.* **1**→**2**.[1] Furthermore, in the same paper we highlighted the importance of alkyl group substitution and stereochemistry of the various alkene double bonds, in determining the regio- and stereo-chemical outcome of these cascade polyene radical cyclisations. In this paper we summarise the extensions of these studies, and show how acyl/alkyl radical cyclisations of polyolefin-selenoates, under clean reductive conditions in the presence of Bu_3SnH–AIBN, can lead to linear and angular six-membered fused polycycles, including steroid ring systems, *via* regio- and stereo-specific consecutive 6-*endo-trig* modes of cyclisation.

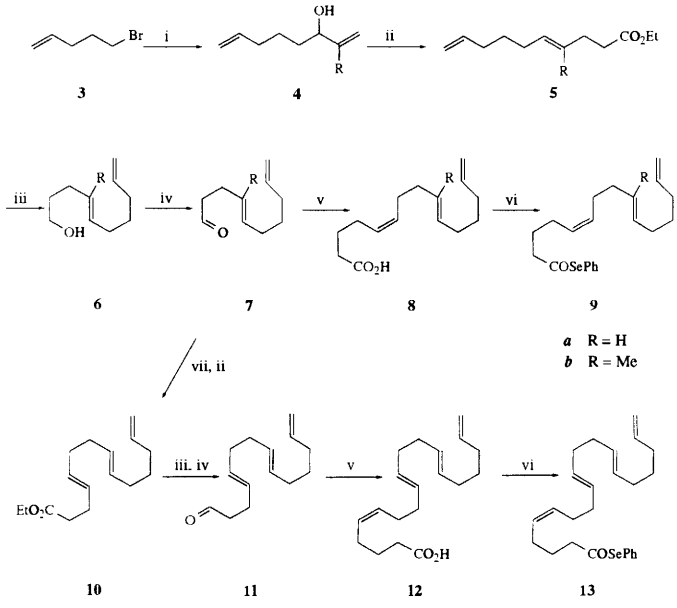


1 **2**

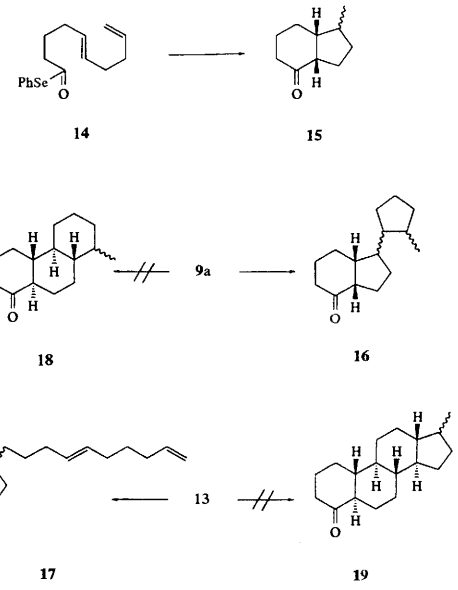
We began the extensions of our earlier studies by first examining the cyclisations of the *Se*-phenyl tri- and tetra-eneselenoates **9a** and **13**, respectively, which were devoid of methyl group substitution on their various olefin double bonds. The (5*Z*,9*E*)-**9a** and (5*Z*,9*E*,13*E*)-**13** isomers of the selenoates were synthesised using methods and conditions developed in earlier studies, and described in the immediately preceding paper. The procedures are shown in outline in Scheme 1.

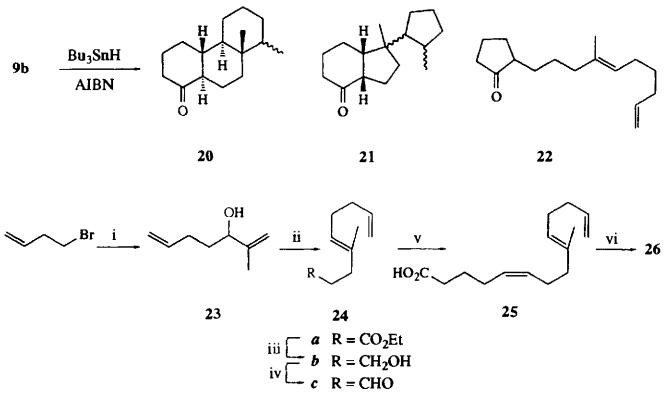
In accord with the outcome of our earlier studies with 5*E*- and 5*Z*-isomers of polyeneselenoates lacking methyl group substitution at C-9, *viz.* **14**→**15**,[1] treatment of the *Se*-phenyl selenoates **9a** and **13** with Bu_3SnH–AIBN led largely to diastereoisomeric mixtures of the corresponding indanone products **16** (~65%) and **17** (~75%) resulting from consecutive 6-*endo*, 5-*exo trigonal* cyclisations. No evidence for the co-formation of products, *e.g.* **18** and **19**, resulting from consecutive 6-*endo* tri- or tetra-cyclisations respectively could be secured from these studies.

By contrast, when the 9-methyl substituted trieneselenoate analogue **9b** was treated with Bu_3SnH–AIBN, under the same conditions, the major product isolated was a mixture of diastereoisomers of the angular-fused 6,6,6-ring ketone **20** (~60%), together with smaller amounts of the substituted indanone **21** and the cyclopentanone **22**. In addition, the related 9-methyl substituted trieneselenoates **26** and **33**, whose syntheses are summarised in Schemes 2 and 3, also underwent

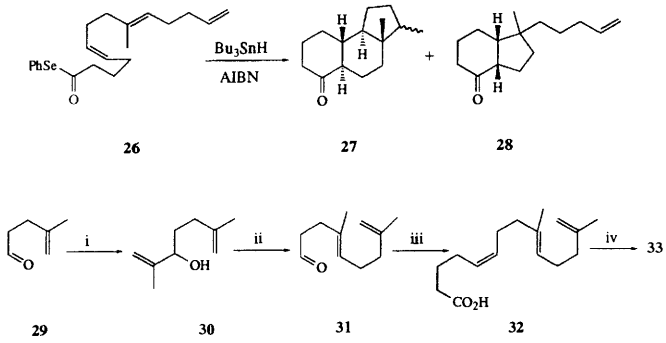


Scheme 1 *Reagents:* i, Mg, then CH_2=C(R)CHO; ii, $(EtO)_3CMe$, $EtCO_2H$; iii, $LiAlH_4$; iv, PCC, CH_2Cl_2; v, $HO_2C(CH_2)_4\overset{+}{P}Ph_3Br^-$, DMSO–NaH; vi, Ph_2Se_2, PBu_3; vii, CH_2=CHMgBr



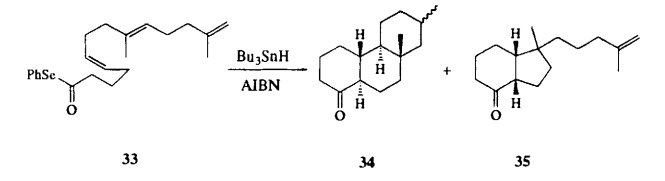


Scheme 2 *Reagents:* i, Mg, then $H_2C{=}C(Me)CHO$; ii, $(EtO)_3CMe$, $EtCO_2H$; iii, $LiAlH_4$; iv, PCC, CH_2Cl_2; v, $HO_2C(CH_2)_4\overset{+}{P}Ph_3Br^-$, NaH–DMSO; vi, Ph_2Se_2, PBu_3



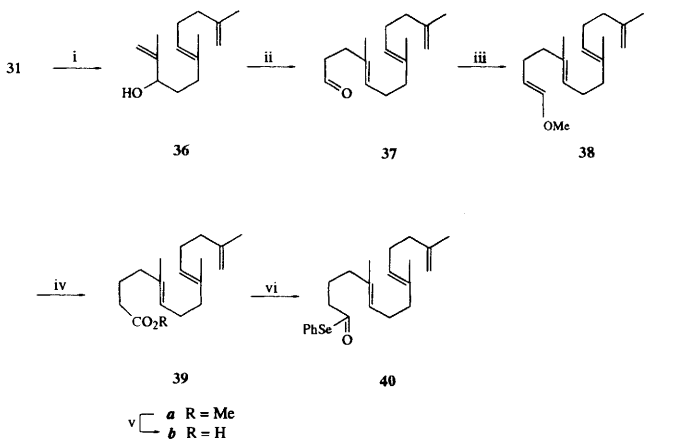
Scheme 3 *Reagents:* i, $H_2C{=}C(Me)MgBr$; ii, $EtOCH{=}CH_2$, $Hg(OAc)_2$, heat; iii, $HO_2C(CH_2)_4\overset{+}{P}Ph_3Br^-$, NaH–DMSO; iv, Ph_2Se_2, PBu_3

successful consecutive 6-*endo-trig* cyclisations leading to the angular fused tricycles **27** (31%) and **34** (31%) respectively. In each instance the formation of **27** and **34** was accompanied by varying amounts of the indanone products **28** (~37%) and **35** (47%) respectively, produced *via* competing 6-*endo*, 5-*exo trig* modes of cyclisation from the polyene acyl radical precursors. The structures and stereochemistries assigned to the polycyclic products **27**, **28**, **34** and **35** followed from inspection and analysis of their ^1H NMR and ^{13}C NMR data, together with comparison and correlation with data for similar compounds described in the literature. These analyses and correlations are discussed at the end of this paper.

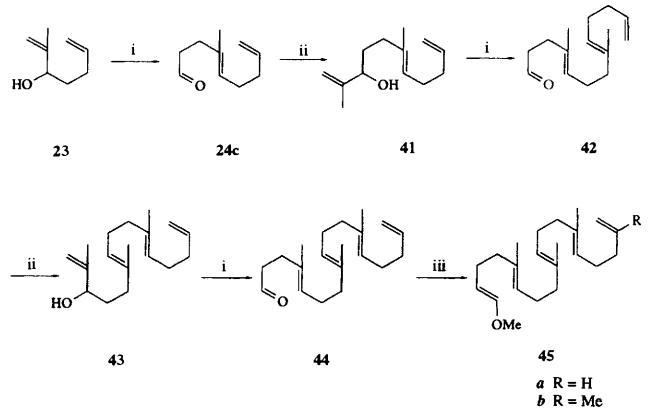


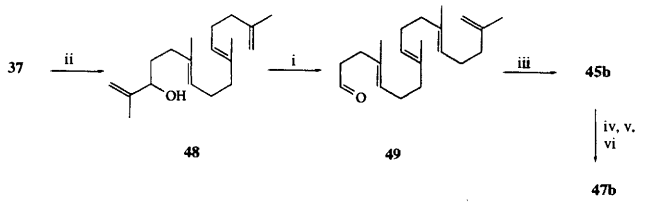
The aforementioned studies provided us with an insight and an appreciation of the importance of methyl group substitution on the various double bonds in determining the regiochemical outcome of the various polyene cyclisations. They also led us to our final series of polyene-selenoates for investigation, *i.e.* those 5,9,13-trienes **40**, **47a** and **47b** containing methyl group substitution on their C-5, C-9 and C-13 centres. The all-*E* isomers of the three *Se*-phenyl selenoates **40**, **47a** and **47b** were all prepared *via* similar routes, using a series of Claisen rearrangements, to establish the geometries of the various trisubstituted double bonds (see Schemes 4 and 5).

Treatment of the *Se*-phenyl trieneselenoate **40** with Bu_3SnH–AIBN produced a 1:1 mixture of the epimeric tricyclic ketones **50** and **51** in approximately 55% yield, accompanied by a smaller amount (*ca.* 18%) of the indanone **52**. Although we were frustrated in our attempts to separate the epimers **50** and **51** by chromatography, we were able to produce a satisfying



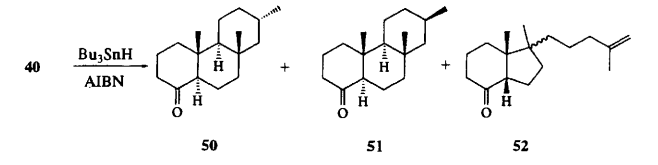
Scheme 4 *Reagents:* i, $H_2C{=}C(Me)MgBr$; ii, $EtOCH{=}CH_2$, $Hg(OAc)_2$, heat; iii, $MeOCH\overset{+}{P}Ph_3Cl^-$–$LiN(SiMe_3)_2$; iv, PCC, CH_2Cl_2; v, K_2CO_3–MeOH; vi, Ph_2Se_2, PBu_3





Scheme 5 *Reagents and conditions:* i, $EtOCH{=}CH_2$, $Hg(OAc)_2$, heat; ii, $H_2C{=}C(Me)MgBr$; iii, $MeOCH_2\overset{+}{P}Ph_3Cl^-$, $LiN(SiMe_3)_2$; iv, PCC, CH_2Cl_2; v, K_2CO_3–MeOH; vi, Ph_2Se_2, PBu_3

crystalline sample of a mixture of epimers of the corresponding 2,4-dinitrophenylhydrazone derivative for X-ray analysis. We were pleased to find that the X-ray analysis indicated a solid solution of the two epimers **50** and **51** of the tricyclic ketone with *trans-anti-trans* stereochemistry in a ratio of approximately 1:1 (Fig. 1).



Finally, when the *Se*-phenyl tetraeneselenoates **47a** and **47b** were treated with Bu_3SnH–AIBN, they both underwent

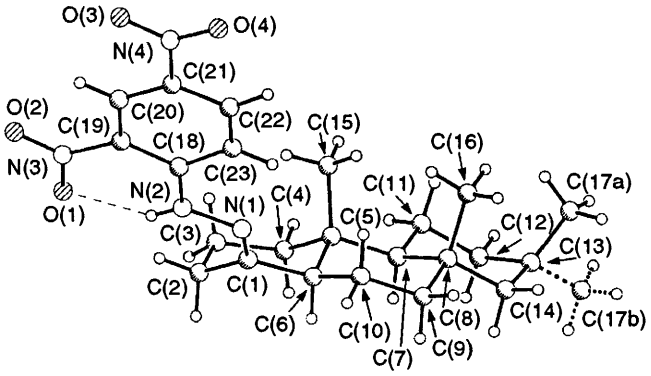
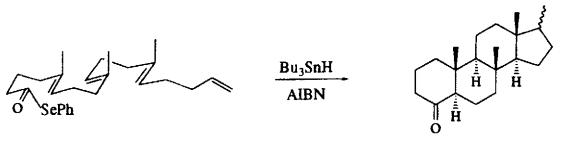
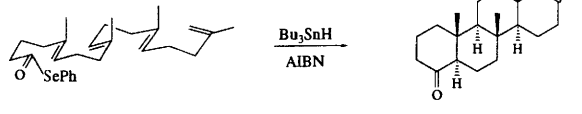


Fig. 1 Molecular structure of 1, showing two positions of the disordered methyl group

extraordinarily clean, and regio- and stereo-specific, tris-cyclisations leading to the all-*trans* isomers of the corresponding tetracycles, **53** and **54**, respectively, in yields of 60–80%. Each of the tetracyclic ketones **53** and **54** was produced as a mixture of ring D methyl epimers, but their structures and stereochemistries followed from analysis of their NMR data, and correlation of these data with those recorded for literature compounds and similar ring systems produced in this study. These important and determining NMR studies will now be described.



47a **53**



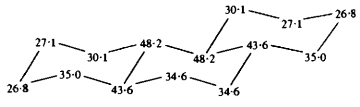
47b **54**

Structural assignments of polycycles

The highfield ^{1}H NMR spectra of the polycyclic ketones prepared in this paper and the accompanying paper[1] were complex and, because of the superposition of many of the signals, could only be partially assigned even with the aid of the various modern irradiation techniques. Hence, the results were not sufficiently unambiguous for the precise definition of the stereochemistry of these systems. However, it has been shown that ^{13}C NMR shift data may be used, in a relatively simple way, for structural and stereochemical assignments in alicyclic systems.[2] The effective use of ^{13}C NMR requires an extensive data collection for suitable model systems and, fortunately, such a compilation exists for *cis*- and *trans*-bicyclo-[4.4.0]decanes.[2]

The validity of the use of $\Delta\delta_C$ effects for substituents in the ring systems prepared in our study was first tested in the assignment of the ^{13}C NMR shifts for *trans,anti,trans*-perhydrophenanthren-1-one,[1] a compound of known stereochemistry. Thus, the ^{13}C shifts for *trans,anti,trans*-perhydrophenanthrene are shown in formula **55**.[3] This molecule may be considered as a $2_{eq},3_{eq}$-butano-*trans*-bicyclo[4.4.0]decane (N.B. *eq* = equatorial). The ^{13}C shifts for the various carbon atoms in *trans*-bicyclo[4.4.0]decane are given in **56**,[2] and the $\Delta\delta$ effects arising from transposing **56** to **55** are then shown in formula **57**. The $\Delta\delta$ values (which are *usually* small beyond the γ-carbon atom) may now be used to estimate the effect of the $7_{eq},8_{eq}$-butano-fusion onto *trans*-bicyclo[4.4.0]decan-2-one **58**[2] to give *trans,anti,trans*-perhydrophenanthren-1-one. These estimated values are now shown in formula **59a**, and the experimentally determined ^{13}C shifts are given in **59b**. There is very close agreement between calculated and experimental values, which mostly lie within the range $\Delta\delta \pm 0.5$ ppm, with the largest differences being $+0.7$ ppm.

Assignment of the ^{13}C NMR shifts for *trans,anti,trans*-perhydrophenanthren-1-one **59** now allows this molecule to be used as a model for calculations in the methyl-substituted tri- and tetra-cyclic ketone systems (*viz.* **20**, **34**), assuming a *trans,anti,trans* ring-fusion stereochemistry. Thus, **59** can alternatively be considered as arising from the $2_{eq},3_{eq}$-fusion of the $CH_2CH_2CH_2CO$ moiety onto *trans*-bicyclo[4.4.0]decane **56**, giving rise to a new set of $\Delta\delta_C$ effects shown in formula **60**. These $\Delta\delta_C$ values can then be used to estimate the effect on the ^{13}C shifts of methyl-substituted *trans*-bicyclo[4.4.0]decanes in their transformation into methyl-substituted *trans,anti,trans*-perhydrophenanthren-1-ones arising from the similar fusion of the $CH_2CH_2CH_2CO$ moiety. Thus, the hypothetical transform-



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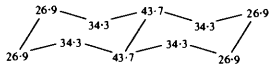

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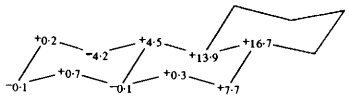

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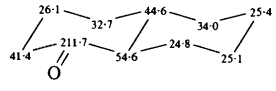

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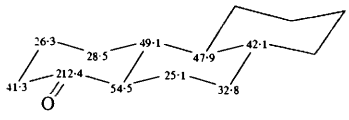
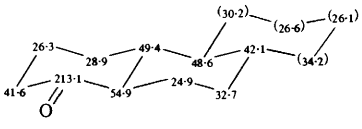
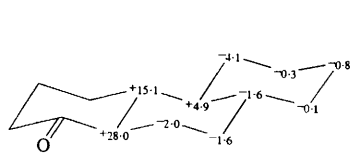


59a (Calculated)



59b (Observed)



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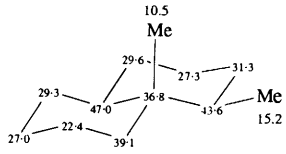

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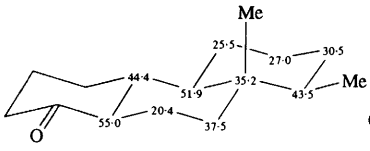
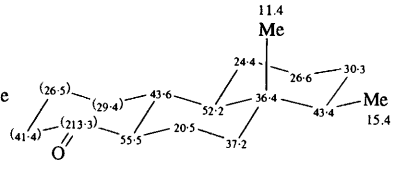
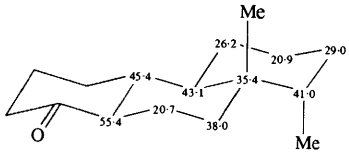


62a



62b



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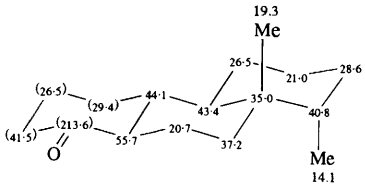
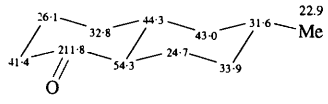


63b



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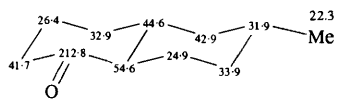

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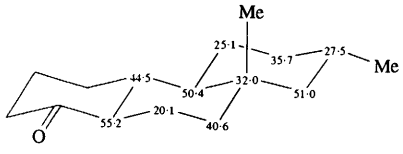

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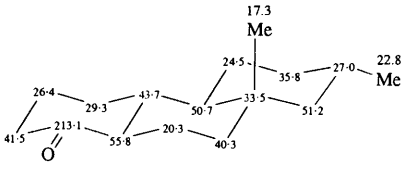
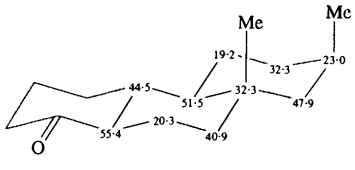


65b



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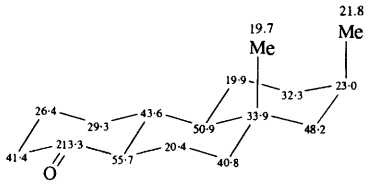


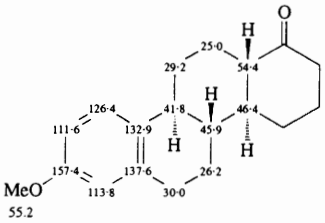
66b

ation of 1,2$_{eq}$-dimethyl-*trans*-bicyclo[4.4.0]decane **61**[2] into the required *trans,anti,trans*-dimethylperhydrophenanthren-1-one gives rise to the calculated shifts shown in formula **62a**. The experimentally observed ^{13}C shifts shown in **62b** are for the major isomer of **20** resulting from the tandem radical cyclisation from **9b**. Agreement between the calculated and observed shifts are remarkably good, and all lie within $\Delta\delta$ ± 1.2 ppm. In order to calculate the ^{13}C NMR shifts for the minor isomer of **20**, which has an 8$_{ax}$- rather than an 8$_{eq}$-methyl substituent, it was first necessary to calculate the ^{13}C shifts for 1,2$_{ax}$-dimethyl-*trans*-bicyclo[4.4.0]decane (N.B. *ax* = axial). This was achieved by correlations using **56** and 1-methyl- and 2$_{ax}$-methyl-*trans*-bicyclo[4.4.0]decanes as model systems.[2] Incorporating the $\Delta\delta_C$ effects due to the appropriate fusion of the $CH_2CH_2CH_2CO$ moiety then led to the calculated shifts shown in **63a**. The experimentally observed ^{13}C shifts for the minor stereoisomer from the aforementioned tandem radical cyclisation are given in **63b**. Differences between **63a** and **b** are all within $\Delta\delta_C$ ± 1.3 ppm, which is a remarkable result in view of the length of the correlation procedure. A unique resonance

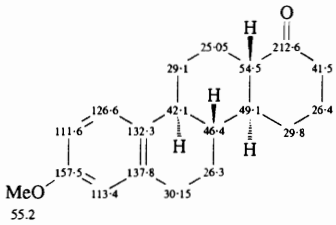
for C-9 was not found in the ^{13}C NMR spectrum, and is tentatively assigned as δ_C 37.2, coinciding with the signal for the major isomer **62b**.

Shift differences for individual carbon atoms in the comparison of *trans*- and *cis*-bicyclo[4.4.0]decan-2-ones can be as high as $\Delta\delta_C = -4.4$ ppm, with an average $\Delta\delta_C = -2.3$ ppm. Differences for individual carbon atoms in the comparison of *trans*- and *cis*-bicyclo[4.4.0]decanes can be as high as $\Delta\delta_C = -8.5$ ppm, with an average $\Delta\delta_C = -4.7$ ppm. These large differences would be expected to translate into similar differences in the ^{13}C shifts for all-*trans*- and the various *cis*-perhydrophenanthrenes and *cis*-perhydrophenanthren-1-ones. Hence, the excellent agreement between the calculated shifts for **62a** and **63a**, and the observed values shown in **62b** and **63b**, can be taken as firm evidence that the presumed *trans,anti,trans* stereochemistry in the products of the above cascade radical cyclisation *is* correct.

Correlations of the type outlined above were also applied in the calculation of the ^{13}C shifts of some of the other ketonic products (*viz.* **34**) arising from this study and also of those (formulae **64a** and **67a**) produced in the immediately preceding paper. The results are summarised in formulae **64a–67a** (calculated) and **64b–67b** (observed). In our calculation for **67a** we used the published ^{13}C shifts for *trans*-7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.[4] In the homoestrone system[1] **67a/b** there is excellent agreement for all carbon atoms other than C-14 (steroid numbering) where $\Delta\delta_C = +2.7$ ppm.



67a



67b

We have been unable to use these correlation procedures for all of the ketonic products produced in our cascade studies because of the lack of literature data for suitable model systems. The effects of multiple methyl substitution is particularly difficult to estimate with accuracy. However, the independent establishment of the *trans,anti,trans*-stereochemistry of the ketones **50** and **51** by X-ray structure analysis lends weight to the above assignments based on ^{13}C shifts. Stereochemical assignments for the indanone products produced in our studies (*e.g.* **17** and **21**) should be taken as tentative at this stage. We hope to clarify the stereochemical problems still outstanding through our continuing efforts in this area.[5]

Experimental

General experimental details and synthetic procedures used in this study are given in the preceding paper.[1]

Octa-1,7-dien-3-ol 4a.[6] The alcohol was prepared from acrolein and the Grignard reagent derived from 5-bromopent-1-ene (52%) following the same procedure used to synthesise 2-methylocta-1,7-dien-3-ol **4b**.[1] It showed ν_{max}/cm^{-1}(film) 3361 br (OH), 3077, 2978, 2934, 2860, 1641, 1424, 992 and 913; δ_H 5.94–5.72 (m, 2 × =CH), 5.25–4.92 (m, 2 × $=CH_2$), 4.14–4.06 (m, CHO), 2.25 (br s, OH), 2.17–1.98 (m, CH_2) and 1.70–1.30 (m, 2 × CH_2); δ_C 141.1 (=CH), 138.5 (=CH), 114.5$_4$ ($=CH_2$), 114.5$_0$ ($=CH_2$), 73.0 (C*H*OH), 36.3 (CH_2), 33.5 (CH_2) and 24.5 (CH_2).

Deca-4,9-dienal 7a. Ethyl (4*E*)-deca-4,9-dienoate **5a**[7] was first prepared (85%) from the alcohol **4a** according to the general procedure[1] and showed δ_H 5.79 (ddt, *J* 17.1, 10.3 and 6.7, C*H*=CH_2), 5.50 (2 × dt, *J* 15.3, 6.1 and 5.3, *E*-CH_2-C*H*=C*H*CH_2), 4.98 (ddt, *J* 17.1, CH=C*H*H), 4.93 (ddt, *J* 10.3, CH=CH*H*), 4.11 (q, *J* 7.1, OCH_2), 2.37–2.27 (m, 2 × CH_2), 2.06–1.96 (m, 2 × CH_2), 1.46–1.39 (m, CH_2) and 1.24 (t, *J* 7.1, CH_3). The *E*-stereochemistry was confirmed by NOE experiments: δ_C 173.3 (CO), 138.8 (=CH), 131.4 (=CH), 128.5 (=CH), 114.5 ($=CH_2$), 60.3 (OCH_2), 34.5 (CH_2), 33.2 (CH_2), 31.9 (CH_2), 28.7 (CH_2), 28.0 (CH_2) and 14.3 (CH_3); the *Z*-isomer was not detected by ^{13}C NMR. Reduction of the ester **5a** using lithium aluminium hydride next produced deca-4,9-dien-1-ol **6a** (74%),[8] an oil showing ν_{max}/cm^{-1}(film) 3328br (OH), 3076, 2928, 2855, 1640, 1439, 1059, 967 and 910; δ_H 5.93–5.78 (m, =CH), 5.51–5.47 (m, CH=CH), 5.09–4.97 (2 × d, *J* 17.2 and 10.0, CH=CH_2), 3.69 (t, *J* 6.5, CH_2O), 2.19–2.02 (m, 3 × CH_2), 1.74–1.63 (m, CH_2) and 1.55–1.44 (m, CH_2); δ_C 138.8 (=CH), 130.7 (=CH), 129.8 (=CH), 114.4 ($=CH_2$), 62.4 (CH_2OH), 33.1 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 28.8 (CH_2) and 28.7 (CH_2). Oxidation of this alcohol **6a** using pyridinium chlorochromate (PCC), according to the general procedure then gave the *aldehyde* **7a** (42%).[8] Alternatively, reduction of **5a** with DIBAL-H in dichloromethane at < -78 °C delivered **7a** directly (90%); δ_H 9.69 (t, *J* 1.0, CHO), 5.80–5.65 (m, =CH), 5.40–5.30 (m, CH=CH), 4.95–4.85 (2 × d, *J* 17.1 and 9.9, CH=CH_2), 2.45–2.40 (m, CH_2), 2.30–2.23 (m, CH_2), 2.00–1.89 (m, 2 × CH_2) and 1.42–1.34 (m, CH_2); δ_C 202.3 (CO), 138.6 (=CH), 131.5 (=CH), 128.0 (=CH), 114.4 ($=CH_2$), 43.4 (CH_2), 33.1 (CH_2), 31.8 (CH_2), 28.5 (CH_2) and 25.1 (CH_2).

(5*Z*,9*E*)-Pentadeca-5,9,14-trienoic acid 8a. The trienoic acid was prepared by Wittig reaction between the aldehyde **7a** and 4-carboxybutyl(triphenyl)phosphonium bromide (46%) according to the general procedure,[1] and gave a *ca.* 3:1 mixture of the *E,Z*- and *E,E*-isomers; ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1709, 1640, 1438, 1414, 1240, 968 and 911; δ_H 9.45 (br s, CO_2H), 5.80 (ddt, *J* 17.0, 10.3 and 6.7, C*H*=CH_2), 5.45–5.30 (m, 2 × CH=CH), 5.00 (dm, *J* 17.0, CH=C*H*H), 4.94 (dm, *J* 10.3, CH=CH*H*), 2.36 (t, *J* 7.5, CH_2CO_2), 2.12–1.97 (m, 5 × CH_2), 1.73–1.66 (m, CH_2) and 1.48–1.40 (m, CH_2); δ_C(*E,Z*-isomer) 180.3 (CO), 139.0 (=CH), 130.7 (=CH), 130.6 (=CH), 130.0 (=CH), 128.6 (=CH), 114.4 ($=CH_2$), 33.3 (CH_2), 32.7 (2 × CH_2), 32.0 (CH_2), 28.9 (CH_2), 27.4 (CH_2), 26.6 (CH_2) and 24.6 (CH_2); δ_C(*E,E*-isomer) 131.3 (=CH), 130.4 (=CH), 130.1 (=CH), 129.1 (=CH), 33.5 (CH_2), 33.4 (CH_2), 31.9 (CH_2) and 24.5 (CH_2).

***Se*-Phenyl pentadeca-5,9,14-trieneselenoate 9a.** The ester was prepared (68%) from the acid **8a** according to the general procedure.[1] Purification by chromatography afforded a *ca.* 9:1 mixture of the *Z,E*- and *E,E*-isomers; δ_H 7.48–7.44 (m, 2 × aryl =CH), 7.34–7.30 (m, 3 × aryl =CH), 5.77 (ddt, *J* 17.1, 10.2 and 6.7, C*H*=CH_2), 5.42–5.23 (m, 2 × CH=CH), 4.94 (dm, *J* 17.1, CH=C*H*H), 4.90 (dm, *J* 10.2, CH=CH*H*), 2.66 (t, *J* 7.4, CH_2CO), 2.07–1.97 (m, 5 × CH_2), 1.76–1.65 (m, CH_2) and 1.46–1.35 (m, CH_2); δ_C(*Z,E*-isomer) 200.1 (CO), 138.8 (=CH), 135.7 (2 × aryl =CH), 130.7 (=CH), 130.5 (=CH), 129.8 (=CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.3 (=CH), 126.4 (quat. C), 114.4 ($=CH_2$), 46.8 (CH_2), 33.2 (CH_2), 32.6 (CH_2), 31.9 (CH_2), 28.7 (CH_2), 27.3 (CH_2), 26.2 (CH_2) and 25.1 (CH_2); δ_C(*E,E*-isomer) 130.3 (=CH), 129.9 (=CH), 129.1 (=CH), 46.7 (CH_2), 31.5 (CH_2), 28.5 (CH_2) and 25.0 (CH_2).

Reductive cyclisation of the *Se*-phenyl selenoate 9a. Cyclisation of the ester according to the general procedure afforded a complex mixture of products. After removal of the tin residues, separation of the mixture (56%) by flash chromatography (light petroleum→light petroleum–ether, 50:1) gave three fractions: (i) 2-deca-4,9-dienylcyclopentanone (~10%); δ_C 221.6 (CO), 139.0 (=CH), 130.3 (=CH), 130.1 (=CH), 114.4 ($=CH_2$), 49.1 (CH), 38.2 (CH_2), 33.2 (CH_2), 32.5

(CH_2), 32.0 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 27.6 (CH_2) and 20.8 (CH_2); (ii) a 5:4 mixture of diastereoisomers of the indanone **16** (24%); δ_H 2.60–1.10 (complex series of m), 0.92 (d, *J* 6.6, CH_3) and 0.69 (d, *J* 7.3, CH_3); δ_C(major) 215.5 (CO), 54.7 (CH), 46.7 (CH), 46.2 (CH), 45.3 (CH), 38.0 (CH_2), 35.3 (CH), 34.0 (CH_2), 28.8 (CH_2), 28.5 (CH_2), 27.4 (CH_2), 25.6 (CH_2), 22.2 (CH_2), 22.0 (CH_2) and 15.6 (CH_3); (minor) 215.4 (CO), 54.1 (CH), 52.5 (CH), 48.7 (CH), 47.1 (CH), 40.5 (CH), 38.0 (CH_2), 35.7 (CH_2), 33.2 (CH_2), 28.0 (CH_2), 27.2 (CH_2), 24.4 (CH_2), 22.0 (CH_2), 21.6 (CH_2) and 15.6 (CH_3); (iii) a mixture of another isomer of the indanone **16** (~35%) and some unidentified compounds (~10%). The latter isomer of **16** showed: δ_H 2.58–1.02 (complex series of m), 0.68 (d, *J* 7.2, CH_3); δ_C 216.0 (CO), 54.5 (CH), 46.9 (CH), 45.4 (CH), 45.3 (CH), 38.0 (CH_2), 35.9 (CH), 33.8 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 27.5 (CH_2), 25.6 (CH_2), 22.1 (CH_2), 21.6 (CH_2) and 14.7 (CH_3).

***Se*-Phenyl nondeca-5,9,13,18-tetraeneselenoate 13.** The title ester was prepared starting from (4*E*)-deca-4,9-dienal **7a**, using the general procedures described earlier. Thus, reaction between vinylmagnesium bromide and (4E)-deca-4,9-dienal **7a** first gave (6*E*)-dodeca-1,6,11-trien-3-ol (48%) as an oil; δ_H 6.12–5.91 (m, 2 × C*H*=CH_2), 5.63–5.59 (m, CH=CH), 5.44–5.09 (m, 2 × CH=CH_2), 4.34–4.26 (m, CHO), 2.31–2.14 (m, 3 × CH_2), 1.83–1.70 (m, CH_2) and 1.69–1.56 (m, CH_2); δ_C 141.0 (=CH), 138.8 (=CH), 130.8 (=CH), 129.8 (=CH), 114.6 (=CH_2), 114.4 (=CH_2), 72.7 (CHOH), 36.7 (CH_2), 33.2 (CH_2), 31.9 (CH_2), 28.7 (CH_2) and 28.5 (CH_2). This compound was converted into ethyl (4*E*,8*E*)-tetradeca-4,8,13-trienoate **10** (89%), uncontaminated with stereoisomers using the Claisen–Ireland rearrangement; δ_H 5.95–5.82 (m, C*H*=CH_2), 5.53–5.47 (m, 2 × CH=CH), 5.08 (dm, *J* 17.1, C*H*H), 5.03 (dm, *J* 10.9, CH*H*), 4.21 (q, *J* 7.2, OCH_2), 2.46–2.38 (m, 2 × CH_2), 2.17–2.09 (m, 4 × CH_2), 1.58–1.47 (m, CH_2) and 1.34 (t, *J* 7.2, CH_3); δ_C 173.2 (CO), 138.8 (=CH), 131.1 (=CH), 130.3 (=CH), 129.9 (=CH), 128.3 (=CH), 114.3 (=CH_2), 60.2 (OCH_2), 34.3 (CH_2), 33.1 (CH_2), 32.6 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 28.7 (CH_2), 27.9 (CH_2) and 14.2 (CH_3). Reduction of **10** with lithium aluminium hydride next gave (4*E*,8*E*)-tetradeca-4,8,13-trien-1-ol (95%); δ_H 5.97–5.82 (m, C*H*=CH_2), 5.58–5.45 (m, 2 × CH=CH), 5.09 (d, *J* 18.1, =C*H*H), 5.03 (d, *J* 10.2, =CH*H*), 3.73 (t, *J* 6.6, CH_2O), 2.18–1.99 (m, 5 × CH_2), 1.77–1.64 (m, CH_2) and 1.58–1.47 (m, CH_2); δ_C 138.9 (=CH), 130.5 (=CH), 130.3 (=CH), 130.0 (=CH), 129.7 (=CH), 114.3 (=CH_2), 62.5 (CH_2OH), 33.2 (CH_2), 32.6 (2 × CH_2), 32.3 (CH_2), 31.9 (CH_2), 28.9 (CH_2) and 28.7 (CH_2) which was oxidised using PCC to the corresponding aldehyde **11** (71%); ν_{max}/cm^{-1}(film) 3075, 2925, 2854, 1726, 1640, 1440 968 and 910; δ_H 9.69 (t, *J* 1.7, CHO), 5.81–5.66 (m, C*H*=CH_2), 5.44–5.28 (m, 2 × CH=CH), 4.91 (dm, *J* 17.1, =C*H*H), 4.87 (dm, *J* 10.2, =CH*H*), 2.45–2.39 (m, CH_2), 2.29–2.23 (m, CH_2), 2.01–1.88 (m, 4 × CH_2) and 1.42–1.31 (m, CH_2); δ_C 202.4 (CO), 138.8 (=CH), 131.3 (=CH), 130.4 (=CH), 129.8 (=CH), 128.0 (=CH), 114.3 (=CH_2), 43.4 (CH_2), 33.1 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 28.7 (CH_2) and 25.1 (CH_2). A Wittig reaction between the aldehyde **11** and 4-carboxybutyl-(triphenyl)phosphonium bromide[1] next led to (5*Z*,9*E*,13*E*)-nonadeca-5,9,13,18-tetraenoic acid **12** (28%); δ_H 10.50 (br s, CO_2H), 5.98–5.83 (m, C*H*=CH_2), 5.56–5.41 (m, 3 × CH=CH), 5.09 (dm, *J* 17.1, =C*H*H), 5.04 (dm, *J* 10.9, =CH*H*), 2.45 (t, *J* 7.3, CH_2CO), 2.29–2.10 (m, 7 × CH_2), 1.79 (pentet, *J* 7.3, CH_2) and 1.59–1.48 (m, CH_2), which was then phenylselenylated to produce the *Se*-phenyl selenoate **13** (68%) as a pale yellow oil; δ_H 7.44–7.38 (m, 2 × aryl =CH), 7.31–7.26 (m, 3 × aryl =CH), 5.80–5.65 (m, C*H*=CH_2), 5.33–5.18 (m, 3 × CH=CH), 4.91 (dm, *J* 18.0, =C*H*H), 4.86 (dm, *J* 9.9, =CH*H*), 2.61 (t, *J* 7.4, CH_2), 2.10–1.92 (m, 7 × CH_2), 1.72–1.60 (m, CH_2) and 1.41–1.30 (m, CH_2); δ_C 200.0 (CO), 138.8 (=CH), 135.7 (2 × aryl =CH), 130.7 (=CH), 130.24 (=CH), 130.17 (=CH), 130.0 (=CH), 129.7 (=CH), 129.2 (2 × aryl =CH), 128.7 (aryl =CH), 128.2 (=CH), 126.4 (quat. C), 114.3 (=CH_2), 46.8 (CH_2), 33.1 (CH_2), 32.6 (2 × CH_2), 32.5 (CH_2), 31.9 (CH_2), 28.7 (CH_2), 27.3 (CH_2), 26.2 (CH_2) and 25.1 (CH_2).

Reductive cyclisation of the *Se*-phenyl selenoate 13. Cyclisation of the title ester, according to the general procedure, led to a 1:1 mixture of diastereoisomers of the indanone **17** (75%) which was separated by further chromatography over flash silica gel (light petroleum–ether, 50:1). The first diastereoisomer showed: ν_{max}/cm^{-1}(film) 3075, 2924, 2855, 1707, 1640, 1457, 1237, 967 and 909; δ_H 5.81–5.66 (m, C*H*=CH_2), 5.37–5.27 (m, CH=CH), 4.96 (dm, *J* 17.0, =C*H*H), 4.89 (dm, *J* 10.2, =CH*H*) and 2.59–1.12 (very complex series of m); δ_C 215.5 (CO), 138.8 (=CH), 130.4 (=CH), 130.1 (=CH), 114.3 (=CH_2), 54.2 (CH), 46.3 (CH), 44.6 (CH), 37.7 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 28.7$_4$ (CH_2), 28.6$_6$ (CH_2), 28.5 (CH_2), 27.2 (CH_2), 25.1 (CH_2) and 21.2 (CH_2); *m*/*z* 274.2261 (M^+. $C_{19}H_{30}O$ requires M^+, 274.2297). The second diastereoisomer showed: ν_{max}/cm^{-1}(film) 3075, 2926, 2855, 1738sh, 1710, 1640, 1456, 1153, 967 and 909; δ_H 5.81–5.66 (m, C*H*=CH_2), 5.34–5.26 (m, CH=CH), 4.92 (dm, *J* 17.0, =C*H*H), 4.87 (dm, *J* 11.5, =CH*H*) and 2.65–0.80 (complex series of m); δ_C 214.1 (CO), 138.8 (=CH), 130.4 (=CH), 130.1 (=CH), 114.3 (=CH_2), 52.5 (CH), 48.3 (CH), 43.0 (CH), 40.3 (CH_2), 34.1 (CH_2), 33.2 (CH_2), 32.7 (CH_2), 31.9 (CH_2), 30.5 (CH_2), 28.7 (CH_2), 28.0 (CH_2), 26.5 (CH_2), 24.7 (CH_2) and 23.2 (CH_2); *m*/*z* 274.2333 (M^+. $C_{19}H_{30}O$ requires M^+, 274.2297).

***Se*-Phenyl (5*Z*,9*E*)-9-methylpentadeca-5,9,14-trieneselenoate 9b.** The title ester was prepared from ethyl 4-methyldeca-4,9-dienoate **5b**[1] following the general procedures, and *via* (i) (4*E*)-4-methyldeca-4,9-dien-1-ol **6b**;[9] ν_{max}/cm^{-1}(film) 3363br (OH), 3076, 2929, 1640, 1454, 1378, 1052, 909 and 734; δ_H 5.82–5.67 (m, =CH), 5.13–5.10 (m, =CH), 4.97–4.85 (*ca.* 2 × d, *J* 17.6 and 9.6, =CH_2), 3.55 (t, *J* 6.5, CH_2OH), 2.10–1.89 (m, 4 × CH_2), 1.65–1.57 (m, CH_2), 1.54 (s, CH_3) and 1.41–1.30 (m, CH_2); δ_C 138.9 (=CH), 134.8 (quat. C), 124.8 (=CH), 114.3 (=CH_2), 62.7 (CH_2OH), 35.9 (CH_2), 33.3 (CH_2), 30.7 (CH_2), 29.0 (CH_2), 27.3 (CH_2) and 15.8 (CH_3); (ii) (4*E*)-4-methyldeca-4,9-dienal **7b**;[9] δ_H 9.68 (br s, CHO), 5.81–5.66 (m, CH=CH_2), 5.09 (t, *J* 6.6, =CH), 4.92 and 4.87 (2 × d, *J* 16.8 and 10.2, CH=CH_2), 2.45 (t, *J* 7.1, CH_2CO), 2.25 (t, *J* 7.1, CH_2), 2.00–1.89 (m, 2 × CH_2), 1.54 (s, CH_3) and 1.40–1.30 (m, CH_2); δ_C 202.6 (CO), 138.8 (=CH), 133.1 (quat. C), 125.4 (=CH), 114.4 (=CH_2), 42.1 (CH_2), 33.2 (CH_2), 31.8 (CH_2), 28.8 (CH_2), 27.2 (CH_2) and 16.0 (CH_3); (iii) (5*Z*,9*E*)-9-methylpentadeca-5,9,14-trienoic acid **8b** contaminated with *ca.* 10% of the *E*,*E*-isomer; ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1709, 1640, 1439, 1414, 1381, 1241, 993 and 911; δ_H 5.82–5.67 (m, C*H*=CH_2), 5.35–5.22 (m, CH=CH), 5.08–5.03 (m, =CH), 4.92 and 4.87 (2 × d, *J* 18.3 and 11.2, CH=CH_2), 2.29 (t, *J* 7.4, CH_2), 2.07–1.88 (m, 5 × CH_2), 1.68–1.59 (m, CH_2), 1.52 (s, CH_3) and 1.41–1.30 (m, CH_2); δ_C 180.5 (CO), 139.1 (=CH), 134.8 (quat. C), 130.9 (=CH), 128.3 (=CH), 124.7 (=CH), 114.4 (=CH_2), 39.6 (CH_2), 33.5 (CH_2), 33.4 (CH_2), 29.1 (CH_2), 27.4 (CH_2), 26.5 (CH_2), 25.9 (CH_2), 24.6 (CH_2) and 16.0 (CH_3).

The *Se*-phenyl selenoate **9b**, essentially a single stereoisomer after chromatographic purification, showed: ν_{max}/cm^{-1}(film) 3074, 3002, 2925, 2854, 1725, 1640, 1580, 1477, 1438, 990, 910, 738 and 689; δ_H 7.58–7.47 (m, 2 × aryl =CH), 7.45–7.33 (m, 3 × aryl =CH), 5.94–5.79 (m, C*H*=CH_2), 5.46–5.32 (m, 2 × dt, *J* 10.5, 6.9 and 6.6, *Z*-CH=CH), 5.21–5.18 (m, =CH), 5.08–4.96 (*ca.* 2 × d, *J* 17 and 10, =CH_2), 2.75 (t, *J* 7.4, CH_2CO), 2.19–2.01 (m, 5 × CH_2), 1.85–1.74 (m, CH_2), 1.64 (s, CH_3), 1.53–1.42 (m, CH_2); δ_C 200.2 (CO), 139.0 (=CH), 135.7 (2 × aryl =CH), 134.6 (quat. C), 130.9 (=CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.0 (=CH), 126.4 (quat. C), 124.7 (=CH), 114.3 (=CH_2), 46.8 (CH_2), 39.5 (CH_2), 33.3 (CH_2), 29.0 (CH_2), 27.3 (CH_2), 26.2 (CH_2), 25.8 (CH_2), 25.2 (CH_2) and 16.0 (CH_3); *m*/*z* (%) 233 (12), 215 (16) and 149 (100) (Found: C, 67.8; H, 7.9. $C_{22}H_{30}OSe$ requires C, 67.9; H, 7.8%).

Reductive cyclisation of *Se*-phenyl selenoate 9b. Cyclisation of the title ester according to the general procedure led to a complicated mixture of products (76%). Separation by flash chromatography over silica gel (light petroleum→light petroleum–ether, 50:1) gave: (i) the cyclopentanone **22** admixed with the isomers of **20** and some unidentified compounds; (ii) a mixture of compounds **21** and **20** (~25%); (iii) a 5:2 mixture of the diastereoisomers of compound **20** (~45%); δ_C(major) 213.3 (CO), 55.5 (CH), 52.2 (CH), 43.6 (CH), 43.4 (CH), 41.4 (CH_2), 37.2 (CH_2), 36.4 (quat. C), 30.3 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 24.4 (CH_2), 20.5 (CH_2), 15.4 (CH_3) and 11.4 (CH_3); δ_C(minor) 213.6 (CO), 55.7 (CH), 44.1 (CH), 43.4 (CH), 41.5 (CH_2), 40.8 (CH), 37.2 (CH_2), 35.0 (quat. C), 29.4 (CH_2), 28.6 (CH_2), 26.5 (2 × CH_2), 21.0 (CH_2), 20.7 (CH_2), 19.3 (CH_3) and 14.1 (CH_3); *m/z* 234.1976. (M^+. CHO requires M^+, 234.1984); *m/z* 234 (100%), 219 (30), 216 (8), 201 (28), 191 (31), 177 (10), 165 (10), 164 (14) and 163 (28).

***Se*-Phenyl (5*Z*,9*E*)-9-methyltetradeca-5,9,13-trieneselenoate 26.** The title ester was prepared starting from 3-hydroxy-2-methylhepta-1,6-diene **23**;[10] δ_H 5.86 (ddt, *J* 16.8, 10.2 and 6.7, C*H*=CH_2), 5.10–4.86 (m, 2 × =CH_2), 4.09 (t, *J* 6.4, CHO), 2.21–2.05 (m, CH_2), 1.75 (s, CH_3) and 1.80–1.59 (m, CH_2); δ_C 147.2 (quat. C), 138.2 (=CH), 114.5 (=CH_2), 110.9 (=CH_2), 75.0 (CHOH), 33.7 (CH_2), 29.7 (CH_2) and 17.2 (CH_3) produced from the addition of but-3-enylmagnesium bromide to methacrolein. According to the general procedures,[1] the alcohol **23** was next converted sequentially into: (i) ethyl(4*E*)-4-methyl-4,8-nonadienoate **24a**;[10] ν_{max}/cm^{-1}(film) 3076, 2978, 2928, 1736, 1640, 1446, 1371, 1296, 1252, 1157, 1035 and 912; δ_H 5.81–5.70 (m, C*H*=CH_2), 5.20–5.10 (m, =CH), 5.05–4.95 (2 × dm, *J* 17.4 and 10.5, CH=CH_2), 4.10 (q, *J* 7.4, OC$H_2$$CH_3$), 2.42–2.22 (m, 2 × CH_2), 2.07–2.03 (m, 2 × CH_2), 1.58 (s, CH_3) and 1.24 (t, *J* 7.4, OCH_2CH_3); δ_C 173.4 (CO), 138.4 (=CH), 133.7 (quat. C), 124.5 (=CH), 114.4 (=CH_2), 60.1 (OCH_2CH_3), 34.6 (CH_2), 33.7 (CH_2), 33.2 (CH_2), 27.2 (CH_2), 15.9 (CH_3) and 14.2 (CH_3); (ii) (4*E*)-4-methylnona-4,8-dien-1-ol **24b**;[11] ν_{max}/cm^{-1}(film) 3346br (OH), 3076, 2935, 1640, 1446, 1381, 1059 and 910; δ_H 5.80–5.72 (m, C*H*=CH_2), 5.20–5.12 (m, =CH), 5.04–4.95 (2 × dm, *J* 17.5 and 10.1, CH=CH_2), 3.65 (t, *J* 7.3, CH_2OH), 2.10–1.98 (m, 3 × CH_2), 1.70–1.62 (m, CH_2) and 1.59 (s, CH_3); δ_C 138.6 (=CH), 135.0 (quat. C), 124.2 (=CH), 114.4 (=CH_2), 62.6 (CH_2OH), 35.9 (CH_2), 33.9 (CH_2), 30.7 (CH_2), 27.3 (CH_2) and 15.9 (CH_3); (iii) (4*E*)-4-methylnona-4,8-dienal **24c** ν_{max}/cm^{-1}(film) 3076, 2920, 2718, 1725, 1669, 1640, 1444, 1414, 1384, 1247 and 912; δ_H 9.75 (t, *J* 1.9, CHO), 5.86–5.75 (m, C*H*=CH_2), 5.19–5.15 (m, =CH), 5.03–4.93 (2 × dm, *J* 16.8 and 10.2, CH=CH_2), 2.55–2.45 (m, CH_2), 2.37–2.20 (m, CH_2), 2.10–2.04 (m, 2 × CH_2) and 1.62 (s, CH_3); δ_C 202.4 (CO), 138.1 (=CH), 133.1 (quat. C), 124.6 (=CH), 114.3 (=CH_2), 41.9 (CH_2), 33.5 (CH_2), 31.6 (CH_2), 27.0 (CH_2) and 15.9 (CH_3) (the aldehyde **24c** was also prepared by Claisen rearrangement of the vinyl ether derived from **23**) and: (iv) (5*Z*,9*E*)-9-methyltetradeca-5,9,13-trienoic acid **25**, containing *ca.* 12.5% of the *E*,*E*-acid; ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1709, 1640, 1438, 1241 and 911; δ_H 5.91–5.78 (m, C*H*=CH_2), 5.45–5.34 (2 × dt, *J* 10.9, 6.9 and 6.7, *Z*-CH=CH), 5.22–5.11 (m, =CH), 5.08–4.98 (2 × d, *J* 18.5 and 11.2, CH=CH_2), 2.38 (t, *J* 7.4, CH_2), 2.19–1.96 (m, 5 × CH_2), 1.75–1.65 (m, CH_2) and 1.61 (s, CH_3); δ_C(*Z*,*E*-isomer) 180.3 (CO), 138.7 (=CH), 134.9 (quat. C), 130.7 (=CH), 128.2 (=CH), 124.1 (=CH), 114.4 (=CH_2), 39.5 (CH_2), 33.9 (CH_2), 33.4 (CH_2), 27.4 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 24.5 (CH_2) and 15.9 (CH_3); δ_C(*E*,*E*-isomer) 138.5 (=CH), 128.7 (=CH), 124.8 (=CH), 114.5 (=CH_2), 39.6 (CH_2), 33.3 (CH_2), 33.0 (CH_2), 31.7 (CH_2) and 24.3 (CH_2).

Phenylselenylation of the acid **25**, according to the general procedure,[1] then gave the *Z*,*E*-ester **26** (72%), containing *ca.* 5% of the corresponding *E*,*E*-isomer, as a pale yellow oil; ν_{max}/cm^{-1}(film) 3074, 2924, 2855, 1725, 1639, 1579, 1477, 1438, 911, 738 and 689; δ_H 7.56–7.50 (m, 2 × aryl =CH), 7.44–7.36 (m, 3 × aryl =CH), 5.94–5.79 (m, C*H*=CH_2), 5.51–5.28 (m, CH=CH), 5.21–5.12 (m, =CH), 5.08–4.96 (m, =CH_2), 2.75 (t, *J* 7.4, CH_2), 2.18–2.04 (m, 5 × CH_2), 1.84–1.75 (m, CH_2) and 1.62 (s, CH_3); δ_C(*Z*,*E*-isomer) 200.1 (CO), 138.6 (=CH), 135.7 (2 × aryl =CH), 134.9 (quat. C), 130.9 (=CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.0 (=CH), 126.4 (quat. C), 124.1 (=CH), 114.4 (=CH_2), 46.8 (CH_2), 39.5 (CH_2), 33.9 (CH_2), 27.4 (CH_2), 26.2 (CH_2), 25.8 (CH_2), 25.2 (CH_2) and 16.0 (CH_3); *m/z* (%) 219 (10), 201 (20), 177 (10), 159 (11), 158 (9), 157 (16), 151 (13), 136 (10) and 135 (100) (Found: C, 67.4; H, 7.7. $C_{21}H_{28}OSe$ requires C, 67.2; H, 7.5%).

Reductive cyclisation of the *Se*-phenylselenoate 26. Cyclisation of the title ester according to the general procedure[1] afforded a mixture of products, separation of which by flash chromatography over silica gel (light petroleum→light petroleum–ether, 50:1) gave: (i) the tricyclic ketone **27** (31%); ν_{max}/cm^{-1}(film) 2932, 2869, 1738sh, 1710, 1454, 1372 and 1313; δ_C 212.6 (CO), 53.5 (CH), 49.5 (CH), 46.3 (CH), 45.4 (CH), 42.0 (CH_2), 32.6 (CH_2), 32.3 (CH_2), 29.8 (CH_2), 29.3 (CH_3), 26.1 (CH_2), 25.6 (CH_2), 17.4 (CH_2) and 14.9 (CH_3) (Found: C, 81.9; H, 11.3%; M^+, 220.1798. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%; M^+, 220.1827) and (ii) the bicyclic ketone **28**, (37%); ν_{max}/cm^{-1}(film) 3075, 2936, 2869, 1705, 1640, 1462, 1377, 1315, 1255, 1172, 993 and 909; δ_H 5.79–5.69 (ddt, *J* 17.2, 10.2 and 6.7, =CH), 4.93 (dm, *J* 17.2 Hz, =C*H*H), 4.90 (dm, *J* 10.2, =CH*H*), 2.89–2.78 (m, CH), 2.32–2.17 (2 H, m), 2.15–1.09 (15 H, complex series of m) and 0.86 (s, CH_3); δ_C 215.3 (CO), 138.8 (=CH), 114.4 (=CH_2), 51.8 (CH), 51.6 (CH), 45.6 (quat. C), 38.0 (CH_2) 36.6 (CH_2), 36.1 (CH_2), 34.6 (CH_2), 25.8 (CH_2), 25.3 (CH_3), 24.4 (2 × CH_2) and 23.2 (CH_2); *m/z* 220.1805 (M^+. $C_{15}H_{24}O$ requires M^+, 220.1827).

***Se*-Phenyl (5*Z*,9*E*)-9,13-dimethytetradeca-5,9,13-trieneselenoate 33.** The title ester was prepared starting from 4-methylpent-4-enal **29**, according to all the general procedures described earlier.[1] Thus, a Grignard reaction between the aldehyde **29** and propenylmagnesium bromide first led (44%) to 2,6-dimethylhepta-1,6-dienol **30**;[12] ν_{max}/cm^{-1}(film) 3354br (OH), 3073, 2970, 2940, 1650, 1446, 1374, 1064, 1022, 1000 and 890; δ_H 5.02–4.78 (m, 2 × =CH_2), 4.14 (t, *J* 6.4, CHO), 2.18–2.03 (m, CH_2), 1.94 (br s, OH), 1.81_5 (s, CH_3), 1.81_0 (s, CH_3) and 1.78–1.71 (m, CH_2); δ_C 147.4 (quat. C), 145.6 (quat. C), 111.1 (=CH_2), 110.0 (=CH_2), 75.5 (CHOH), 33.7 (CH_2), 32.7 (CH_2), 22.5 (CH_3) and 17.5 (CH_3), which by Claisen rearrangement was next converted into (4*E*)-4,8-dimethylnona-4,8-dienal **31** (98%);[13] ν_{max}/cm^{-1}(film) 3074, 2967, 2932, 2854, 2717, 1726, 1684, 1649, 1446, 1374 and 887; δ_H 9.68 (t, *J* 2.0, CHO), 5.11–5.06 (m, =CH), 4.63 (s, =C*H*H), 4.59 (s, =CH*H*), 2.48–2.41 (m, CH_2), 2.28–2.22 (m, CH_2), 2.10–1.93 (m, 2 × CH_2), 1.64 (s, CH_3) and 1.55 (s, CH_3); δ_C 202.6 (CO), 145.4 (quat. C), 133.0 (quat. C), 125.0 (=CH), 109.9 (=CH_2), 42.0 (CH_2), 37.5 (CH_2), 31.7 (CH_2), 26.0 (CH_2), 22.3 (CH_3) and 15.2 (CH_3) *via* the corresponding vinyl ether; ν_{max}/cm^{-1}(film) 3074, 2971, 2948, 1649, 1635, 1614, 1448, 1374, 1318, 1195, 1166, 1067, 892 and 828; δ_H 6.37 (dd, *J* 14.0 and 6.4, C*H*=CH_2), 5.08–5.00 (m, =CH_2), 4.83 (br s, =C*H*H), 4.79 (br s, =CH*H*), 4.42 (s, =C*H*H), 4.37 (s, =CH*H*), 4.18 (t, *J* 6.8, OCH), 2.19–2.05 (m, CH_2), 1.97–1.85 (m, CH_2), 1.82 (s, CH_3) and 1.77 (s, CH_3); δ_C 150.5 (=CH), 145.0 (quat. C), 144.1 (quat. C), 113.4 (=CH_2), 110.2 (=CH_2), 88.7 (=CH_2), 83.1 (OCH), 33.5 (CH_2), 31.3 (CH_2), 22.5 (CH_3) and 16.9 (CH_3).

A Wittig reaction between the aldehyde **31** and the ylide from 4-carboxybutyl(triphenyl)phosphonium bromide, according to the general procedure,[1] next led to (5*Z*,9*E*)-9,13-dimethyltetradeca-5,9,13-trienoic acid **32** (62%), containing *ca.* 10% of the *E*,*E*-isomer; ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1709, 1649, 1443, 1241 and 887; δ_H(br s, CO_2H), 5.51–5.41 (m, CH=CH), 5.24 (m, =CH), 4.81 (s, =CHH), 4.78 (s, =CH*H*), 2.46

(t, J 7.6, CH_2), 2.24–2.13 (m, 5 × CH_2), 1.83 (s, CH_3), 1.82–1.77 (m, CH_2) and 1.71 (s, CH_3); δ_C 181.0 (CO), 146.9 (quat. C), 135.6 (quat. C), 131.4 (=CH), 128.8 (=CH), 125.0 (=CH), 110.4 (=CH_2), 40.1 (CH_2), 38.4 (CH_2), 34.0 (CH_2), 27.0 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 25.2 (CH_2), 23.1 (CH_3) and 16.5 (CH_3). This compound was phenylselenylated in 48% yield, after chromatographic purification, to produce the *Se*-phenyl selenoate, a single stereoisomer, as a pale yellow oil; ν_{max}/cm^{-1}(film) 3073, 3003, 2929, 2854, 1724, 1649, 1580, 1477, 1439, 886, 737 and 689; δ_H 7.64–7.61 (m, 2 × aryl =CH), 7.50–7.45 (m, 3 × aryl =CH), 5.58–5.38 (2 × dt, J 10.8, 6.9 and 6.6, *Z*-CH=CH), 5.29–5.24 (m, =CH), 4.84 (s, =C*H*H), 4.81 (s, =CH*H*), 2.83 (t, J 7.4, CH_2), 2.25–2.14 (m, 5 × CH_2), 1.93–1.82 (m, CH_2), 1.85 (s, CH_3) and 1.74 (s, CH_3); δ_C 200.4 (CO), 146.0 (quat. C), 136.0 (2 × aryl =CH), 134.8 (quat. C), 131.1 (=CH), 129.5 (2 × aryl =CH), 129.0 (aryl =CH), 128.2 (=CH), 126.8 (quat. C), 124.6 (=CH), 110.0 (=CH_2), 47.0 (CH_2), 39.7 (CH_2), 38.0 (CH_2), 26.44 (CH_2), 26.40 (CH_2), 26.0 (CH_2), 25.4 (CH_2), 22.7 (CH_3) and 16.2 (CH_3); m/z (%) 233 (9), 215 (18), 177 (14), 159 (13), 157 (10), 155 (8) and 149 (51) (Found: C, 68.0; H, 7.9. $C_{22}H_{30}OSe$ requires C, 67.9; H, 7.8%).

Reductive cyclisation of the *Se*-phenyl selenoate 33. Cyclisation of the title ester according to the general procedure,[1] followed by chromatography over silica gel (light petroleum→light petroleum–ether, 50:1), gave: (i) the tricyclic ketone **34** (31%) as a *ca.* 5:3 mixture of ring C methyl epimers; ν_{max}/cm^{-1}(film) 2934, 2867, 1709, 1447, 1379, 1313, 1149 and 733; δ_H 2.42–0.88 (complex series of m); δ_C(major isomer **65**) 213.1 (CO), 55.8 (CH), 51.2 (CH_2), 50.7 (CH), 43.7 (CH), 41.5 (CH_2), 40.3 (CH_2), 35.8 (CH_2), 33.5 (quat. C), 29.3 (CH_2), 27.0 (CH), 26.4 (CH_2), 24.5 (CH_2), 22.8 (CH_3), 20.3 (CH_2) and 17.3 (CH_3); δ_C(minor isomer **66**) 213.3 (CO), 55.7 (CH), 50.9 (CH), 48.2 (CH_2), 43.6 (CH), 41.4 (CH_2), 40.8 (CH_2), 33.9 (quat. C), 32.3 (CH_2), 29.3 (CH_2), 26.4 (CH_2), 23.0 (CH) 21.8 (CH_3), 20.4 (CH_2), 19.9 (CH_2) and 19.7 (CH_3); m/z 234.1976 (M^+. $C_{16}H_{26}O$ requires M^+, 234.1984) and (ii) the bicyclic ketone **35** (47%); ν_{max}/cm^{-1}(film) 3072, 2938, 2869, 1703, 1649, 1458, 1376 and 885; δ_H 4.63 (s, =C*H*H), 4.59 (s, =CH*H*), 1.64 (s, CH_3), 0.86 (s, CH_3) and 2.33–0.75 (complex series of m); δ_C 215.3 (CO), 145.8 (quat. C), 109.8 (=CH_2), 51.9 (CH), 51.6 (CH), 45.6 (quat. C), 38.6 (CH_2), 38.0 (CH_2), 36.7 (CH_2), 36.1 (CH_2), 25.8 (CH_2), 25.3 (CH_3), 24.3 (CH_2), 23.2 (CH_2), 22.9 (CH_2) and 22.3 (CH_3); m/z 234.1967 (M^+. $C_{16}H_{26}O$ requires M^+, 234.1984).

1-Methoxy-5,9,13-trimethyltetradeca-1,5,9,13-tetraene 38. A set of identical Grignard and Claisen rearrangements identical with those described earlier were used to convert the aldehyde **31** into (6*E*)-2,6,10-trimethylundeca-1,6,10-trien-3-ol **36** (66%);[13,14] ν_{max}/cm $^{-1}$(film) 3384br (OH), 3073, 2969, 2937, 1649, 1447, 1374, 1059 and 887; δ_H 4.98–4.93 (m, =CH), 4.73–4.72 (m, =CHH), 4.63–4.62 (m, =CH*H*), 4.49–4.48 (m, =C*H*H), 4.47–4.46 (m, =CH*H*), 3.83 (t, J 6.4, CHO), 1.96–1.75 (m, 3 × CH_2), 1.51$_1$(s, CH_3), 1.50$_8$ (s, CH_3), 1.49–1.38 (m, CH_2) and 1.41 (s, CH_3); δ_C 147.5 (quat. C), 145.8 (quat. C), 134.9 (quat. C), 124.5 (=CH), 111.0 (=CH_2), 109.8 (=CH_2), 75.6 (CHOH), 37.7 (CH_2), 35.6 (CH_2), 33.1 (CH_2), 26.1 (CH_2), 22.4 (CH_3), 17.6 (CH_3) and 16.0 (CH_3) and also into (4*E*,8*E*)-4,8,12-trimethyltrideca-4,8,12-trienal **37** (93%);[15] ν_{max}/cm^{-1}(film) 3073, 2967, 2918, 2853, 2716, 1727, 1649, 1445, 1384 and 886; δ_H 9.82 (t, J, 1.8, CHO), 5.23–5.18 (m, 2 × =CH), 4.78 (s, =C*H*H), 4.75 (s, =CH*H*), 2.61–2.55 (m, CH_2) 2.44–2.36 (m, CH_2), 2.19–1.90 (m, 4 × CH_2), 1.80 (s, CH_3), 1.69 (s, CH_3) and 1.68 (s, CH_3); δ_C 202.9 146.1 (quat. C), 135.1 (quat. C), 133.2 (quat. C), 125.7 (=CH), 124.7 (=CH), 110.2 (=CH_2), 42.5 (CH_2), 39.8 (CH_2), 38.2 (CH_2), 32.2 (CH_2), 26.8 (CH_2), 26.5 (CH_2), 22.8 (CH_3), 16.4 (CH_3) and 16.3 (CH_3). Lithium bis(trimethylsilyl)-amide (15.8 cm^3, 15.8 mmol) was added dropwise over 20 min to a stirred solution of methoxymethyl(triphenyl)phosphonium chloride (5.6 g, 15.8 mmol) in THF (35 cm^3) under nitrogen at 0 °C. The reaction mixture was stirred for 1 h, after which a solution of the aldehyde **37** (3.4 g, 14.4 mmol) in THF (35 cm^3) was added dropwise over 30 min. The mixture was stirred at room temperature for 20 h and then quenched by cautious addition of saturated aqueous ammonium chloride. The aqueous phase was extracted with ether, and the combined ether extracts were dried and then evaporated under reduced pressure. The residue was purified by chromatography over silica gel (light petroleum–ether, 5:1) to give the *vinyl ether* **38** (2.6 g, 68%), a *ca.* 3:2 mixture of the *Z*,*E*,*E*- and *E*,*E*,*E*-isomers, as an oil; ν_{max}/cm^{-1}(film) 3073, 3034, 2930, 2852, 1655, 1450, 1385, 1210, 1112, 933 and 886; δ_H 6.11 and 5.67 (2 × d, J 12.9 and 6.3, CH=CH), 4.95 (m, 2 × =CH), 4.53 (s, =C*H*H), 4.50 (s, =CH*H*), 3.39 and 3.31 (2 × d, J 2 and 1.3, OCH_3), 2.10–1.75 (m, 6 × CH_2), 1.55 (s, CH_3), 1.43 (s, CH_3) and 1.41 (s, CH_3); δ_C 146.9 and 145.9 (=CHO), 135.0$_9$ and 135.0$_6$ (=*C*Me), 134.7 and 134.4 (=*C*Me), 124.5 and 124.3 (=CH), 124.0 and 124.0 (=CH), 109.7 and 109.7 (=CH_2), 106.5 and 102.7 (*C*H=CHO), 59.4 and 55.7 (OCH_3), 40.9 (CH_2), 39.7 (CH_2), 39.6 (CH_2), 37.8 (2 × CH_2), 26.5$_4$ (2 × CH_2), 26.4$_7$ (CH_2), 26.4 (CH_2), 26.2 (2 × CH_2), 23.4 (CH_3), 22.4 (2 × CH_3), 22.3 (CH_2), 15.9 (2 × CH_3) and 15.8 (CH_3).

Methyl 5,9,13-trimethyltetradeca-5,9,13-trienoate 39a. A solution of the vinyl ether **38** (2.5 g, 9.5 mmol) in dichloromethane (20 cm^3) was rapidly added to a suspension of PCC (4.1 g, 19.0 mmol) in dichloromethane (20 cm^3). After the mixture had been stirred at room temperature for 1.5 h it was diluted with ether (40 cm^3). The supernatant liquid was poured into a beaker and the residue solid was then washed with ether (3 × 20 cm^3). The combined etheral solutions were passed through a column of silica gel and magnesium sulfate, and then evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (light petroleum–ether, 5:1) to give the *ester* **39a** (1.9 g, 73%) as an oil; ν_{max}/cm^{-1}(film) 3074, 2934, 2853, 1742, 1650, 1436, 1374, 1209, 1155 and 887; δ_H 5.26–5.15 (m, 2 × =CH), 4.80 (s, =C*H*H), 4.77 (s, =CH*H*), 3.76 (s, OCH_3), 2.36 (t, J 7.6, CH_2), 2.21–1.94 (m, 5 × CH_2), 1.90–1.70 (m, CH_2), 1.82 (s, CH_3), 1.70 (s, CH_3) and 1.68 (s, CH_3); δ_C 174.4 (CO), 146.1 (quat. C), 135.2 (quat. C), 134.0 (quat. C), 125.5 (=CH), 124.4 (=CH), 110.0 (=CH_2), 51.6 (OCH_3), 39.8 (CH_2), 39.1 (CH_2), 38.0 (CH_2), 33.6 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 23.2 (CH_2), 22.7 (CH_3), 16.2 (CH_3) and 15.9 (CH_3).

5,9,13-Trimethyltetradeca-5,9,13-trienoic acid 39b. Potassium carbonate (4.6 g, 33.5 mmol) was added to a solution of the trienoate **39a** (1.9 g, 6.7 mmol) in aqueous methanol (7%; 46 cm^3) and the mixture was then stirred and heated under reflux overnight. After it had cooled to room temperature, the reaction mixture was acidified with 2 mol dm^{-3} hydrochloric acid, and extracted with ethyl acetate (3 × 35 cm^3). The organic extracts were washed with brine (35 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (light petroleum–ether, 5:1) to give the *acid* **39b** (1.3 g, 76%) as an oil; ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1710, 1650, 1443, 1383, 1275, 1243 and 886; δ_H 10.2 (br s, CO_2H), 5.29–5.10 (m, 2 × =CH), 4.80 (s, =C*H*H), 4.78 (s, =CH*H*), 2.41 (t, J 7.6, CH_2CO), 2.34–1.90 (m, 5 × CH_2), 1.89–1.65 (m, CH_2), 1.82 (s, CH_3), 1.71 (s, CH_3) and 1.69 (s, CH_3); δ_C 181.6 (CO), 147.5 (quat. C), 137.9 (quat. C), 136.1 (quat. C), 126.8 (=CH), 125.5 (=CH), 111.0 (=CH_2), 40.9 (CH_2), 40.1 (CH_2), 39.1 (CH_2), 34.6 (CH_2), 27.8 (CH_2), 27.5 (CH_2), 24.0 (CH_2), 23.8 (CH_3), 17.3 (CH_3) and 17.0 (CH_3).

***Se*-Phenyl (9*E*,13*E*)-5,9,13-trimethyltetradeca-5,9,13-triene-selenoate 40.** The title ester was prepared according to the general procedure (68%), and showed: ν_{max}/cm^{-1}(film) 3073, 2930, 2854, 1725, 1649, 1580, 1478, 1439, 1374, 886, 738 and 689; δ_H 7.64–7.61 (m, 2 × aryl =CH), 7.60–7.43 (m, 3 × aryl

=CH), 5.30–5.20 (m, 2 × =CH), 4.83 (s, =C*H*H), 4.80 (s, =CH*H*), 2.77 (t, *J* 7.4, CH_2), 2.30–2.00 (m, 5 × CH_2), 1.93–1.78 (m, CH_2), 1.84 (s, CH_3), 1.73 (s, CH_3) and 1.70 (s, CH_3); δ_C 200.5 (CO), 145.8 (quat. C), 135.7 (2 × aryl=CH), 134.9 (quat. C), 133.4 (quat. C), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 126.5 (quat. C), 125.7 (=CH), 124.2 (=CH), 109.8 (=CH_2), 46.8 (CH_2), 39.6 (CH_2), 38.5 (CH_2), 37.8 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 23.4 (CH_2), 22.5 (CH_3), 16.0 (CH_3) and 15.7 (CH_3); *m/z* (%) 247 (19), 229 (12), 191 (11), 179 (12), 173 (12), 158 (12), 149 (17), 123 (31) and 81 (100) (Found: C, 68.8; H, 8.0. $C_{23}H_{32}OSe$ requires C, 68.5; H, 8.0%).

Reductive cyclisation of the *Se*-phenyl selenoate 40. Cyclisation of the title ester, according to the general procedure, followed by chromatography over silica gel (light petroleum→ light petroleum–ether, 50:1) led to: (i) the indanones **52** (18%) as a mixture of diastereoisomers; δ_H 4.63–4.59 (m, =CH_2), 2.59–0.61 (complex series of m), 1.64 (s, CH_3), 0.82 (s, CH_3) and 0.78 (s, CH_3); δ_C 215.7 and 215.5 (CO), 145.3 (quat. C), 109.9 and 109.8 (=CH_2), 59.1 and 58.7 (CH), 51.9, 48.1 and 47.9 (quat. C), 38.8 and 38.6 (CH_2), 37.4 (CH_2), 36.9 (CH_2), 36.4 (CH_2), 35.6 (CH_2), [34.8 (CH_2)], 33.6 (CH_2), [30.1 (CH_2)], 29.0 (CH_2), 25.6 (CH_2), 24.6 (CH_2), 23.2 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.3 (CH_3), 22.1 (CH_2), 21.3 (CH_3), 19.4 (CH_3), 19.0 (CH_3) and 18.4 (CH_3). Further chromatographic purification afforded essentially a single stereoisomer: δ_C 215.5 (CO), 145.3 (quat. C), 109.8 (=CH_2), 59.1 (CH), 51.9 (quat. C), 48.1 (quat. C), 38.8 (CH_2), 36.9 (CH_2), 36.4 (CH_2), 35.6 (CH_2), 29.0 (CH_2), 25.6 (CH_2), 23.2 (CH_2), 22.7 (CH_2), 22.3 (CH_3), 21.3 (CH_3) and 18.4 (CH_3); *m/z* 248.2103 (M^+. $C_{17}H_{28}O$ requires M^+, 248.2140) and (ii) a *ca.* 1:1 mixture of the epimeric tricyclic ketones **50** and **51** (53%); ν_{max}/cm^{-1}(film) 2953, 2844, 1712, 1454, 1383, 933 and 733; δ_H 2.52–0.72 (very complex series of m), 1.01 (s, CH_3), 0.89 (d, *J* 6.6, CH_3) and 0.76 (s, CH_3); δ_C 213.4, 43.0, 34.7 and 34.5 (all quat. C), 60.1$_6$, 60.1$_1$, 56.7, 55.9, 27.7, and 27.3 (all CH), 54.9, 51.7, 41.5, 40.8, 40.7, 38.1, 38.0, 36.4, 33.5, 22.2, 21.6, 17.5, 17.3, and 16.9 (all CH_2), 22.9, 22.7, 21.7, 20.6 and 13.6 (all CH_3); *m/z* 248.2092 (M^+. $C_{17}H_{28}O$ requires M^+, 248.2140). The 2,4-dinitrophenylhydrazone derivative of the tricyclic ketone was prepared in DMF, and several fractional crystallisations (CH_2Cl_2–Et_2O) afforded very small samples of the enriched epimers. One of the epimers showed: δ_H 11.16 (s, NH), 9.04 (d, *J* 2.5, aryl =CH), 8.20 (dd, *J* 9.8 and 2.5, aryl =CH), 7.90 (d, *J* 9.8, aryl =CH), 2.79–2.73 (1 H, m), 2.05–0.61 (complex series of m), 0.92 (s, CH_3), 0.76 (d, *J* 6.6, CH_3) and 0.61 (s, CH_3); δ_C 162.7 (quat. C), 145.7 (quat. C), 137.4 (quat. C), 130.0 (aryl =CH), 128.8 (quat. C), 123.7 (aryl =CH), 116.5 (aryl =CH), 56.0 (CH), 55.0 (CH_2), 54.9 (CH), 41.6 (CH_2), 41.5 (quat. C), 38.5 (CH_2), 36.6 (CH_2), 34.8 (quat. C), 27.5 (CH), 26.9 (CH_2), 22.9 (CH_3), 21.7 (CH_2), 21.5 (CH_2), 20.8 (CH_3), 19.5 (CH_2) and 13.9 (CH_3); the other epimer showed: δ_H 11.16 (s, NH), 9.04 (d, *J* 2.6, aryl =CH), 8.21 (dd, *J* 9.6 and 2.6, aryl =CH), 7.90 (d, *J* 9.6, aryl =CH), 2.78–2.74 (1 H, m), 2.05–0.61 (complex series of m), 1.01$_5$ (s, CH_3), 1.01$_0$ (d, *J* 7.6, CH_3) and 0.64 (s, CH_3); δ_C 162.7 (quat. C), 145.7 (quat. C), 137.4 (quat. C), 130.0 (aryl =CH), 128.8 (quat. C), 123.7 (aryl =CH), 116.5 (aryl=CH), 56.9 (CH), 54.8 (CH), 51.8 (CH_2), 42.3 (CH_2), 38.4 (CH_2), 35.0 (quat. C), 34.8 (quat. C), 33.7 (CH_2), 28.0 (CH), 26.9 (CH_2), 23.1 (CH_3), 21.9 (CH_3), 21.5 (CH_2), 19.0 (CH_2), 17.5 (CH_2) and 13.9 (CH_3).

The mixture of 2,4-dinitrophenylhydrazones was recrystallised from dichloromethane–ether, to afford crystals which proved to be satisfactory for X-ray analysis.

X-Ray crystal structure determination of 2,4-dinitrophenylhydrazone derivative of tricyclic ketones 50 and 51

The derivative crystallised as a solid solution of two diastereoisomers, differing by the orientation of the ring 17-methyl group, in approximately equal amounts (see Fig. 1). All the cyclohexane rings adopt chair conformations, with *cis*-orientation of the C(15) and C(16) angular methyl groups. The hydrazone and nitro groups are essentially coplanar with the benzene ring. Such a conformation is stabilised by an intramolecular hydrogen bond, N(2)–H···O(1) [N···O 2.59(1) Å]; [N–H 0.79(8), H···O 1.98(8) Å, N–H–O angle of 135(8)°], which causes lengthening of the N(3)–O(1) bond to 1.250(9) Å, *versus* the average of 1.214(9) Å for the other three N–O bonds. The C(1)N(1)N(2)C(18) torsion angle of −169.7(7)° indicates significant twisting round the N–N bond.

The single-crystal X-ray diffraction experiment was carried out on a CAD-4 four-circle diffractometer at room temperature.

Crystal data. $C_{23}H_{32}N_4O_4$, M = 428.532 monoclinic, space group $P2_1/n$, a = 17.214(2), b = 6.012(1), c = 22.800(4) Å, β = 108.91(1)°, U = 2232.1(6) Å^3 (from 18 reflections with 20 < θ < 24°), Z = 4, D_x = 1.28 g cm^{-3}, $F(000)$ = 920, Ni-filtered Cu-Kα radiation (λ = 1.541 78 A), U = 7.2 cm^{-1}. Orange plate-like crystal (0.07 × 0.18 × 0.45 mm) was obtained from the solvent (dichloromethane–ether, 1:2). The intensities of 3194 reflections, including 2281 independent, were measured in a 2θ/ω scan mode (θ < 50°). The structure was solved by direct methods (SHELXS-86)[16] and refined by full-matrix least squares (SHELXL-93)[17] against F^2 of 2274 reflections with Chebyshev weighting scheme. The 17-methyl group appeared to be disordered over two positions, A and B, the occupancies of which were refined to 0.54(1) and 0.46(1), and which correspond to two co-crystallised isomers. Oxygen atoms were refined with anisotropic displacement parameters; N, C and the hydrazone H atoms in isotropic approximation, and the rest of the H atoms were treated in riding model. The refinement of 153 variables converged at $R = \Sigma(F_o - F_c)/\Sigma(F_o) - 0.071$ for 899 (observed) reflections with $I > 2\sigma(I)$ and R = 0.233 for all data. The final difference map exhibited the max. and min. residual electron density features of 0.29 and −0.22 e Å^{-3}, respectively. Lists of atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

(4*E*,8*E*,12*E*)-4,8,12-Trimethylheptadeca-4,8,12,16-tetraenal 44. The aldehyde was produced from 2-methylhepta-1,6-dien-1-ol **23** using three successive Claisen rearrangements. Thus, conversion of **23** into the corresponding vinyl ether followed by Claisen rearrangement first led to (4*E*)-4-methylnona-4,8-dienal **24c** (95%)–see above for spectroscopic data. A Grignard reaction between **24c** and propenylmagnesium bromide next produced (6*E*)-2,6-dimethylundeca-1,6,10-trien-3-ol **41** (74%);[14] ν_{max}/cm^{-1}(film) 3365br (OH), 3075, 2976, 2921, 2857, 1641, 1446, 1374, 1063, 995 and 908; δ_H 5.96–5.86 (m, C*H*=CH_2), 5.27 (m, =CH), 5.13–4.92 (m, 2 × =CH_2), 4.13 (t, *J* 6.4, CHO), 2.19–2.05 (m, 3 × CH_2), 2.02–1.74 (m, CH_2), 1.82 (s, CH_3) and 1.71 (s, CH_3); δ_C 147.4 (quat. C), 138.6 (=CH), 135.1 (quat. C), 124.2 (=CH), 114.4 (=CH_2), 111.0 (=CH_2), 75.5 (CHOH), 35.6 (CH_2), 33.9 (CH_2), 33.1 (CH_2), 27.3 (CH_2), 17.5 (CH_3) and 16.0 (CH_3) and a second Claisen rearrangement from the allyl alcohol **41** then led to (4*E*,8*E*)-4,8-dimethyltrideca-4,8,12-trienal **42** (71%); ν_{max}/cm^{-1}(film) 3076, 2919, 2853, 2717, 1727, 1640, 1444, 1384, 1119, 995 and 911; δ_H 9.83 (br s, CHO), 5.96–5.80 (m, C*H*=CH_2), 5.30–5.15 (m, 2 × =CH), 5.09 (d, *J* 19.8, =C*H*H), 5.04 (d, *J* 11.2, =CH*H*), 2.62–2.50 (m, CH_2), 2.50–2.30 (m, CH_2), 2.30–1.95 (m, 4 × CH_2), 1.70 (s, CH_3) and 1.68 (CH_3); δ_C 202.6 (CO), 138.7 (=CH), 135.0 (quat. C), 132.8 (quat. C), 125.3 (=CH), 124.0 (=CH), 114.3 (=CH_2), 42.1 (CH_2), 39.4 (CH_2), 33.9 (CH_2), 31.8 (CH_2), 27.3 (CH_2), 26.4 (CH_2), 16.0 (CH_3) and 15.9 (CH_3). A second Grignard reaction leading to the allylic alcohol **43** (58%); ν_{max}/cm^{-1}(film) 3363br (OH), 3075, 2922, 2856, 1641, 1448, 1382, 1065, 994 and 909; δ_H 6.02–5.82 (m, C*H*=CH_2), 5.35–4.95 (m, 2 × =CH +

2 × =CH_2), 4.15 (t, *J* 6.4, CHO), 2.30–1.95 (m, 5 × CH_2), 1.84 (s, CH_3), 1.73 (2 × CH_3) and 1.90–1.65 (m, CH_2); δ_C 147.4 (quat. C), 138.7 (=CH), 135.2 (quat. C), 134.6 (quat. C), 124.6 (=CH), 123.8 (=CH), 114.3 (=CH_2), 111.0 (=CH_2), 75.6 (CHOH), 39.6 (CH_2), 35.7 (CH_2), 33.9 (CH_2), 33.0 (CH_2), 27.3 (CH_2), 26.5 (CH_2), 17.6 (CH_3) and 16.0 (2 × CH_3), followed by a third Claisen rearrangement finally gave the tetraenaldehyde **44** (74%)[18] which was used directly for the next stage without purification.

(4*E*,8*E*,12*E*)-4,8,12,16-Tetramethylheptadeca-4,8,12,16-tetraenal 49. *Addition of* propenylmagnesium bromide to the trienal **37** first led to the allylic alcohol **48** (74%); ν_{max}/cm^{-1}(film) 3360br (OH), 3073, 2934, 1650, 1448, 1374, 1059 and 887; δ_H 5.23–5.18 (m, 2 × =CH), 5.00 (br s, =C*H*H), 4.89 (br s, =CH*H*), 4.78 (s, =C*H*H), 4.76 (s, =CH*H*), 4.09 (t, *J* 6.3, CHO), 2.31–2.00 (m, 5 × CH_2), 1.90–1.60 (m, CH_2), 1.80 (s, CH_3) and 1.69 (2 × CH_3); δ_C 147.4 (quat. C), 145.5 (quat. C), 134.8 (quat. C), 134.5 (quat. C), 124.5 (=CH), 124.0 (=CH), 110.8 (=CH_2), 109.7 (=CH_2), 75.4 (CHOH), 39.5 (CH_2), 37.7 (CH_2), 35.5 (CH_2), 33.0 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 22.3 (CH_3), 17.4 (CH_3) and 15.8 (2 × CH_3), which was then converted by Claisen rearrangement into the tetraenal **49** (90%);[13,14] ν_{max}/cm^{-1}(film) 3073, 2966, 2921, 2853, 2717, 1728, 1649, 1445, 1383, 886 and 735; δ_H 9.84 (t, *J* 2.0, CHO), 5.28–5.15 (m, 3 × =CH), 4.80 (s, =C*H*H), 4.78 (s, =CH*H*), 2.63–2.57 (m, CH_2), 2.47–2.38 (m, CH_2), 2.35–1.95 (m, 6 × CH_2), 1.82 (s, CH_3), 1.71 (2 × CH_3) and 1.69 (CH_3); δ_C 202.6 (CO), 145.8 (quat. C), 135.1 (quat. C), 134.6 (quat. C), 132.8 (quat. C), 125.4 (=CH), 124.4 (=CH), 124.0 (=CH), 109.7 (=CH_2), 42.1 (CH_2), 39.7 (CH_2), 39.5 (CH_2), 37.8 (CH_2), 31.8 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 22.5 (CH_3), 16.0_5 (CH_3) and 16.0_0 (2 × CH_3).

***Se*-Phenyl (5*E*,9*E*,13*E*)-5,9,13-trimethyloctadeca-5,9,13,17-tetraeneselenoate 47a.** According to the general procedures, a Wittig reaction between the aldehyde **44** and methoxymethyl(triphenyl)phosphoranylide first led to a *ca.* 3:2 mixture of the *cis*- and *trans*- isomers of the vinyl ether **45a** (75%); ν_{max}/cm^{-1}(film) 3076, 3040, 2926, 2851, 1656, 1641, 1450, 1384, 1210, 1112 and 911; δ_H 6.11 and 5.75–5.58 (d and m, *J* 12.9, C*H*=C*H* and C*H*=CH_2), 5.03–4.75 (m, 3 × =CH + =CH_2), 3.39 and 3.31 (OCH_3), 2.05–1.85 (m, 8 × CH_2), 1.82 (s, CH_3), 1.51 (s, CH_3) and 1.42 (2 × CH_3); δ_C 146.9 and 145.9 (=*C*HOMe), 138.7 (*C*H=CH_2), 135.4, 134.9 and 134.6 (quat. C), 124.6, 124.4, 124.2_4 124.1_9, and 123.8 (=CH), 114.3 (=CH_2), 106.5 and 102.7 (*C*H=CHOMe), 59.4 and 55.8 (OCH_3), 41.0, 39.7, 39.6, 34.0, 32.5, 27.4, 26.6, 26.4 and 22.3 (CH_2), 23.3, 16.0_3, 16.0_0, (CH_3), 15.9_5 and 15.8_1 (CH_3). Oxidation of **45a** using PCC in CH_2Cl_2 next led to the methyl ester **46a** (R′ = Me; 75%); ν_{max}/cm^{-1}(film) 3076, 2922, 2852, 1742, 1640, 1437, 1382, 1245, 1210, 1156, 994 and 911; δ_H 5.88–5.75 (m, C*H*=CH_2), 5.15–5.08 (m, 3 × =CH), 4.99 (d, *J* 17.1, =C*H*H), 4.94 (d, *J* 10.2, =CH*H*), 3.65 (s, OCH_3), 2.30–2.24 (m, CH_2CO), 2.10–1.95 (m, 7 × CH_2), 1.76–1.62 (m, CH_2), 1.60 (s, CH_3), 1.59 (s, CH_3) and 1.58 (s, CH_3); δ_C 174.2 (CO), 138.7 (=CH), 135.3 (quat. C), 134.8 (quat. C), 133.7 (quat. C), 125.3 (=CH), 124.3 (=CH), 123.8 (=CH), 114.3 (=CH_2), 51.4 (OCH_3), 39.6 (2 × CH_2), 38.9 (CH_2), 34.0 (CH_2), 33.4 (CH_2), 27.4 (CH_2), 26.6 (2 × CH_2), 23.0 (CH_2), 16.0 (2 × CH_3) and 15.7 (CH_3) which was then saponified to the corresponding carboxylic acid **46a** (R′ = H; 73%); ν_{max}/cm^{-1}(film) 3500–2500br (CO_2OH), 1710, 1640, 1441, 1414, 1384, 1286, 1243 and 911; δ_H 9.90 (br s, CO_2H), 6.00–5.83 (m, C*H*=CH_2), 5.28–5.18 (m, 3 × =CH), 5.11 (d, *J* 17.1, =C*H*H), 5.05 (d, *J* 12.2, =CH*H*), 2.41 (t, *J* 7.4, CH_2CO), 2.20–2.00 (m, 7 × CH_2), 1.89–1.78 (m, CH_2) and 1.71 (br s, 3 × CH_3); δ_C 180.6 (CO), 138.8 (=CH), 135.5 (quat. C), 134.9 (quat. C), 133.7 (quat. C), 125.6 (=CH), 124.4 (=CH), 123.9 (=CH), 114.4 (=CH_2), 39.8 (CH_2), 39.7 (CH_2), 38.9 (CH_2), 34.1 (CH_2), 33.5 (CH_2), 27.5 (CH_2), 26.7 (2 × CH_2), 22.8 (CH_2), 16.1 (2 × CH_3) and 15.8 (CH_3). Phenylselenylation of **46a** (R′ = H) finally gave the *Se*-phenyl selenoate **47a** (73%) as a pale yellow oil; ν_{max}/cm^{-1}(film) 3075, 3060, 2923, 2854, 1726, 1640, 1580, 1478, 1439, 1383, 1065, 1021, 999, 911 and 737; δ_H 7.65–7.56 (m, 2 × aryl =CH), 7.56–7.45 (m, 3 × aryl =CH), 6.02–5.88 (m, C*H*=CH_2), 5.30–5.20 (m, 3 × =CH), 5.13 (d, *J* 17.1, =C*H*H), 5.08 (d, *J* 10.9, =CH*H*), 2.78 (t, *J* 7.1, CH_2), 2.30–2.00 (m, 7 × CH_2), 1.98–1.72 (m, CH_2), 1.74 (s, 2 × CH_3) and 1.71 (s, CH_3); δ_C 200.2 (CO), 138.7 (=CH), 135.7 (2 × aryl =CH), 135.3 (quat. C), 134.7 (quat. C), 133.3 (quat. C), 129.2 (2 × aryl =CH), 128.7 (aryl =CH), 126.5 (quat. C), 125.7 (=CH), 124.3 (=CH), 123.8 (=CH), 114.3 (=CH_2), 46.8 (CH_2), 39.7 (CH_2), 39.6 (CH_2), 38.5 (CH_2), 34.0 (CH_2), 27.4 (CH_2), 26.5_4 (CH_2), 26.4_9 (CH_2), 23.3 (CH_2), 16.0_3 (CH_3), 15.9_6 (CH_3) and 15.6 (CH_3); *m/z* 301 (28), 283 (7), 191 (25), 179 (19), 173 (17), 163 (9), 161 (13), 157 (14), 149 (11), 137 (12), 135 (20) and 81 (100) (Found: C, 71.0; H, 8.6. $C_{27}H_{38}OSe$ requires C, 70.9; H, 8.4%).

***Se*-Phenyl (5*E*,9*E*,13*E*)-5,9,13,17-tetramethyloctadeca-5,9,13,17-tetraeneselenoate 47b.** The title ester was prepared from the tetraenal **49** using the general procedures, and proceeding *via* (i) the vinyl ether **45b** (38%), obtained as a *ca.* 3:2 mixture of *cis*- and *trans*-isomers; ν_{max}/cm^{-1}(film) 3072, 3055, 2928, 2852, 1655, 1586, 1449, 1434, 1383, 1210, 1111, 886, 743 and 696; δ_H 6.02 and 5.58 (2 × d, *J* 12.5 and 6.3, =CHO), 4.92–4.80 (m, C*H*=CHO + 3 × =CH), 4.44 (s, =C*H*H), 4.42 (s, =CH*H*), 3.30 and 3.22 (OMe), 1.90–1.68 (m, 8 × CH_2), 1.46 (s, CH_3), 1.35 (s, CH_3) and 1.33 (s, 2 × CH_3); δ_C 146.9 and 145.9 (=*C*HOMe), 137.3, 137.1, 135.1, 134.9_0, 134.8_6, 134.7_1 and 134.4 (quat. C), 133.9 and 133.6 (=CH), 128.7, 128.5 and 128.4 (=CH), 124.6, 124.4, 124.2 and 124.0 (=CH), 109.8 (=CH_2), 106.5 and 102.8 (CH=CHO), 59.4 and 55.8 (OCH_3), 41.0, 40.0, 39.7, 39.6, 37.8, 26.6, 26.5, 26.4, 26.2 and 26.1 (CH_2), 23.4, 22.5, 22.4, 16.0 and 15.8 (CH_3); (ii) the ester **46b** (R′ = Me; 38%); ν_{max}/cm^{-1}(film) 3073, 2920, 1742, 1649, 1437, 1374, 1204, 1155 and 886; δ_H 5.28–5.08 (m, 3 × =CH), 4.80 (s, =C*H*H), 4.77 (s, =CH*H*), 3.76 (s, OCH_3), 2.36 (t, *J* 7.4, CH_2CO), 2.30–1.90 (m, 8 × CH_2), 1.88–1.65 (m, CH_2), 1.82 (s, CH_3), 1.71 (s, CH_3) and 1.69 (s, 2 × CH_3); δ_C 174.5 (CO), 145.8 (quat. C), 135.1 (quat. C), 134.7 (quat. C), 133.7 (quat. C), 125.3 (=CH), 124.3 (=CH), 124.0 (=CH), 109.7 (=CH_2), 51.4 (OCH_3), 39.6 (2 × CH_2), 38.9 (CH_2), 37.8 (CH_2), 33.4 (CH_2), 26.6 (2 × CH_2), 26.2 (CH_2), 23.0 (CH_2), 22.4 (CH_3), 15.9 (2 × CH_3) and 15.7 (CH_3) and (iii) the acid **46b** (R′ = H; 73%); ν_{max}/cm^{-1}(film) 3500–2500br (CO_2H), 1709, 1649, 1442, 1382, 1274, 1242 and 886; δ_H 10.2 (br s, CO_2H), 5.26–5.18 (m, 3 × =CH), 4.80 (s, =C*H*H), 4.79 (s, =CH*H*), 2.41 (t, *J* 7.4, CH_2CO), 2.30–2.00 (m, 7 × CH_2), 1.89–1.75 (m, CH_2), 1.83 (s, CH_3), 1.71 (s, CH_3) and 1.70 (s, 2 × CH_3); δ_C 180.4 (CO), 145.8 (quat. C), 135.1 (quat. C), 135.0 (quat. C), 134.7 (quat. C), 125.5 (=CH), 124.3 (=CH), 124.0 (=CH), 109.7 (=CH_2), 39.6_4 (CH_2), 39.5_9 (CH_2), 38.8 (CH_2), 37.8 (CH_2), 33.3 (CH_2), 26.6 (2 × CH_2), 26.2 (CH_2), 22.7 (CH_2), 22.4 (CH_3), 15.9 (2 × CH_3) and 15.7 (CH_3). Phenylselenylation of the carboxylic acid **46b** (R′ = H) then gave the ester **47b** (53%) as a pale yellow oil; ν_{max}/cm^{-1}(film) 3073, 2927, 2852, 1726, 1649, 1580, 1478, 1439, 1382, 1022, 886, 737 and 689; δ_H 7.44–7.40 (m, 2 × aryl =CH), 7.31–7.27 (m, 3 × aryl =CH), 5.10–5.00 (m, 3 × =CH), 4.63 (s, =C*H*H), 4.60 (s, =CH*H*), 2.57 (t, *J* 7.4, CH_2CO), 2.10–1.80 (m, 7 × CH_2), 1.76–1.55 (m, CH_2), 1.64 (s, CH_3) 1.53 (s, 2 × CH_3) and 1.50 (s, CH_3); δ_C 200.2 (CO), 145.8 (quat. C), 135.7 (2 × aryl =CH), 135.1 (quat. C), 134.7 (quat. C), 133.3 (quat. C), 129.2 (2 × aryl =CH), 128.7 (aryl =CH), 126.5 (quat. C), 125.7 (=CH), 124.3 (=CH), 124.0 (=CH), 109.7 (=CH_2), 46.7 (CH_2), 39.7 (CH_2), 39.6 (CH_2), 38.5 (CH_2), 37.8 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 23.3 (CH_2), 22.4 (CH_3), 16.0 (2 × CH_3) and 15.6 (CH_3).

Reductive cyclisation of *Se*-phenyl selenoate 47a. Cyclisation of the title ester, according to the general conditions, gave the

bicyclic analogue of **52** (trace), but mainly a mixture of ring-D methyl epimers of the tetracyclic ketone **53** (78%) as an oil. Partial enrichment in one isomer was achieved by HPLC: δ_H 2.35–2.22 (2 H, m), 2.22–2.05 (1 H, m), 2.05–1.80 (4 H, m), 1.80–1.65 (2 H, m), 1.65–1.54 (2 H, m), 1.54–1.41 (4 H, m), 1.41–1.29 (3 H, m), 1.29–1.14 (2 H, m), 1.14–0.98 (2 H, m), 0.98–0.90 (2 H, m), 0.87 (s, CH_3), 0.87–0.75 (1 H, m), 0.80 (s + d, *J* 7.3, CH_3 + $CHCH_3$) and 0.74 (s, CH_3); δ_C 213.7 (CO), 60.2 (CH), 59.8 (CH), 56.4 (CH), 43.9 (CH), 43.5 (quat. C), 43.3 (quat. C), 40.9 (CH_2), 39.5 (CH_2), 38.4 (CH_2), 36.9 (quat. C), 35.4 (CH_2), 30.0 (CH_2), 24.1 (CH_3), 22.4 (CH_2), 20.7 (CH_2), 19.0 (CH_2), 18.9 (CH_3), 17.0 (CH_2), 16.7 (CH_3) and 13.9 (CH_3).

Reductive cyclisation of the *Se*-phenyl selenoate 47b. Cyclisation of the title ester, according to the general conditions, led to a mixture of ring-D methyl epimers of the tetracyclic ketone **54** (78%) as an oil. Partial enrichment in one isomer was achieved by HPLC; δ_H 2.33–2.22 (*ca.* 2 H, m), 2.19–2.08 (*ca.* 1 H, *ca.* dd), 2.03–1.85 (*ca.* 3 H, m), 1.85–1.68 (*ca.* 2 H, m), 1.68–1.41 (*ca.* 7 H, m), 1.41–1.14 (*ca.* 5 H, m), 1.11–0.97 (*ca.* 2 H, m), 0.97–0.75 (*ca.* 2 H, m), 0.92 (s, CH_3), 0.83 (m, 2 × CH_3) and 0.74 (s, CH_3); δ_C 213.3 (CO), 56.2 (CH), 55.5 (CH), 55.2 (CH_2), [54.2 (CH)], [43.6 (quat. C)], 43.2 (CH), 42.8 (CH_2), 41.6 (CH_2), 37.7 (CH_2), 36.6 (CH_2), 36.5 (quat. C), 34.7 (quat. C), 34.5 (quat. C), 29.4 (CH_2), 27.6 (CH), 26.6 (CH_2), 23.3 (CH_3), 22.9 (CH_3), 21.8 (CH_3), 21.1 (CH_2), 21.0 (CH_2), 20.2 (CH_2) and 13.7 (CH_3).

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